

Luminescence of surface polaritons in CdS crystals

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The luminescence spectrum of CdS crystals reveals two new lines, one of which is attributed to emission resulting from the scattering of surface polaritons by a surface roughness. This identification is based on studies which have been made. The second new line is attributed to an emission due to a scattering of surface polaritons by phonons and impurities.

On a perfectly flat surface and in the absence of scattering processes, surface polaritons cannot convert into observable radiation.¹ It was shown theoretically in Refs. 2 and 3 that a scattering by a roughness and by phonons can give rise to manifestations of surface polaritons in the exciton luminescence spectra. Specifically, there will be two lines, between the energies E_L and E_T , which correspond to the bottoms of the bands of longitudinal and transverse excitons. Results from Ref. 3. are shown in the inset in Fig. 1. Scattering by acoustic phonons should give rise to a line on the long-wave side of E_S , which can be found from the condition $\epsilon(E_S) = -1$, where $\epsilon(E)$ is the dielectric constant, in the case of contact with vacuum and if spatial dispersion is ignored. A scattering by a roughness should give rise to a line on the short-wave side of E_T . A possible manifestation of surface polaritons in photoluminescence spectra was reported earlier in studies of Xe (Ref. 5) and ZnTe crystals.⁴ The basic argument for a surface-polariton identification of the observed structural features reduces to a determination of their positions with respect to the energies E_L and E_T (but see Ref. 6). No active experiments aimed at verifying the proposed interpretation have been carried out. In the present study we have not only observed two lines in the region of the longitudinal-transverse splitting (the *LT* region) in the photoluminescence spectrum of CdS crystals but also found evidence from several experiments to justify the identification of these lines with surface polaritons.

The photoluminescence spectra of the $n = 1A$ exciton state of CdS crystals are studied at $T = 2$ K with excitation by the 476.5-nm line of an Ar⁺ laser. The use of clean surfaces, obtained by cleavage in liquid helium (the cleavage was carried out along the *C* axis), was important for observing manifestations of surface polaritons in the photoluminescence spectra. Another important step is the recording of the luminescence in the forbidden geometry $\mathbf{E} \parallel \mathbf{C}$ (with $\mathbf{k} \perp \mathbf{C}$), where \mathbf{E} and \mathbf{k} are the polarization vector and wave vector of the light being studied, and *C* is the optic axis of the crystal. The particular features of the manifestation of surface polaritons in the geometry $\mathbf{E} \perp \mathbf{C}$ will be reported later. From previous work on the forbidden geometry in the *LT* region of the $n = 1A$ state of CdS crystals we have only the report of an observation of the line A_L , corresponding to the emission of longitudinal excitons, and of the line A_F , corresponding to the emission of ortho-excitons. In the present study we have observed two lines, *B* and *C* (spectrum 1 in Fig. 2), between the A_L and A_F lines in the

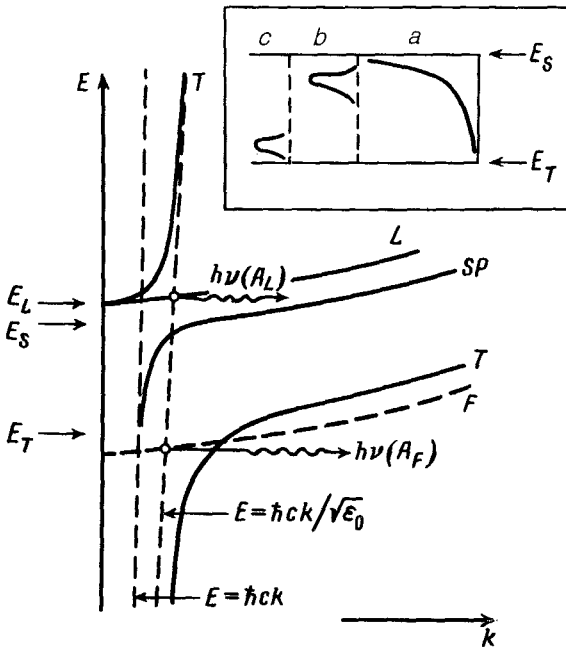


FIG. 1. Generalized dispersion curves of the $n = 1A$ state of CdS crystals (the details which stem from the anisotropy are not included). Curves T , L , F , and SP correspond to the dispersion of transverse polaritons ($E \perp C$), longitudinal excitons, forbidden ortho-excitons, and surface polaritons. The inset shows results of the calculations of Ref. 3, which ignore spatial dispersion and anisotropy. a —State density of surface polaritons; b, c —probabilities for the scattering of surface polaritons by acoustic phonons and a roughness.

spectra of clean surfaces, immediately after cleavage. Comparison of Figs. 1 and 2 reveals that the energy positions of these lines agree well with the predictions of Refs. 2 and 3 regarding manifestations of surface polaritons in luminescence spectra. It would be natural to suggest that line B corresponds to emission which occurs during the scattering of surface polaritons by phonons, while C corresponds to an emission during the scattering of surface polaritons by a roughness (for the lines we are adopting the notation proposed in Chapter 5 in Ref. 1 for some analogous lines).

Spectrum 2 in Fig. 2 was found at an excitation intensity (I_{exc}) about an order of magnitude lower than the value of I_{exc} at which spectrum 1 was obtained (for convenience in comparison, we have drawn spectra 1 and 2 to scales such that the intensities of the A_L lines are the same). We see that the relative intensity of line B increases with increasing I_{exc} . In principle, such an increase might be explained within the framework of the interpretation which we are offering here on the basis that an increase in I_{exc} is accompanied by an increase in the number of nonequilibrium acoustic phonons, which appear near the surface as a result of an energy relaxation of electronic excitations generated in the crystal. However, an elastic scattering of surface polaritons by impurities may also be contributing to line B . As I_{exc} is increased, the probability for such processes increases, because the polariton trapping centers convert into elastic-scattering centers with increasing I_{exc} (Ref. 7). We believe that scattering by impuri-

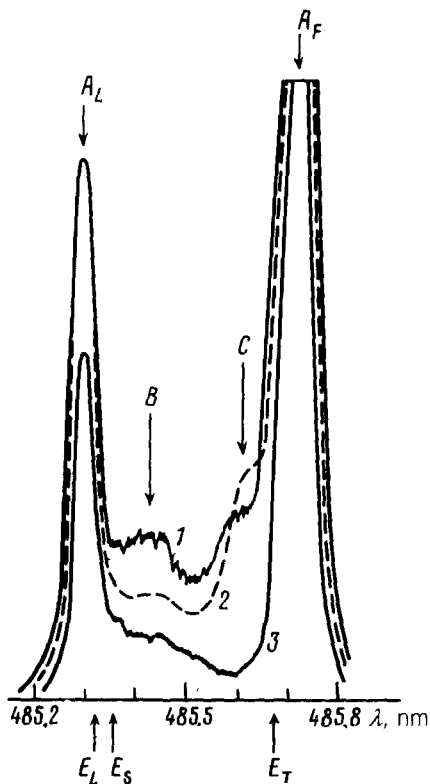


FIG. 2.

ties is basically responsible for line *B*, since there could hardly be any substantial change in the probability for scattering by a phonon over the I_{exc} range which we studied.

Spectrum 3 in Fig. 2 was found under the same excitation and measurement conditions and from the same surface as spectrum 1, but after the sample had been heated to room temperature and held in air. Oxidation significantly reduces the intensity of line *B*; line *C* essentially disappears from the spectrum. Oxidation is accompanied by the appearance of a space-charge region. The electric field of the space-charge region reaches high values at a boundary (Ref. 8, for example). This effect evidently reduces the amplitude of a surface-polariton at the boundary and therefore reduces the intensity of line *C*. Line *B*, which results from the scattering by phonons and impurities, is formed by the entire region in which surface polaritons exist (with a depth on the order of the wavelength of the polariton). Oxidation would naturally not have as strong an effect on this line as it does on *C*.

Reduction of the solid angle in which the emission is observed makes it possible to clearly determine the shape of line *B* (Fig. 3). This approach corresponds to reducing the relative intensity of line A_L , which is known to be proportional to $\cos^2\alpha$, where α is the angle between the wave vector of a "nearly longitudinal exciton" and the *C* axis.⁹ It can be seen from Fig. 3 that line *B* has a half-width considerably greater than those

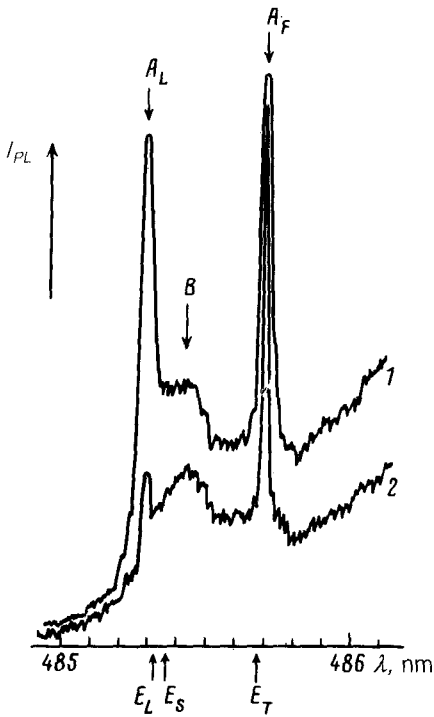


FIG. 3. Photoluminescence spectra of an oxidized surface for identical values of I_{exc} and for two values of the measured solid angle. The aperture ratio of the "measuring" objective for spectrum 1 is 1:2.8, while that for spectrum 2 is 1:22. The spectra have been drawn to scales such that the intensities of the A_F line for spectra 1 and 2 are the same, for convenience in comparison.¹⁾

of forbidden lines, and its short-wave tail stretches out above the energy E_S . In view of the continuous nature of the dispersion of surface polaritons and also the circumstance that the surface-polariton branch stretches out above E_S when spatial dispersion is taken into account (Chapter 2 in Ref. 1; spatial dispersion was not considered in Refs. 2 and 3), we conclude that the observed shape of line B also conforms to the interpretation proposed here.

In summary, all of the properties observed for lines B and C —their energy positions, their spectral shapes, the effect of oxidation on the absolute intensities, and the dependence of their relative intensities on I_{exc} —agree with the suggestion that line B appears in the photoluminescence spectrum as a result of scattering of surface polaritons by phonons and impurities, while line C appears as a result of the scattering of surface polaritons by a roughness. Further evidence in favor of this interpretation comes from the fact that the energy structure of the $n = 1A$ state of CdS crystals is known quite well, and in the region studied by us there are no other spectral features of any sort. Refining the mechanism for the conversion of surface polaritons into observable emission in the case studied here will require an analysis incorporating spatial dispersion and anisotropy.

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¹The increasing background in the long-wave direction seen in Fig. 3 is interesting. It increases appreciably after oxidation. It was subtracted from the spectra in Fig. 2 in order to allow a better comparison of the spectra of clean and oxidized surfaces.

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