Influence of near-surface layer on the anomalies in the spectrum of exciton reflection of CdS single crystals at $T = 4.2°K$

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It was observed that the exciton-reflection spectra can be reversibly altered by irradiating CdS single crystals with low-energy electrons. Depending on the radiation dose, an exciton-free ("dead") layer of different depth is produced at the surface of the crystal, and this makes it possible to obtain quite definite curves of reflection spectra with different anomalies.

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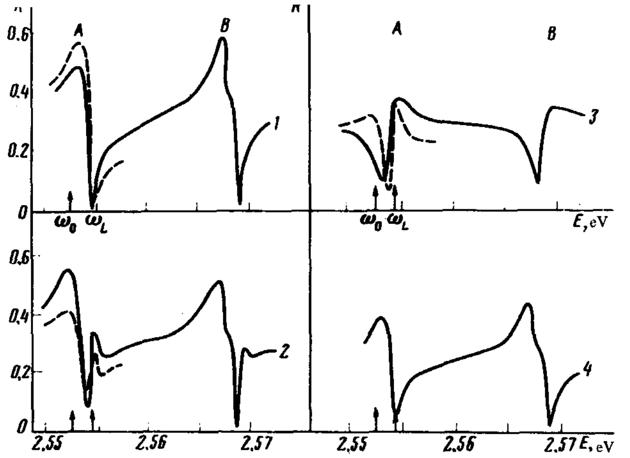
Exciton reflection spectra at low temperatures frequently exhibit anomalies which are determined to a considerable degree by effects of spatial dispersion.[1-3] In particular, the reflection spectra of CdS frequently reveal narrow peaks ("spikes") at the longitudinal-exciton frequency ω_L. The nature of these anomalies was first considered by Thomas and Hopfield.[1] For a spike to appear, it is necessary that a "dead" layer exist at the surface of the crystal. The second condition for the presence of a spike is that the dissipative damping be small ($\Gamma < 10^{-5}$ eV).[3]

To assess the role of the surface in the manifestation of the indicated anomalies, the CdS single crystals were bombarded by electrons[4] of low energy, 3.5 keV. The reflection spectra were registered photoelectrically in a geometry with $\mathbf{E} \perp \mathbf{C}$ and $\mathbf{K} \perp \mathbf{C}$ for different incidence angles $\phi = 6$, 30, 45, and 60°. The character of the variation of the spectra after the electron bombardment was common to all the incidence angles.[1)] The maximum intensity of a spike, when it was present in spectrum, was observed at $\phi = 60°$. Each investigated crystal was bombarded several times, each for a longer time



Reflection spectra of CdS single crystal at $T=4.2\,^\circ$K, $\mathbf{E}\perp\mathbf{C}$, $\mathbf{K}\perp\mathbf{C}$, $\phi=6^\circ$. Dashed curves—theoretical calculation[1]: 1) initial state $l\approx 0$ Å, 2) after electron bombardment at 3.5 keV for one minute; $l\approx 110$ Å, 3) after electron bombardment at 3.5 keV and 12 min; $l\approx 160$ Å, 4) after heating the crystal to room temperature.

(larger dose).

The regularities common to all the crystals were the following: 1) After the first electron bombardment session, the intensity at the maximum of the reflection increased by a factor $\sim 1/2$. Further increase of the electron bombardment time led to a decrease of the intensity and to a change in the shape of the curve.
2) Heating the crystal to room temperature returned the reflection spectrum to its initial form. 3) After prolonged bombardment (~ 15 min), the reflection curves had an "inverted" form. 4) In crystals with $\sim 10^{-4}$ eV, the spike appeared after the first bombardment session (~ 1 min). Crystals with $\Gamma > 10^{-4}$ eV revealed no spike at the frequency ω_L.

The figure shows a series of spectra of number of reflections of one crystal, which revealed a spike after electron bombardment. In the initial state, the curve has the usual shape (curve 1). The shoulder on the short-wave slope of the reflection maximum $B_{s=1}$ of the exciton indicates that the damping is small. After the first electron bombardment session (curve 2), a spike appears at the frequency ω_L. A similar anomaly is observed also in the region $B_{s=1}$ of the exciton. A gradual increase of the electron bombardment time leads to an increase of the spike intensity. Bombardment of the crystal for 12 minutes "inverts" the spectrum (curve 3). Heating the crystal to room temperature from any state (curve 2 or 3) returns the reflection to the initial form (curve 4). Illumination of the crystal with light in the intrinsic-adsorption region increases the intensity of the spike. A comparison of the experimental curve with the theoretical calculation of the reflection,[1] with account taken of the spatial dispersion with variable parameter of the dead layer l, results in good qualitative agreement.

With increasing irradiation dose, an increase seems to occur in the depth l of the exciton-free layer. The total change in the form of the reflection curve with inversion (without allowance for the spike) is, as shown by calculation,[5] the consequence of the interference of the waves reflected from the crystal boundary and from the boundary of the dead layer of different depths l. The picture of the inverted reflection corresponds to $l \approx 200$ Å. The result described above make it now possible to regard it as proved that the appearance of the spike at definite values of l is connected precisely with the allowance, in the interference, of the additional wave due to effects of spatial dispersion. At large damping these effects vanish, and no spike appears in the reflection spectra.

We assume that the dead layer is due principally to ionization of the excitons in the near-surface field.[2)] As a result of the electron bombardment, the electric field near the surface increases and this causes an increase in the effective depth l. The increase of the field is due to the increase in the number of charged centers in the space-charge region. An additional increase of the field is achieved by illuminating the sample.

The existence of a thin surface layer in which the excitons are ionized should play an important role in processes of photoelectrically active decay of excitons. We assume that it is precisely this layer which causes many singularities on the spectral photocurrent curves of crystals subjected to electron bombardment.[6]

The presence of a spike for the $B_{s=1}$ exciton offers evidence of an appreciable role of spatial dispersion for this exciton state. The similar character of the variation of the spikes A and B of the excitons and the simultaneous inversion of the reflection spectra indicate that the dead layer for these exciton states is of the same order. The lower intensity of the B-exciton spike is probably due to the fact that this state is of higher energy and its damping is larger.

[1)] In the case of normal incidence, the spike occurs at the longitudinal-exciton frequency ω_L. With increasing incidence angle, a shift of the spike takes place towards higher energies, reaching 0.4 Å at $\phi=60^\circ$. From the position of the spike it is possible to calculate the upper branch of the dispersion curve of the transverse polaritons.[2]

[2)] It is assumed that the exciton ionization sets in the case when the potential drop across the exciton radius is equal to its binding energy. For CdS, this amounts to $F_{cr}\approx 10^5$ V/cm.

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