

Exciton spectra of clean and oxidized surfaces of CdS crystals

V. V. Travnikov

A. F. Ioffe Physicotechnical Institute, Academy of Sciences of the USSR, Leningrad

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Surface exciton states of two types have been observed. It is suggested that the states of one type stem from surface defects, while those of the other type stem from a space-charge region.

One method for studying the properties of a real surface is to compare its optical spectra with those of atomically clean surfaces. In the present letter we report a study of the exciton spectra of clean surfaces of CdS crystals, produced by cleavage in liquid helium, in comparison with the spectra of oxidized surfaces of these crystals.

The experiments are carried out at $T = 2$ K. The cleavage is carried out along the C optic axis. Figures 1 and 2 show the photoluminescence spectra (solid lines) of a cleaved surface of one of the samples in the vicinity of the $n = 1A$ exciton state. Spectra 1 were obtained directly after cleavage in the liquid helium, while spectra 2 were obtained after a heating to room temperature, a hold in air, and a subsequent cooling to $T = 2$ K. The dashed lines show the corresponding reflection spectra (1' and 2'). The structural features in the spectra of the surface exposed to the air coincide with structural features found in the spectra of ordinary surfaces of CdS crystals—surfaces not subjected to a special treatment. The hold in air significantly changes the observed spectra. Most of the changes occur in the region between the polariton luminescence line (PL) and the intense line I_2 , which corresponds to the emission of an exciton-impurity complex and which is associated with lines I_{s1}^i in the spectrum of the clean surface and the lines I_{s1}^o and I_{s2}^o in the spectrum of the oxidized surface (the unlabeled narrow lines correspond to the emission of various states of exciton-impurity complexes). The nature of the spectra of the oxidized and clean surfaces, on the one hand, and the extent to which they differ, on the other, depend on both the intensity of the exciting light (I_{exc}) and the intensity and duration of the preliminary illumination of the oxidized surface by the exciting light. The photoluminescence spectra shown in Fig. 1 (curves 1 and 2) were obtained at a minimum I_{exc} [$I_0 \sim 10^{16}$ photons/($\text{cm}^2 \cdot \text{s}$)], without preliminary illumination of the surfaces. In this case, after the hold in air, an intense line I_{s1}^o appears in place of the line I_{s1}^i , while in the reflection

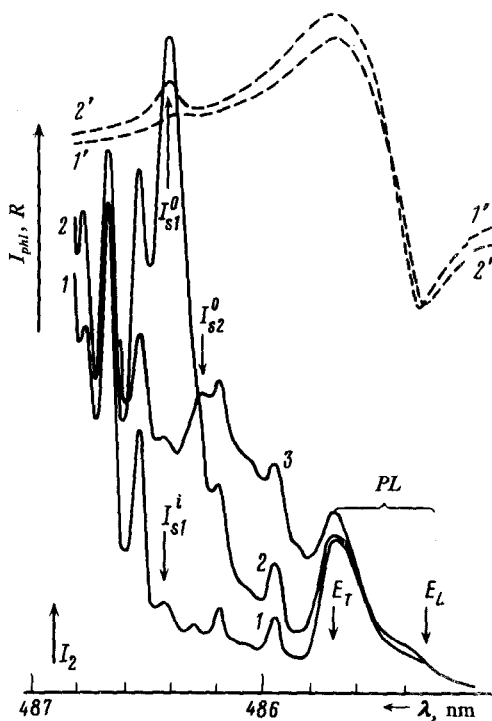


FIG. 1. Photoluminescence spectra (1, 2) and reflection spectra (1', 2') of a clean surface (1, 1') and of an oxidized surface (2, 2') of CdS crystals without preliminary illumination. The photoluminescence spectra were recorded at the minimum I_{exc} (I_0). E_L , E_T —Positions of the bottom of the bands of longitudinal and transverse excitons.

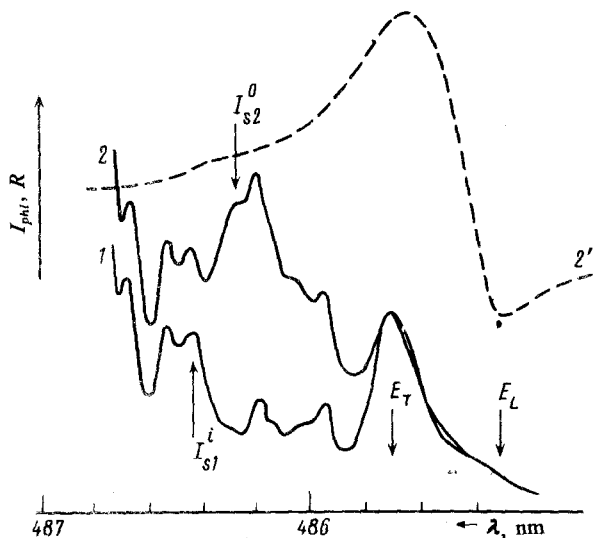
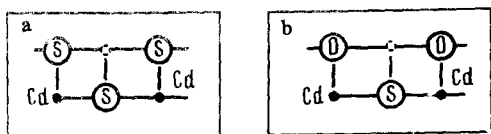


FIG. 2. Photoluminescence spectra of a clean surface (1) and of an oxidized surface (2) recorded at $I_{exc} = 400I_0$. Reflection spectrum 2' was recorded after illumination of the oxidized surface at this I_{exc} . The insets are schematic diagrams of (a) a region of a clean surface with a Cd vacancy and (b) a region of an oxidized surface on which O atoms attach to surface Cd atoms.

spectrum there is an increase in the amplitude of the slight structure observed near the I_{s1}^i line in the spectrum of the clean surface. As I_{exc} is increased, a line I_{s2}^0 splits off from the I_{s1}^0 peak in the spectrum of the oxidized surface and shifts down the wavelength scale with increasing I_{exc} , decreasing in relative intensity. In the spectrum of the clean surface, an increase in I_{exc} is accompanied by an increase in the relative intensity of the line I_{s1}^i . Figure 2 shows photoluminescence spectra of these surfaces at $I_{exc} = 400I_0$. In this case the intensities of lines I_{s1}^i and I_{s1}^0 are essentially identical. The shift of I_{s2}^0 is irreversible, as can be seen from Fig. 1, which shows spectrum 3 at $I_{exc} = I_0$ after the recording of spectrum 2 (Fig. 2). The photoluminescence spectrum of the clean surface depends on only I_{exc} ; a preliminary illumination has no effect on it. In the reflection spectra, the preliminary illumination again affects only the spectra of the oxidized surface. In the reflection spectrum of the oxidized surface found before any illumination, the amplitude of the structure, which coincides resonantly with the I_{s1}^0 line, is substantially higher than the amplitude of the corresponding structure in the spectrum of the clean surface (Fig. 1). As the illumination is intensified, this amplitude decreases, as can be seen from Fig. 2, where spectrum 2 was obtained after illumination of the oxidized surface at the maximum I_{exc} .

The hold in air can change only the surface properties of the sample, so that the intensification of the I_{s1}^0 line is proof that this line is of surface origin. The properties of the I_{s1}^0 line are the same as those of I_{s1}^i : (1) The spectral positions of the I_{s1}^i and I_{s1}^0 peaks are essentially identical. (2) Resonant structures in the reflection spectra correspond to both lines, in contrast with the lines of interior electron-impurity complexes. (3) The half-widths of these lines are substantially greater than the half-width of the lines of the exciton-impurity complexes. Since this coincidence can hardly be fortuitous, we believe that the states corresponding to I_{s1}^i and I_{s1}^0 have a common surface origin. The number of such states increases after the hold in air, as is indicated by the intensification of the corresponding structures in the reflection and photoluminescence spectra. After the illumination of the oxidized surface, the number of such states decreases to values characteristic of the clean surface (see spectra 1 and 3 in Fig. 1). The line I_{s2}^0 is not found in the spectrum of the clean surface. This line can naturally be linked with surface states which are peculiar to an oxidized surface.

The surface nature of these lines of the oxidized surface has been discussed previously in studies of CdS (Ref. 1) and CdS (Refs. 2 and 3) crystals. In Refs. 1 and 2, the line I_{s1}^0 and the line I_{s2}^0 , split off from the latter, were perceived as a single line I_s . On the basis of the pronounced sensitivity to electron bombardment, the line I_s was concluded to be of surface origin, and it was suggested that it was due to states of mechanical surface excitons,⁴ which arise from a shift of the bottom of the exciton band in the electric field of a space-charge region. A correlation between the line I_s and a space-charge layer was established in Ref. 3.

The shift of the line I_{s1}^0 with respect to the energy E_T observed experimentally is ~ 3.7 meV, roughly the same as an estimate of the maximum energy shift of an exciton in an electric field,⁵ ~ 3.4 meV. However, the fields corresponding to this shift should cause a broadening of the exciton state (~ 8 meV; Ref. 5) considerably greater than the half-width of the I_{s1}^i and I_{s1}^0 lines (~ 1 meV). This circumstance rules out an

interpretation of the lines in the model of mechanical surface excitons. We suggest that the states corresponding to I_{s1}^i and I_{s1}^o are excitons localized near surface centers. Such centers might be structural defects where S atoms may be replaced by O atoms, e.g., Cd surface vacancies (see the inset in Fig. 2). By virtue of the isoelectronic structure of the outer shells of the S and O atoms, the regions on the oxidized surface in which O atoms attach to Cd atoms may have electronic properties similar to those of clean surfaces with Cd vacancies. In particular, the parameters of the Coulomb potentials, which determine the binding energy of excitons near such defects, may be approximately the same; this similarity would help explain the essentially identical spectral positions of I_{s1}^i and I_{s1}^o . The model proposed here explains the change in the number of surface states. The increase in the number of states due to the hold in air may be due to the appearance of Cd surface vacancies with surroundings in the form of O atoms instead of S atoms, while the decrease during illumination may be due to a decrease in the number of such vacancies as a result of the desorption of oxygen.

The line I_{s2}^o , not found in the spectrum of the clean surface, is evidently due to a space-charge region. The desorption that occurs during illumination may, by changing the properties of the space-charge region, cause the change in the spectral position and relative intensity of the line I_{s2}^o . The nature of the state I_{s2}^o suggests that it may correspond to either mechanical surface excitons or excitons bound to ionized donors in the space-charge region.¹⁻³ The presence of a space-charge region explains why the line I_{s2}^o becomes more intense in the photoluminescence spectrum than in the reflection spectrum. In the reflection spectrum, the intensity is proportional to only the number of states, while in the photoluminescence spectrum there is the further probability of a filling of existing states. As a result of the electric field of the space-charge region, the excitons are drawn toward the surface.⁶ This effect should lead to an increase in the probability for the filling of surface states. The decrease in the field during the illumination also reduces the relative intensity of the emission.

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