LOW-TEMPERATURE SPECTRAL DISTRIBUTION OF THE INTERNAL PHOTOEFFECT OF CADMIUM SELENIDE AND CADMIUM SULFIDE

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Abstract

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LOW-TEMPERATURE SPECTRAL DISTRIBUTION OF THE INTERNAL PHOTOEFFECT OF CADMIUM SELENIDE AND CADMIUM SULFIDE

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I. To explain a wide range of phenomena of the photosensitivity of CdS crystals (^{1}) and Cu_2O (^{2}), hypotheses based on exciton mechanisms have been proposed. The most direct method for testing these hypotheses could be the detection of complex photoconductivity structures and their comparison with the structure of absorption spectra in the region of the long-wavelength edge of the fundamental absorption of crystals. For the first time, a fine structure of the spectral curve of the photocurrent of semiconductors was found in CdS (^{3}) at $T = 77.3^\circ$ K. However, the comparison of the photocurrent peaks and the intrinsic-absorption maxima of CdS in (^{3}) was carried out not quite reliably and convincingly: 1) the spectral photocurrent curves were obtained at $T = 77.3^\circ$ K (4 peaks) and compared with the maxima of the line structure of absorption at $T = 4.2^\circ$ K (about 20 lines and bands!); 2) the dispersion of the monochromator was insufficient for a convincing resolution of the complex structure of the photocurrent curves. Therefore, an important step in investigating the nature of the structures of edge spectra of the photocurrent, absorption, and emission would be the study of the spectral curves of the photocurrent of CdSe and CdS at $T = 4.2^\circ$ K using a monochromator of sufficiently large dispersion.

The CdSe and CdS single crystals investigated by us had dark currents of 10^{-9} -10^{-11} A and photocurrents of 10^{-8}–10^{-9} A at $T = 77.3^\circ$ K and $T = 4.2^\circ$ K. The photocurrent curves were recorded in polarized light (without interrupting the light) on an apparatus with a linear dispersion of 5 Å/mm and a scan time for a spectral interval of 200 Å of $t = 5$–30 min, with a spectral slit width not exceeding 0.5 Å.

II. In the spectral distribution of the photocurrent we found 6 peaks (dips) at 77.3° K and 8 peaks (dips) at 4.2° K in CdSe, and, respectively, 6 and 9 peaks (dips) in CdS (Fig. 1). In many of the "pure" CdSe and CdS single crystals studied by us, the peaks coincide in their position in the spectrum with the dips*.

The introduction of impurities, various kinds of heat treatments in different gaseous atmospheres, damage to the surface, and gluing of crystals to different substrates—all this, as a rule, strongly changes the appearance of the spectral photocurrent curves of such "disturbed" crystals relative to the "pure" ones ([4,5]): 1) the sharpness of resolution of the peaks (dips), and even the number of peaks (dips), may change greatly; 2) the peaks (dips) may be shifted into the ultraviolet or infrared region of the spectrum; 3) the relative magnitudes of the peaks (dips) may change greatly, etc.

Detailed investigations carried out by us on a large number of "pure" CdSe and CdS single crystals at $T = 77.3°$ K made it possible further to establish the following:

1) If a crystal is cooled from 290 to 77.3° K in complete darkness and then the spectral curves of the photocurrent are studied (also in darkness), then at first no structure of the photocurrent curves can be detected (Fig. 2)—

* In some crystals, photocurrent curves with peaks are observed; in others, with dips. In Figs. 1 and 2, photocurrent curves with peaks are shown; below, in schematic form, are given the absorption spectra at $T = 4.2°$ K—the most intense absorption lines.

the spectral curve has the form of a monotonic dark-current curve. However, after several hours of repeated measurements against the background of the dark-current initial curve (Fig. 2, curve 1), peaks (dips) appear (Fig. 2, curves 2-4), which gradually increase as the time of irradiation of the crystal by light from the region of intrinsic absorption increases. Prolonged illumination of the crystal at $T = 77.3°$ K with low-intensity light (from the monochromator slit) or short-time illumination with high-intensity light can increase the photocurrent by many times (in comparison with non-photoactivated crystals) and yield very sharply expressed peaks (dips).

2) Illumination of the crystal by a light probe can be carried out in two ways: the light probe illuminates only the crystal, or the crystal and both electrodes. Our investigations showed that often the two illumination methods have unequal effects on the sharpness of the appearance of peaks (dips): in the first illumination method the structure of the photocurrent curves is much better expressed than in the second method; sometimes, when the crystal and its electrodes are illuminated, the structure of the photocurrent cannot be detected at all.

3) Quenching of the edge photoconductivity by infrared light is approximately the same for all peaks (dips): the photocurrent curve of the crystals measured by us under the simultaneous action of strongly photocurrent-quenching infrared light agrees well with the photocurrent curve without quenching illumination in the positions and relative magnitude of the peaks (dips).

Fig. 1. Spectral distribution of the intrinsic photoeffect of CdSe and CdS single

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Fig. 2. Spectral distribution of the intrinsic photoeffect of single crystals at different levels of photoactivation

Figure 2: Fig. 2. Spectral distribution of the intrinsic photoeffect of single crystals at different levels of photoactivation

crystals at $T = 4.2^\circ$ K

Fig. 2. Spectral distribution of the intrinsic photoeffect of single crystals at different levels of photoactivation

4) In some crystals we have found the formation of charges that disappear so slowly with time that it is possible to obtain spectral photocurrent curves even without applying the previously used voltage to the electrodes, with the structure of the photocurrent curves remaining the same without noticeable changes.

III. The main results obtained by us for the spectral photocurrent curves of CdSe and CdS single crystals at low temperatures:

1) "Pure" crystals are divided into two groups—crystals with peaks and crystals with dips on the photocurrent curves; in their position in the spectrum the peaks coincide with the dips and possess great stability. In "na-

"disturbed" crystals, two groups of crystals are also observed; however, a greater variety and variability is found in the position and number of peaks (dips).

2) The peaks (dips) of the spectral photocurrent curves of "pure" crystals coincide, to an accuracy of 1-2 Å, with the maxima of the intense lines and bands ($K \approx 10^5$ cm^{-1}) of the line structure of the edge of fundamental absorption (Fig. 1).

3) One of the most interesting and important results is the clearly expressed strong dependence of the manifestation of the structure of the photocurrent curves on the state of photoactivation of the crystals: photocurrent peaks (dips) arise only in the presence of a certain minimum photoactivation of the samples.

4) In CdS at 4.2°K, it was not possible to reliably detect the structure of the photocurrent curves on any of the "variable" absorption lines caused by immobile exciton-impurity complexes.*

It seems to us that two principal experimental results discovered by us—the coincidence of peaks (dips) of the spectral photocurrent curves with the maxima of the intense lines of edge absorption ($K \approx 10^5$ cm^{-1}) and the strong dependence of the manifestation of the structure of the photocurrent curves on the photoactivation of the crystals—convincingly prove the excitonic origin of the peaks (dips) of the photocurrent curves of CdSe and CdS single crystals, as well as of the corresponding lines of the line structure of edge absorption and emission. The excitonic structure of edge absorption appears in the form of peaks (dips) in the spectral distribution of the photocurrent owing to the interaction of excitons with photocenters arising upon irradiation of the crystal from the fundamental-absorption region ($E > E_g$).**

Our experimental detection of peaks (dips) on the photocurrent curves of CdSe and CdS crystals, coinciding with high accuracy in their position in the spectrum with the absorption lines of excited states of excitons ($n > 1$), confirms, together with our data on the properties of edge emission (8), the absence in these crystals of a quasi-equilibrium distribution between the energy levels of different excitons (A and B) and between the levels of one and the same exciton.

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CITED LITERATURE

[1] V. E. Lashkarev, G. A. Fedorus, Izv. AN SSSR, ser. fiz., **16**, 84 (1952).
[2] V. P. Zuze, S. M. Ryvkin, DAN, **58**, 1629 (1947); ZhETF, **20**, 152 (1950); Izv. AN SSSR, ser. fiz., **16**, 93 (1952).
[3] E. F. Gross, A. A. Kaplyanskii, B. V. Novikov, ZhETF, **26**, 913 (1956).
[4] V. V. Sobolev, Abstract of Candidate' s dissertation, L., 1962.
[5] E. F. Gross, V. V. Sobolev, Abstracts of reports, First All-Union Conference on Photoelectric and Optical Phenomena in Semiconductors in Kiev, November 1957, Kiev, 1957.
[6] V. L. Broude, V. V. Eremenko, M. K. Sheinkman, ZhETF, **28**, 2142 (1958).
[7] V. V. Eremenko, Fiz. tverd. tela, **2**, 2596 (1960).
[8] V. V. Sobolev, Abstracts of reports at the Eighth All-Union Conference on Low-Temperature Physics in Kiev, October 1961, Kiev, 1961.

* The principal results presented in the present work were obtained by us in 1957 (5). The complex structure of the photocurrent curves of CdSe and CdS at $T = 20$°K is partly repeated in (6,7). The use of a monochromator with greater resolving power allowed us, with much greater certainty than in (6,7), to establish the existence of two groups of CdSe and CdS crystals (peaks and dips) and the correlation of the peaks (dips) on the photocurrent curves with the linear exciton structure of the absorption spectra.

** The photocenters in CdSe and CdS are possibly sticking levels, whose filling is regulated by light with energy $E > E_g$.