

# Detection of quasi-surface excitons in the reflection spectra of layered $\text{BiI}_3$ single crystals

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Quasi-surface excitons are observed for the first time in the reflection spectra of layered  $\text{BiI}_3$  semiconductors.

Surface excitons were predicted by Selivanenko<sup>1</sup> and Pekar<sup>2</sup> and their dynamics was developed by Sugakov.<sup>3</sup> The possibility for the existence of quasisurface excitons in molecular lattices was pointed out by Tovstenko.<sup>4</sup> The energy levels of surface excitons are situated outside the exciton band, whereas the levels of quasi-surface excitons are located inside it. The former have been reliably detected in the spectra of molecular crystals,<sup>5–7</sup> whereas the latter thus far have not been observed.

Our purpose in this study was to detect quasi-surface excitons in semiconductors. At  $T = 4.2$  K in  $\text{E} \perp \text{C}$  polarization we studied the reflection spectra of layered  $\text{BiI}_3$  single crystals in the region of excitonic transitions with allowance for the controllable states of the surface.

The samples were obtained by Bridgman's method. The state of the surface was altered by mechanical grinding and polishing, treatment with ethyl alcohol, and cleavage with a chisel along the cleavage surface in air and with a knife in liquid helium. In the latter case, special attention was given to the possibility of avoiding deformations. Although the surface of the samples obtained by cleavage with both methods were

mirror-smooth, small inclusions in the form of islands, formed by residues of the upper layers, appeared nevertheless at some sites due to cleavage in liquid helium.

The reflection spectra were recorded using the apparatus described in Ref. 8 with a spectral resolution better than 1 Å.

As is well known, the surface of real crystals contains an abundance of different types of structural defects: cracks, dislocations, vacancies or groups of vacancies, foreign atoms that come to the surface, adsorbed atoms and molecules, etc. As a result, the spectra of the surface excitonic states are very sensitive to the state of the surface.

As expected, the reflectivity of BiI<sub>3</sub> single crystals which were treated with ethyl alcohol and mechanically ground and polished turned out to be lower than that of the cleaved single crystals. The excitonic reflection spectra of the former single crystals reproduced those described previously.<sup>9</sup> We have therefore focused our attention mainly on the study of the spectra of the cleaved samples. Typical curves are shown in Fig. 1. Curve 1 shows the reflection spectra of crystals cleaved in air; curve 2 shows the same spectra for crystals cleaved in liquid helium. In the first case we see the usual dispersion curve  $R(\lambda)$  with a structural feature in the form of a small dip at  $\lambda = 642$  nm in the long-wavelength wing of the fundamental oscillation. This dip, which coincides in frequency with the peak of the absorption and photoluminescence bands, is associated with the surface defects of the crystal lattice.<sup>10</sup> The stronger and weaker oscillations, whose reflection peaks are situated at  $\lambda = 598.0$  and  $\lambda = 568.2$  nm, correspond to the ground state  $n = 1$  and the excited state  $n = 2$  of the allowed "direct" exciton, respectively.<sup>9</sup> The inflection point of the first oscillation is located at  $\lambda = 591.2$  nm and its half-width amounts to 39.6 meV.

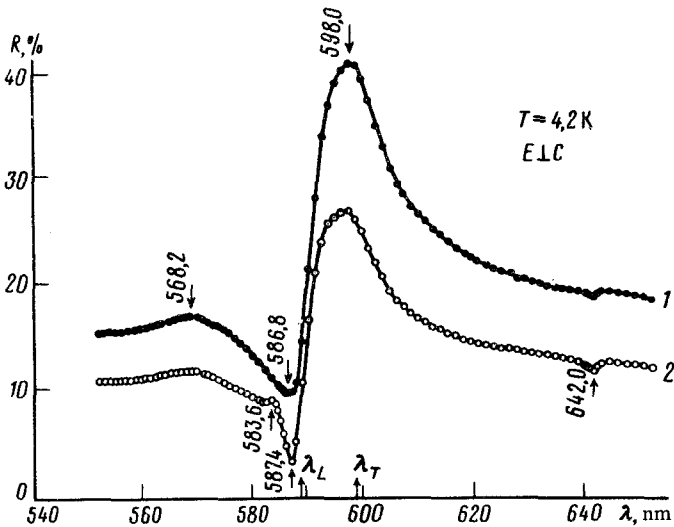


FIG. 1. Excitonic reflection spectra of layered BiI<sub>3</sub> single crystals cleaved in air (1) and in liquid helium (2).  $T = 4.2$  K;  $E \perp C$ . ( $\lambda_L$  and  $\lambda_T$  are the wavelengths of optical transitions for longitudinal and transverse excitons, respectively<sup>11</sup>).

In the second case, we have an atomically pure surface that is protected from contamination by the external medium, which accounts for the slightly different spectra. The entire curve  $R(\lambda)$  dips significantly due to light-scattering defects produced by the cleavage. We clearly see a sharp drop in intensity and a long-wavelength shift of the minimum by 2.2 meV, although the energy position of the peak of the first oscillation remains constant, a decrease of its half-width by 3.6 meV, and an insignificant increase in the depth of the dip at  $\lambda = 642$  nm. In addition to these changes, a new peak appears at  $\lambda = 583.6$  nm on the short-wavelength side of the minimum in the main excitonic band, which was also detected by Komatsu *et al.*<sup>11</sup> The fact that this band has been observed in the reflection spectra of only the samples cleaved in liquid helium indicates that this band is linked to the atomically pure surface. The following experimental data lend additional support to this assertion: (a) the high sensitivity of the intensity of the 583.6-nm band to the surface state, (b) its shift toward lower energies as a result of the deposition of oxygen on the surface of the cooled sample, and (c) return to the starting energy position when the oxygen is removed by heating the sample to 60 K.<sup>11</sup> Since the depths of the dips at  $\lambda = 642$  nm in the spectra represented by curves 1 and 2 are approximately the same, the defects responsible for them cannot be the reason for the appearance of this band.

Curve 2 in Fig. 1 shows that the energy position of the reflection peak at  $\lambda = 583.6$  nm falls in the band of volume excitonic states between the states  $n = 1$  and  $n = 2$  on the short-wavelength side of the position of the longitudinal exciton ( $E_L = 2.105$  eV; Ref. 11). Therefore, the band under study cannot be linked to purely surface excitons,<sup>11</sup> since the energy levels of the latter lie outside the region of the continuous excitonic spectrum.<sup>12</sup> Its appearance also cannot be linked to the macroscopic step of the surface layer examined in Ref. 13, since the structural features predicted in this study are not the same as those observed experimentally in many samples cleaved in liquid helium. It also seems unlikely that the nature of this band can be explained by invoking Sugakov's<sup>14</sup> theory, which examines the creation of longitudinal excitons because of the presence of imperfections in the crystal lattice in view of its dependence on the atomically pure surface. It is also not associated with surface polaritons,<sup>15</sup> since it appears in the reflection spectra under normal incidence of light. All these factors taken collectively allow us to assert that the new band at  $\lambda = 583.6$  nm is attributable to quasi-surface excitons predicted in Ref. 4.

The absence of a 583.6-nm band in the reflection spectra of a sample with a natural surface and a sample freshly cleaved in air can be explained by its broadening due to the inhomogeneity of the oxidized surface, screening of the exciton-surface interaction potential<sup>16</sup> (if the carrier density at this surface is high), and damping<sup>4</sup> caused by scattering of the excitons.

It can thus be asserted that the quasi-surface excitons that are formed account for the new band at  $\lambda = 583.6$  nm detected at  $T = 4.2$  K in E $\perp$ C polarization in the reflection spectra of BiI<sub>3</sub> single crystals cleaved in liquid helium.

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