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Exciton Spectra of BiI3 bulk crystals

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The luminescence, reflection and absorption spectra of layered BiI_3 crystals on samples of different quality are studied in a wide temperature range. Based on the data obtained, the parameters of the direct exciton, which has a high oscillator strength, are estimated.

Keywords: Bismuth(III) iodide, exciton, localized states

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1. Introduction

Optical and electric properties of a layered rhombohedral bismuth(III) iodide crystal have long since been attracting attention. This crystal is considered as a promising topological insulator, a transition of the metal–insulator [1] type occurs in BiI_3 under pressure. Some papers study the usability of BiI_3 as a material for photovoltaic cells and some other applications [2,3]. According to [4], bulk BiI_3 is a non-direct-band crystal with the band gap of 1.67 eV. The band gap for a direct optical transition is significantly larger, the reflection and absorption spectra in the region of 2.05 eV feature a free exciton stripe (FE). Bismuth(III) iodide spectra were studied both on bulk crystals and on microcrystal injected into crystal and glass matrices [5–7]. A technology for the making of monolayers of BiI_3 [8] is being developed recently. According to [8,9], dispersion and mutual location of electron bands in a monolayer and in thicker BiI_3 crystals differ significantly.

At the early stage of study of BiI_3 optical properties, it was supposed that a stable group of lines, usually observed in the absorption and luminescence spectra, refers to the bound state of two same-sign charge carriers [10,11]. This supposition was not subsequently proven. At present, this group of lines is interpreted as a spectrum of stacking fault excitons (SFE) [5,6]. Stacking faults (SF) are caused by violations in the regular alternation of BiI_3 layers, each of which consists of four atomic layers. An elementary cell extends to four BiI_3 layers, due to which stacking faults cause elementary cell distortion. Domains of different thickness with the D_{3d} symmetry may occur in the BiI_3 lattice having the C_{3i}^2 symmetry. Such domains also bind excitons, since the band gap BiI_3 decreased upon transition from C_{3i}^2 to D_{3d}.

This paper studies the typical spectra for bulk samples of BiI_3 having different quality, and their temperature behavior in order to clarify the origin of certain spectrum elements and parameters of exciton states.

2. Experiment details

BiI_3 crystals were grown from bismuth(III) iodide powder obtained by heating a mixture of iodine and bismuth powders in vacuum to 300°C. Then the BiI_3 powder with a small amount of crystalline iodine was slowly heated in vacuum to 350°C in a temperature-gradient furnace. BiI_3 monocrystals in the shape of plane hexagons or their fragments grew in the cold region of the furnace. During recording of reflection and luminescence spectra, the light ray direction was close to the normal line to crystal layers.

3. Results and discussion

The absorption spectrum of BiI_3 has five narrow lines of bound excitons usually designated as P, Q, R, S and T. In luminescence, one can usually see the R, S and T lines, which refer to SFE. The P and Q lines, apparently, should be interpreted as the radiation of excitons bound on fine impurities. Let us consider the low-temperature luminescence spectra of BiI_3 given in Fig. 1. Radiation of the R, S and T lines prevails in the spectrum of sample 1. The spectrum of sample 2, in addition to these lines, has wider intensive stripes II and III that refer to excitons localized in mesoscopic domains with the D_{3d} symmetry [12]. The spectrum of sample 3 has one more stripe I of identical origin. Attention should be paid to the fact that the T line in the radiation of sample 3 is more intensive than the other SFE lines. This is probably due to the high SF concentration in sample 3. In this case the SFE, moving in the layers' plane, manage to relax to deeper SF levels within their lifetime. The spectrum of sample 4 has stripes I, II and III, while the SFE radiation is weak. Temperature at which the SFE lines are no longer observed varies from sample to sample. The luminescence spectra of some samples have wider stripes with the maxima of 1.76 and 1.45 eV, which should be referred to native defects, in particular, iodine vacancies typical for BiI_3.

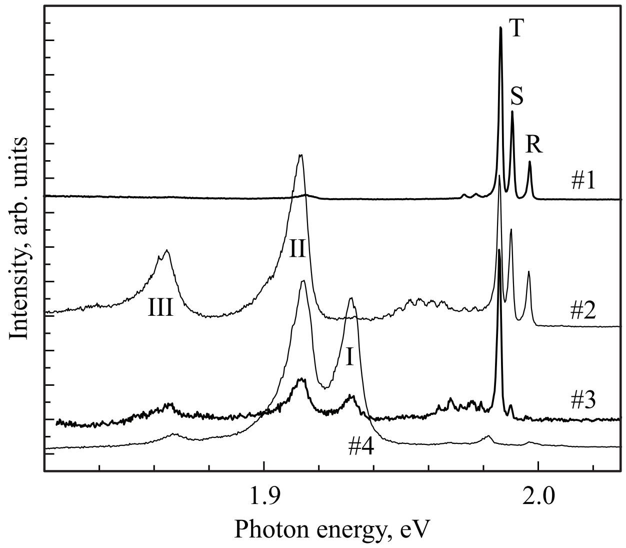

Figure 1. Luminescence spectra of BiI_3 (samples 1–4) at $T = 5\,K$. Lines R, S, T refer to stacking fault excitons (SFE), stripes I, II, III refer to excitons of domains with the D_{3d} symmetry.

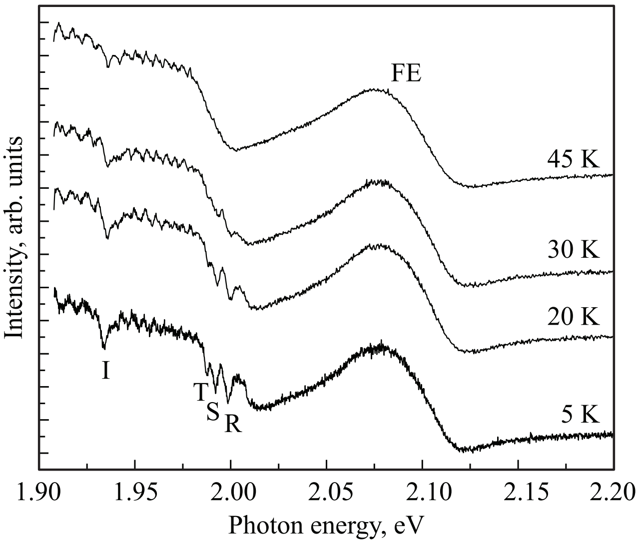

Figure 2. BiI_3 spectra obtained in the reflection geometry in the temperature interval of 5–40 K. FE is the contour of free exciton stripe.

Figure 2 shows the BiI_3 spectra obtained in the reflection geometry. In the temperature interval of 5–45 K, the contour of FE reflection varies little, the SFE lines are already absent at $T = 45\,K$. In addition to FE and SFE, this spectrum has stripe I. It should be noted that the SFE lines and stripe I are observed because the crystalline plate absorbs the light reflected from the substrate. Figure 3 shows that when temperature rises, the SFE lines move towards higher energies, above $T > 40\,K$ there is an abrupt increase in continuous absorption that can be explained by the presence of one more indirect transition with an energy close to the energy of a direct FE.

Judging by the dependence of FE energy on temperature, the band gap of BiI_3 increases in the interval of 5–60 K, probably due to larger distance between crystalline layers. The band gap narrows upon further heating of the crystal.

Analysis of the shape of the FE reflection stripe shows that TO–LO splitting of the FE lower level in BiI_3 is about 50 meV. Let us state for reference that in the conventional „exciton“ crystals of CdS and ZnO the TO–LO splitting of the exciton is equal to 2 and 10 meV, respectively. This means a greater force of the oscillator of the exciton optical transition in BiI_3. The contour

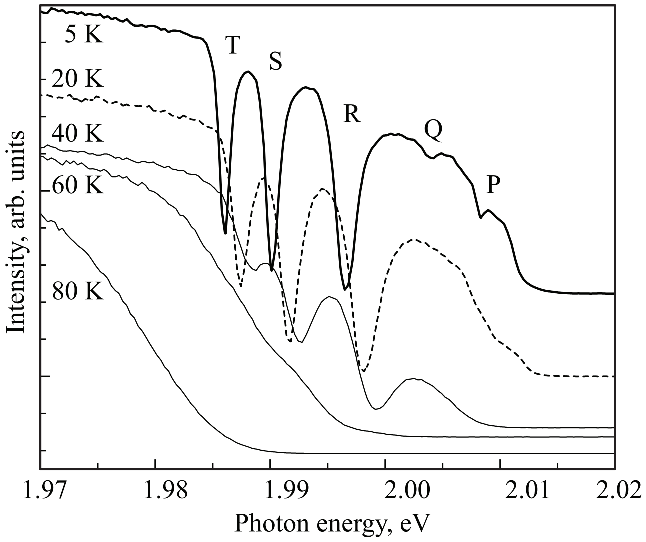

Figure 3. BiI_3 absorption spectra in the temperature interval of 5–45 K. R, S and T lines are the stacking fault excitons (SFE), P and Q lines are excitons bound on fine impurities.

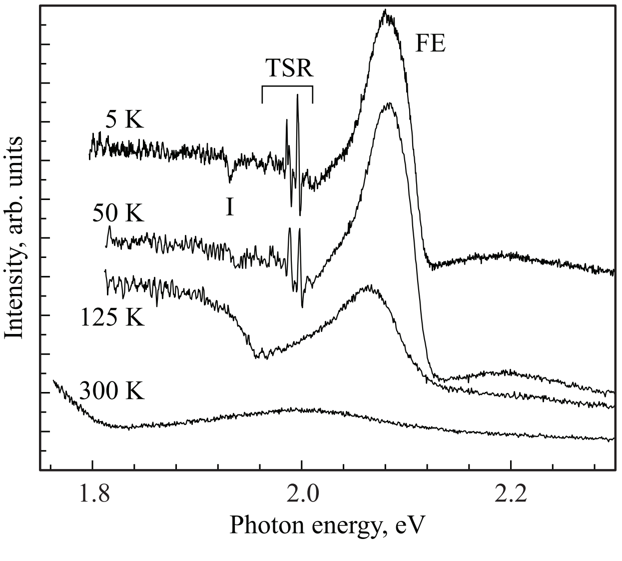

Figure 4. Evolution of the BiI_3 crystal spectrum obtained in the reflection geometry in the temperature interval of 5–300 K.

of BiI_3 exciton reflection is clearly seen in the reflection spectrum even at room temperature (Fig. 4). A change of the FE reflection contour depending on temperature and comparison of this dependence with similar measurements on crystals with a known exciton bond energy make it possible to draw certain conclusions about the exciton parameters in BiI_3. If the average value of dielectric permeability between it low-frequency and high-frequency values is taken, the bond energy and the FE radius can be estimated as 100 meV and 0.7 nm, respectively, and reduced effective mass as $1.1m_0$.

It should be noted that radiation of a direct FE in the luminescence of BiI_3 is not observed. The reason is probably the excitation relaxation into the indirect transition region.

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Conflict of interest

The authors declare that they have no conflict of interest.

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