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Saddle point excitonic resonances in BiI_3 layered single crystals

O.O. Kudryavtsev, M.P. Lisitsa, F.V. Motsnyi, S.V. Virko
Institute of Semiconductor Physics, NAS of Ukraine
45, prospect Nauky, 03028 Kyiv, Ukraine, E-mail: motsnyi@sun.semicond.kiev.ua

Abstract. Excitonic resonances near the critical saddle point of M_1 sort by van Hove have been revealed for the first time in the BiI_3 layered semiconductor. Their main parameters are estimated.

Keywords: reflectance spectum, saddle point, resonances, hyperbolic excitons.

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1. Introduction

Excitons related with a saddle point (the so-called «hyperbolic excitons») were theoretically predicted by Phillips [1,2] more than 30 years ago. Despite that, the hyperbolic excitons are studied rather weakly. Such excitons can be observed in optical spectra as bands situated near energies considerably exceeding a band-gap width, E_G [1-8], which makes some difficulties for searching them in view of absence of detailed calculations for energy band structures characterizing most of substances.

On the other hand, the BiI_3 energy band structure calculated in [9] with the empirical pseudopotential method without accounting spin-orbit interaction is rather compicated. It consists of 26 subbands of the valence band and 9 subbands of the conduction one with a set of branching in every band. Therefore, one can expect to observe the saddle point excitonic resonances in this semiconductor. Moreover, as known [1], these can be favored by heavy atoms, which are, in particular, the Bi and I atoms. In connection with stated above, it was interesting to analyse bands near 3.804 and 4.103 eV that have a shape of clear-cut features, namely, intensive peaks in BiI_3 reflection spectra (RS) [10–12], from the standpoint of the mentioned approach.

The main purpose of this work was to detect hyperbolic excitons in BiI_3 layered single crystals using temperature investigations of RS in the photon energy range of $h\nu > E_G$.

2. Experimental

BiI_3 single crystals were grown by the Bridgman technique. Prepared samples had the shape of rectangular plates with optical *C*-axis orientated normally to the spalling plane. To avoid any surface influence, we used only the atomically pure planes. These were prepared either by spalling samples with a knife in liquid helium or by peeling layers with a scotch in cold helium vapor. The surface prepared in such manner has mirror reflection, special care was taken into account to avoid sample deformation. Light of stabilized incandescent filament lamp was directed onto the sample under an angle less than 5° relatively to *C*-axis. Reflection spectra were recorded using PGS-2 spectrometer with resolution 0.15 meV and $E \perp C$ polarization at temperatures 5–300 K. Accuracy of temperature measurements was ±0.5 K. Data upon refraction index dispersion $n(h\nu)$ and absorption æ$(h\nu)$ in $E \perp C$ polarization at 4.2 K were derived using the Kramers – Kronig classical relations since spatial dispersion effects in BiI_3 are not essential [11,12].

3. Results and discussion

Typical RS as well as $n(h\nu)$ and æ$(h\nu)$ dependences for BiI_3 single crystals with atomically pure surfaces in the range of energies $h\nu$ from 1.5 to 5.5 eV at 4.2 K are shown in Fig. 1. Along with well-known bands 2.098, 2.206 and 2.214 eV caused by free [10–12] and quasi-surface [12,13] excitons, respectively, there are 3.804 and 4.103 eV bands, which are also found in RS of samples with natural surface. Therefore these bands cannot be associated with any surface state. The absorption coefficients at the peak positions are equal to $5.0 \cdot 10^5$ and $3.7 \cdot 10^5$ cm^{-1}, respectively. These values are rather large and cannot be caused by impurities or other defects of a crystal lattice.

The influence of the temperature on 3.804 and 4.103 eV bands is shown in Figs 2 and 3. It is seen that with increasing temperature the both bands change considerably. Their maxima remain on their places up to $T \approx 45$ K and at $T > 45$ K begin to shift into the lower energy side with the rate of

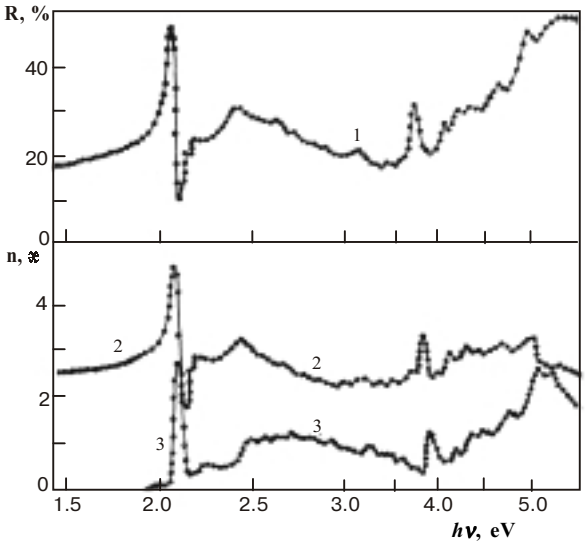

Fig. 1. The reflectance spectra (1), dispersion of the reflective index $n(h\nu)$ (2) and absorption index $æ(h\nu)$ (3) of BiI_3 layered single crystals with atomically pure surface at T = 5 K and **E** ⊥ **C**.

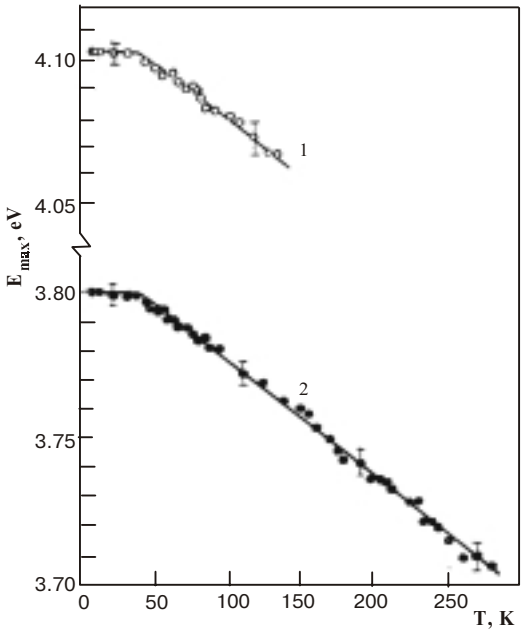

Fig.3. Temperature dependence of the reflectance maxima of the bands 3.804 and 4.103 eV of BiI_3 layered single crystals at **E** ⊥ **C**.

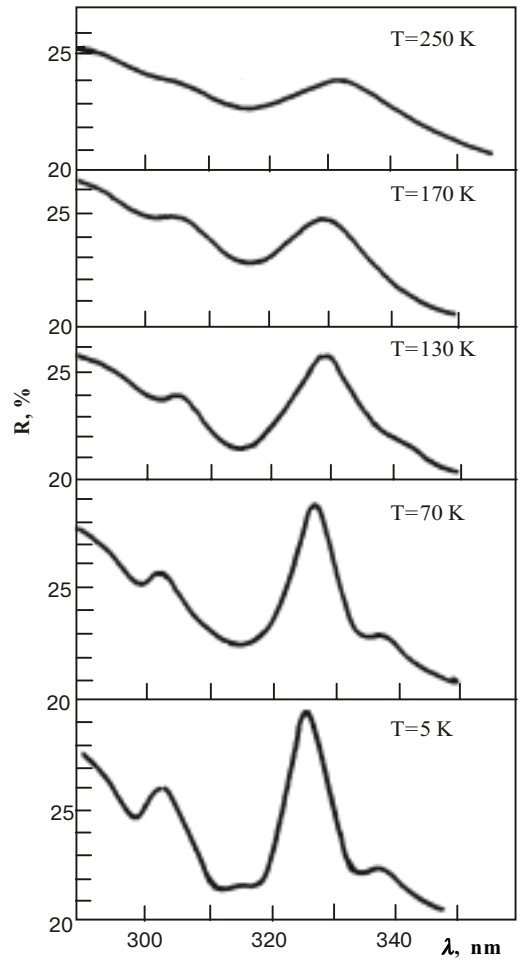

Fig. 2.Influence of the temperature on the behaviour of the reflectance bands 3.804 and 4.103 eV of BiI_3 layered single crystals at **E** ⊥ **C**.

dE_{max}/dT = -3.6·10^{-4} eV/K (Fig. 3). The peaks obey a regularity found empirically in the form:

$$E_{max}(T) = E - 6.2 \cdot 10^{-4}\, T^2/(T + 240\ \mathrm{K})\ (\mathrm{eV}), \qquad (1)$$

where E is the energy position of considered bands at T = 5 K. It should be noted that this regularity was also found to be valid for hyperbolic excitons in GaSe [3].

Temperature broadening was possible to follow only for 3.804 eV band (Fig. 4). As background influence on the shape of this band appears to be essential at T = 140 K, we corrected its shape subtracting this background from the experimental reflection contour (see insert in Fig. 4). It is typical that 3.804 eV band halfwidth at T = 270 K exceeds more than twice its meaning at T = 5 K. It can be well described by the next empirical relation:

$$\Gamma(T) = (\Gamma_O^2 + A \cdot T^2)^{1/2}\ , \qquad (2)$$

where Γ_O = 85 meV, A = 150 meV^2/K^2.

Thus, the extremely large absorption coefficient values along with strong dependences of 3.804 and 4.103 eV bands on temperature are sufficient signs of their excitonic nature.

Taking E_G = 2.242 eV for BiI_3 at T = 4.2 K [10,12] one can notice that the excitonic levels corresponding to these bands are situated near 1.56 and 1.86 eV above the fundamental absorption edge. Strictly speaking, these levels can be caused by both parabolic excitons stemmed from more deep subbands of respective valence and conduction bands and by hyperbolic excitons.

As known [1,2], during interband transition in the van Hove M_0 point, the density of states changes with energy E as $dN/dE \sim (E - E_G)^{1/2}$, while during transitions near the critical saddle point of M_1 sort it behaves as $dN/dT \sim [C - b\cdot(E_c - E)]^{1/2}$ and $dN/dE \cong C$ for $E > E_c$ and $E > E_c$,

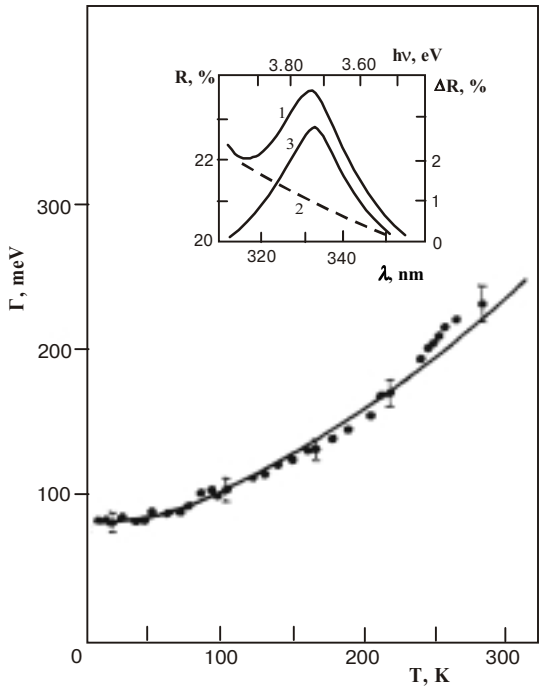

Fig. 4. Dependence of halfwidth of the reflectance band 3.804 eV on temperature of BiI_3 layered single crystals at $\mathbf{E} \perp \mathbf{C}$.

respectively, where E_c is the energy of the van Hove M_1 saddle point, and C, b are some constants [1].

On the other hand, $K \sim æ \sim dN/dE$, therefore as a typical sign of difference for hyperbolic excitons from the parabolic ones could serve, for instance, the presence of plateau on curves $K(h\nu)$ or $æ(h\nu)$ from the short-wave side of an excitonic resonance. Such plateau is realy observed in absorption spectra of hyperbolic excitons in layered GaSe [3]. It can be simply watched on the curve $æ(h\nu)$ for layered BiI_3 at the energy $h\nu = 4.4$ eV, too (Fig.1, curve 3). Validity of this conclusion is also confirmed by the next factors:

1. For all known semiconductors, coefficients of a temperature shift of deeper valence subbands and higher conduction ones are less than those of subbands forming the fundamental absorption edge. In the case of BiI_3, dE_G/dT is equal to $+8 \cdot 10^{-3}$ eV/K and $-1.3 \cdot 10^{-4}$ eV/K at $T \le 45$ and $T > 45$, respectively. Therefore, the different temperature behaviour of $E_{\max}(T)$ and $E_G(T)$ at $T \le 45$ K and exceeding by 1.7 times the rate of longwave shifting the former as compared to the latter at $T > 45$ K cannot be explained by contribution of above subbands in appearing 3.804 and 4.103 eV bands.
2. Temperature broadening of both bands are extraordinarily strong. For example, it reaches 153 meV for band 3.804 eV at 270 K and considerably exceeds respective broadening of the main excitonic absorption band ($n = 1$) [10,12].
3. The temperature shift of considered peaks in BiI_3 are identical to that of hyperbolic excitons in GaSe [3].

Consequently, all taken together enables us to conclude that 3.804 and 4.103 eV bands belong to the van Hove M_1 singularity and not to the M_0 one, i.e. to hyperbolic excitons.

A possible reason for such appearance of found excitonic resonances may be spin-orbit splitting of BiI_3 valence band near a saddle point. The saddle point excitons splitted by spin-orbit interaction have been detected earlier in alkali metal iodides [14].

In view of absence of rigorous theory for the saddle point resonance, the hyperbolic exciton binding energy value was estimated like that for M_0- excitons considering $E_{ex}^{hyp} = E_{M1} - E_{\max}$. Taking $E_{M1} = 4.4$ eV at $T = 5$ K one can obtain $E_{ex}^{hyp} = 0.6$ eV and $E_{ex}^{hyp} = 0.3$ eV for excitonic resonances near 3.804 and 4.103 eV, respectively.

At last, one estimate more. The halfwidth of the 3.804 eV absorption band is equal to 85 eV at 5 K and by the factor 2.4 exceeds that of the main excitonic band with $n = 1$. Assuming $\tau \sim 1/\Gamma$ one can conclude that the lifetime τ_{ex}^{hyp} of hyperbolic excitons in BiI_3 is 2.4 times less than that of the parabolic ones. It is obviously caused by dynamic instability of considered excitons near the saddle point of the M_1 sort. Unfortunately, available estimate of the band structure for BiI_3 [9] do not enable us to identify it with definite points of the Brillouin zone.

Conclusions

1. Optical characteristics $n(h\nu)$ and $æ(h\nu)$ of BiI_3 layered single crystals with an atomically pure surface are determined in the range of energies 1.5–5.5 eV using light polarization $E \perp C$ at 4.2 K.
2. Excitonic resonances associated with the van Hove critical saddle point of the M_1 sort are found for the first time at investigation of reflection spectra of BiI_3 layered semiconductor samples with atomically pure and natural surfaces in the range of energies $h\nu > E_G$.
3. The binding energies of hyperbolic excitons were estimated that are equal to 0.6 and 0.3 eV, respectively. It is shown that lifetime of hyperbolic excitons in BiI_3 is 2.4 times less than that of the parabolic ones. It was assumed that the small value of the hyperbolic exciton lifetime is caused by dynamic instability of excitons near the van Hove critical saddle point of M_1 sort.

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