Observation of surface mechanical excitons in crystals

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The exciton optical spectra have been measured in CdSe crystals with a natural surface and in crystals which had been subjected to electron bombardment. The exciton reflection spectra and exciton photoluminescence spectra at $T = 4.2$ K reveal a structure caused by a surface mechanical exciton {V. A. Kiselev, Fiz. Tverd. Tela (Leningrad) **20**, 1191 (1978) [Sov. Phys. Solid State **20**, 685 (1978)]}.

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Gribnikov and Rashba[2] report that excitons can be attracted to a strong-field region near a surface. Kiselev has studied the manifestations of this attraction in the exciton reflection spectra with the help of several model potentials[3] and also the attraction in the electric field of a Schottky barrier.[5] If there is a sufficiently strong attraction of excitons toward the surface in a crystal exhibiting spatial dispersion, a bound state corresponding to a surface mechanical exciton can be expected to appear in the potential well.[1,3] A surface mechanical exciton sensitive to the state of the surface should appear in the exciton reflection spectra as structure on the main reflection maximum. Figure 1a shows the exciton reflection spectra calculated for CdS crystals for various well depths.[3]

For an experimental test of these theoretical ideas, we adopted electron bombardment as a method for modifying the surface of a crystal. As has been shown in the cases of CdS (Ref. 5) and CdSe (Ref. 6), electron bombardment changes the electric field at the surface, initially weakening it as a result of the desorption of gases from the surface and later strengthening it, because of the formation of surface defects. These effects are seen in the exciton reflection spectra as characteristic changes in the spike region; as the dose is increased, there is a general change in the shape of the reflection line.

Figure 1b shows the exciton reflection spectra of a plate-shaped CdSe single crystal at $T = 4.2$ K before and after bombardment by 2-keV electrons in various doses; Fig. 2 shows the photoluminescence spectra of the samples under the same conditions.

The exciton reflection spectra of these crystals have several distinctive features, specifically, an intense spike and structure on the long-wave side of the main maximum, which we denote[1)] by I_s, and clear evidence of the $A_{n=2}$ reflection line. It can be seen from Fig. 1 that electron bombardment in small doses changes the shape of the exciton reflection spectrum near the spike (the spike is on the left of the minimum on curve 3), causes I_s to shift in the short-wave direction, and causes $A_{n=2}$ to

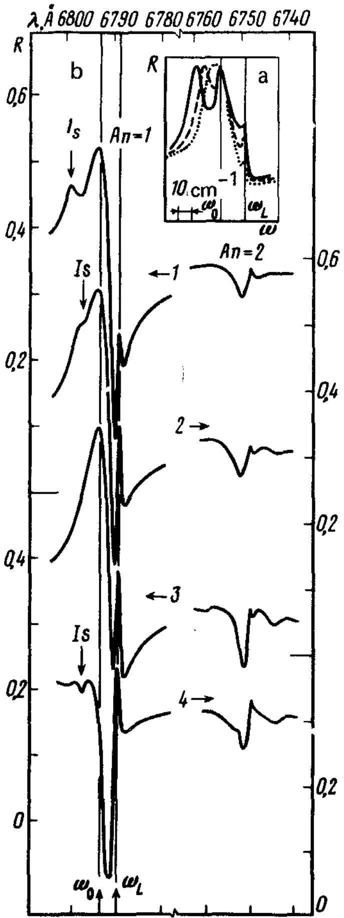

FIG. 1. (a) Calculated exciton reflection spectra of CdS crystals.[3] (b) Experimental exciton reflection spectra of a CdSe sample ($T = 4.2$ K, $\mathbf{E} \perp C$, $\mathbf{k} \perp C$, $\phi \approx 10°$). 1–Original spectrum; 2–$\sim 1 \times 10^{16}$ e/cm^2; 3–$\sim 5 \times 10^{16}$ e/cm^2; 4–$\sim 3 \times 10^{17}$ e/cm^2.

intensify. At doses $\sim 5 \times 10^{16}$ e/cm^2 (curve 3) there are increases in the maximum and minimum values of the reflection near the $A_{n=1}$ main resonance; the I_s structure disappears, and the $A_{n=2}$ amplitude goes to its maximum. Large bombardment doses (curve 4) cause characteristic changes in the shape of the reflection line. An additional reflection structure is again observed on the long-wave side.

In the photoluminescence spectrum (Fig. 2), the $A_{n=1}$ structure can be seen in the original state, along with several identified lines corresponding to bound excitons, the most intense of which is the line I_2 ($\lambda = 6804.2$ Å), which corresponds to the emission of excitons bound by neutral donors (this line is not shown in Fig. 2). In addition to these lines, there is an I_s resonance line at $\lambda \approx 6799$ Å. Electron bom-

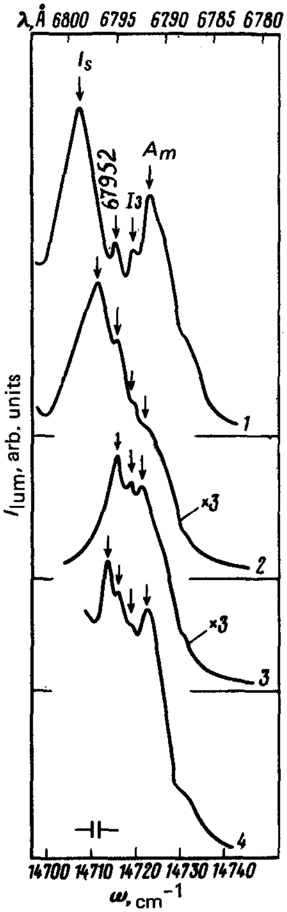

FIG. 2. Experimental photoluminescence spectra of the CdSe sample ($T = 4.2$ K, $E \perp C$). 1–Original spectrum; 2–~1×10^{16} e/cm^2; 3–~5×10^{16} e/cm^2; 4–~3×10^{17} e/cm^2.

bardment in small doses causes a sharp intensification of I_2 and also $A_{n=1}$. The line I_s, as in the reflection spectrum, shifts in the short-wave direction, initially intensifying and later fading. At high bombardment doses, the line $\lambda \approx 6796$ Å intensifies (curve 4).

We believe that the I_s structure observed in the exciton reflection spectrum and the luminescence, which is at resonance with this structure, are spectral manifestations of surface mechanical excitons.

In the original state of the crystal there is an electric field at the natural surface, caused by surface states. A potential well for excitons formed near the surface, and a bound state accordingly appears in this well; this is a surface mechanical exciton. Electron bombardment of the surface weakens this field, causes the potential well to become shallower, and thus reduces the bindng energy of the state. As a result, a short-wave displacement of the level corresponding to the surface mechanical exciton occurs in the spectra.[2)]

The general form of the spectrum after bombardment in small doses—the maximum possible value of the reflection near the maximum and minimum of the main resonance and the position and shape of the spike—correlates well with the shape of the experimental spectra found after electron bombardment of CdS crystals in small doses[5] and with the spectra calculated for low surface electric potentials.[4] Special measurements of the surface photo-emf[6] confirm that curve 3 in Fig. 1 corresponds to low values of the surface potential. The intensification of the $A_{n=2}$ feature corresponds to a low value of this potential. At fields near zero, the potential well for excitons is no longer capable of holding a bound state; as a result, no structure corresponding to a surface mechanical exciton is observed in the spectra.

Electron bombardment leads to the appearance of donor centers near the surface as a result of a subthreshold defect-formation mechanism. This effect is seen as a substantial intensification of the I_2 line, which is the emission of excitons bound by neutral donors. The energy-loss profile during the electron bombardment goes through a maximum at a certain distance from the surface. As a result, a spatially inhomogeneous distribution of donor centers is produced near the surface during the electron bombardment. A potential well for excitons can form in the field of the defects, so that a bound state may appear in this well. It may be suggested that the structure at $\lambda \approx 6796$ Å, which appears in the spectra after a high bombardment dose, is a manifestation of a surface mechanical exciton in the field of inhomogeneously distributed defects. Such states have apparently been observed in the exciton reflection and photoluminescence spectra of CdS crystals after electron bombardment and annealing.[5,7] In general, the spectral manifestations of surface mechanical excitons are determined by the properties of the well and also by the damping.

[1)] In most of the crystals studied, the maximum of this structure is usually at $\lambda \approx 6799$ Å, but in several samples I_S lies 1-2 Å from this point.

[2)] Strictly speaking, we cannot completely rule out at this stage of the research the possibility that the formation of the structure in the I_S region is affected by the capture of excitons by molecules adsorbed on the surface or by a possible intensification of forbidden exciton transitions in the surface electric field.

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