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Influence of Mn and Cr impurities on quasi-surface exciton states of BiI_3 layered single crystals

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Abstract. The influence of Mn and Cr impurities on quasi-surface excitons of BiI_3 single crystals was studied. The broadening of their band was found which may be caused by ionization of quasi-surface excitons by the electric field of Mn^{2+} and Cr^{3+} ions.

Keywords: layered crystals; quasi-surface excitons; influence of Mn and Cr impurities.

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Quasi-surface excitons were theoretically predicted by Tovstenko [1] for molecular lattices. They were experimentally found at the temperature T = 4.2 K in light polarization $\vec{E} \perp \vec{C}$ by Lisitsa and Motsnyi [2] in the reflectance spectra of BiI_3 layered single crystals with atomically clean surface. In connection with problems of spintronics [3,4], it was interesting to study the influence of Mn and Cr impurities introduced as Mn^{2+} and Cr^{3+} ions into BiI_3 crystal lattice and placed instead of Bi^{3+} ions [5] on quasi-surface excitons. This was the aim of the present work.

Pure (specially non-doped) and doped (with 1 mass % Mn and 1 mass % Cr impurities) BiI_3 single crystals were grown by the Bridgman method. The concentration of paramagnetic impurities was estimated using electron paramagnetic resonance signals. It was $\sim 10^{18}$ cm^{-3}. The samples with dimensions $5 \times 5 \times 0.5$ mm^2 were obtained by breaking off a bulk crystal with a blade. Special attention was paid to avoid the deformations. The atomically clean surface was obtained by taking off the layers with the scotch tape in cold helium vapor or with a special knife in liquid helium. The samples had the mirror-smooth surface. The reflectance spectra were registered with experimental setup based on PGS-2 spectrograph with a spectral resolution better than 1 Å.

The typical reflectance spectra are shown in Fig. 1. Curve 1 corresponds to non-doped samples. Curves 2 and 3 correspond to samples doped with Mn and Cr, correspondingly. The band at λ = 5836 Å is related to quasi-surface excitons [2]. It is observed only in reflectance spectra of samples taken off in cold helium vapor or cleaved in liquid helium. This indicates that the band at λ = 5836 Å is related with atomically clean surface. Additional argument in favor of this statement may be high sensitivity of the band to surface conditions. It shifts to low energies at deposition of oxygen on the cooled sample surface and turns back to the initial energy position when oxygen is removed with heating up to 60 K [6].

The band at λ = 5836 Å appears as a broadened band in reflectance spectra of BiI_3 samples containing Mn^{2+} and Cr^{3+} ions. It should be noticed that this band was not observed when the samples were cleaved in air.

Thus, the experimental data obtained indicate that the band at λ = 5836 Å caused by atomically clean surface.

Let us analyze the obtained data in more details. It is well known [7,8] that the band of surface exciton states is splitted from the band of the three-dimensional excitons due to some surface disturbances much more than certain

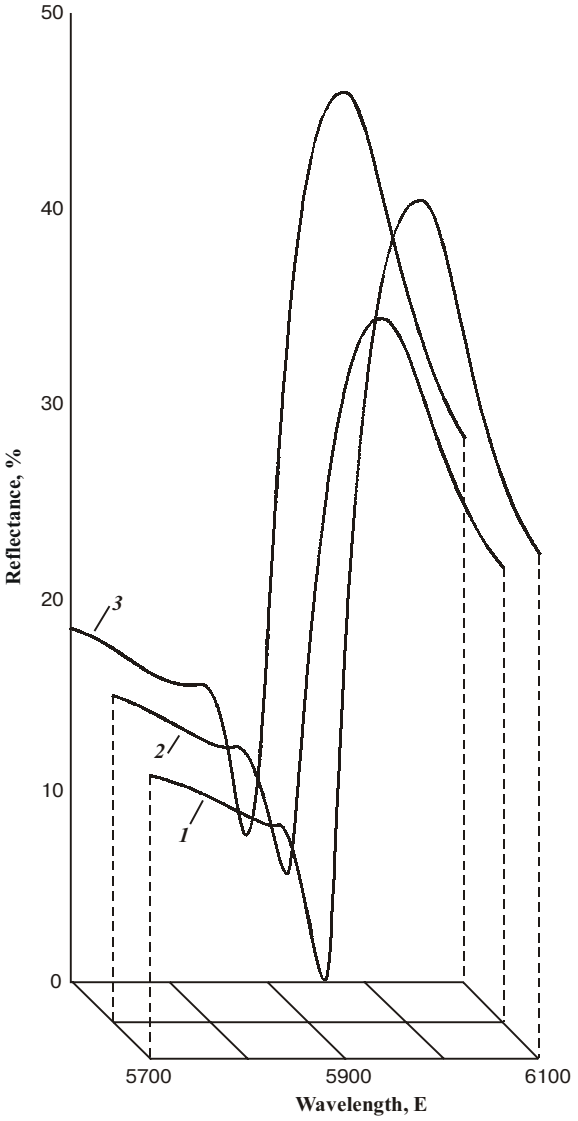

Fig. 1. Exciton reflectance spectra of BiI_3 single crystals cleaved in liquid helium: *1* – pure (specially non-doped); *2*, *3* – containing Mn^{2+} and Cr^{3+} ions, respectively, with the concentration 10^{18} cm^{-3}. T = 4.2 K, $\vec{E} \perp \vec{C}$.

value ones. The position of surface exciton levels is determined by the following formula [9,10]:

$$E_{\mu}^{surf.} = E_{\mu}(0) + \frac{(\Delta - M_{\mu})^2}{\Delta}. \qquad (1)$$

Here $E_{\mu}(0)$ is the energy position of the bottom of μ band of the three-dimensional excitons; $\Delta = (E_0' - E_0)$ is the difference between energies of excited molecules located near the surface and in the bulk of crystal; M_{μ} is some value proportional to the width of the three-dimensional exciton band. It is easy to see, if $|\Delta| > |M_{\mu}|$, then there is the possibility of existence of surface excitons together with the three-dimensional ones. In this case, the energy levels of surface excitons respective to the exciton band are determined by Δ parameter. If Δ is negative (the excitation energy of molecules at surface less than the excitation energy in the crystal depth) the level of surface exciton is located below the exciton band. Such situation is typical, for example, for II-VI compounds [11], GaAs [12] and others. However, if Δ is positive the surface exciton level is located above the exciton band, which is typical for the most of molecular crystals [13]. Moreover, at definite correlations between Δ and M_{μ} parameters this level can get into the exciton band causing the formation of quasi-surface exciton states [1,14]. Consequently, the appearance of quasi-surface exciton band in BiI_3 reflectance spectra indicates that the energy of the excited surface layer packet is larger than the energy of the bulk layer packet. This can be caused by both strong anisotropy of chemical bonding in the BiI_3 crystals and unusually small radius of Wannie-Mott exciton as for semiconductors (< 10 Å).

It should be noticed that the band at λ = 5836 Å was also registered by authors [15] in absorption and reflectance spectra of high quality thin layers of BiI_3 single crystals with the thickness 540, 300 and 70 Å (T = 4.2 K; $\vec{E} \perp \vec{C}$) obtained by hot wall technique on PbI_2 and CdI_2 substrates. They established that this band disappeared after deposition of PbI_2 thin layer on the BiI_3 film while the band of the direct three-dimensional exciton transition (n = 1) did not have any changes. This is in a very good agreement with data obtained.

The absence of the band at λ = 5836 Å in reflectance spectra of samples with natural and just cleaved in air surface can be caused by its broadening at the expense of inhomogeneity of oxidized surface. Together with the first reason, there may be another one due to screening of the interaction potential of exciton with surface [16] in assumption that the concentration of carriers in such surface is higher than in the bulk.

At last, the broadening of quasi-surface exciton band in crystals with paramagnetic impurities may be caused by their ionization by the electric field of Mn^{2+} and Cr^{3+} ions. Similar situation was concidered for three-dimensional excitons in crystals with charged impurities [17].

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