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Effect of temperature variation on shift and broadening of exciton band in $Cs_3Bi_2I_9$ layered crystals

V.F. Machulin[1], F.V. Motsnyi[1], E.Yu. Peresh[2], O.M. Smolanka[1], and G.S. Svechnikov[1]

[1] *V. Lashkaryov Institute of Semiconductor Physics of the National Academy of Sciences of Ukraine 41 Nauky Ave., Kyiv 03028, Ukraine*
E-mail: motsnyi@sun.semicond.kiev.ua

[2] *Uzhgorod National University, Chemical Faculty, 46 Pidgirna Str., Uzhgorod 88000, Ukraine*

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The exciton reflection spectra of $Cs_3Bi_2I_9$ layered crystals is investigated in the temperature region 4.2–300 K with light polarization $\mathbf{E} \perp \mathbf{c}$. It is estimated that the energy gap E_g equals 2.857 eV (T = 4.2 K) and the exciton binding energy Ry is 279 meV. A nontraditional temperature shift of $E_g(T)$ for the layered substances is found for the first time. It is learned that this shift is described very well by the Varshni formula. A transition region in the temperature broadening of the half-width $H(T)$ of the exciton band with the increase of temperature is registered in the interval between 150 and 220 K. It is shown that this region may be identified as the heterophase structure region where ferroelastic and paraelastic phases coexist. A surge of $H(T)$ at the point of the ferroelastic phase transition (T_c = 220 K) is also observed.

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1. Introduction

$Cs_3Bi_2I_9$ crystals belong to an extensive family of little-studied three-component $A_3B_2X_9$ layered compounds (A are alkaline atoms, B = As, Sb, Bi, Fe, Cr, Mo, or W, and X = Br, Cl or I) [1,2], which are kindred to the well-known perovskites. Interest in these crystals is caused by the manifestation of a ferroelastic second-order phase transition at the temperature T_c = = 220 K [2–4] accompanied by a reversible change of crystal symmetry class from hexagonal $6/mmm$ to centrosymmetric monoclinic $2/m$, the prediction of an incommensurate phase at $T < 220$ K [1,5], and the possibilities of practical use in recorder systems, pressure and γ-emission sensors, and acousto- and optoelectronics.

The optical data on $Cs_3Bi_2I_9$ crystals concern to the birefrigence [2], exciton states [6,7], phonon spectra [8], and low-temperature optical characteristics [9].

On the other hand, one of the important physical properties of layered crystals is the anomalous temperature dependence of energy gap $E_g(T)$, which increases at $T < T_m$ and decreases at $T > T_m$. For different layered crystals T_m varies within a temperature range of 30–45 K [10–14]. The phenomenon originates from high anisotropy of the chemical bonding due to the strong ionic–covalent bonding in separate sandwich layers and the weak van der Waals binding between neighboring sandwiches. This is confirmed by the presence of low-frequency optical vibrations in the Raman spectra of layered crystals [8,13,15–18] which determine the exciton–phonon interaction [14,19,20], spin–lattice relaxation [21], temperature dependence of electron paramagnetic resonance (EPR) spectra [21,22], and also a large difference in linear broadening coefficients in directions perpendicular to the layers and in the planes of the layers [23]. Anomalous temperature behavior of $E_g(T)$ can be explained on the basis of the essential influence of anharmonic optical vibrations of the layered lattice starting at low temperature and of low-frequency optical phonons starting at higher temperatures [14,24]. However, this temperature dependence has not been studied for $A_3B_2X_9$ compounds in general and for $Cs_3Bi_2I_9$ crystals in particular.

The aim of this paper is to study the temperature behavior of the exciton band of $Cs_3Bi_2I_9$ layered crystals.

2. Experimental

$Cs_3Bi_2I_9$ layered crystals were grown by the Bridgman method. The peculiarities of this technology are given in [25,26]. Samples with dimensions approximately 7×5×0.02 mm were cut off from a bulk crystal in air with a blade. Special care was taken to avoid deformations. The samples had the mirror-smooth surface with optical **c** axis perpendicular to cleavage surface. The reflection spectra were measured in the heating regime. They were recorded with an automated experimental setup based on a MDR-23 monochromator in the energy interval of 2.0–3.5 eV in the temperature range of 4.2–300 K and with light polarization $\mathbf{E} \perp \mathbf{c}$. The energy resolution was better than 0.5 meV. The relative error of measurement of the reflection spectra did not exceed 3%. The temperature was stabilized with accuracy better than 0.1 K.

The resonance energies of the exciton absorption bands were determined from the inflection point of the exciton oscillation with quantum number $n = 1$ by setting the second derivative of the reflection coefficient with respect to energy equal to zero ($d^2R/dE^2 = 0$). The inflection point found in such a way coincides up to $T \le 200$ K with the one determined in the ordinary way as the half energy interval or the half distance on the reflectance scale between the extrema of the exciton oscillation. The half-width $H(T)$ of the exciton absorption band was found as the energy difference between the maximum and the minimum of the fundamental exciton oscillation. The insertion errors in the measured values of the temperature variations of the energy position of the exciton band $E_{ex}(T)$ and its half-width are insignificant [11] and do not influence their qualitative course.

3. Results and discussion

A typical reflection spectrum at 4.2 K and $\mathbf{E} \perp \mathbf{c}$ and the dependence of $[\varepsilon_2(\omega)\hbar\omega]^2$ as a function of energy $\hbar\omega$ for $Cs_3Bi_2I_9$ crystals are shown in Fig. 1. The intense oscillation with inflection point at energy 2.578 eV and the two shorter-wave length maxima at energies of 2.961 and 3.073 eV (Fig. 1,*a*) are caused by excitons in the ground state ($n = 1$) and interband electron transitions, respectively [6,7]. On the basis of this spectrum, the extrapolation by the Yahoda method*, and the Kramers–Kronig relations, we have previously [9] found the real $\varepsilon_1(\omega)$ and imaginary $\varepsilon_2(\omega)$ parts of the complex dielectric function $\varepsilon(\omega)$. Knowing $\varepsilon_2(\omega)$, we estimated the direct band gap E_g of $Cs_3Bi_2I_9$ crystals at 4.2 K and $\mathbf{E} \perp \mathbf{c}$. The dependence of $[\varepsilon_2(\omega)\hbar\omega]^2$ as a function of energy $\hbar\omega$ was constructed in accordance with [27] (Fig. 1,*b*). One can see three intense bands with maxima at energies of 2.548, 2.986, and 3.079 eV. The calculated spectrum satisfactorily correlates with the experimental reflection spectrum. The value of E_g in such a case is estimated as the energy of the cut off. It equals 2.857 eV. The binding energy Ry of the exciton is found as the difference between E_g and the maximum of the exciton band, that is Ry = 279 meV. It should be noted that Ry in the $Cs_3Bi_2I_9$ crystals is high, and higher than in basic BiI_3 (Ry = 144 meV) [19]. This may be explained by that fact that $Cs_3Bi_2I_9$ crystals are alkali halide compounds. In such substances the polar type of chemical bonding takes place, and therefore Ry may be high.

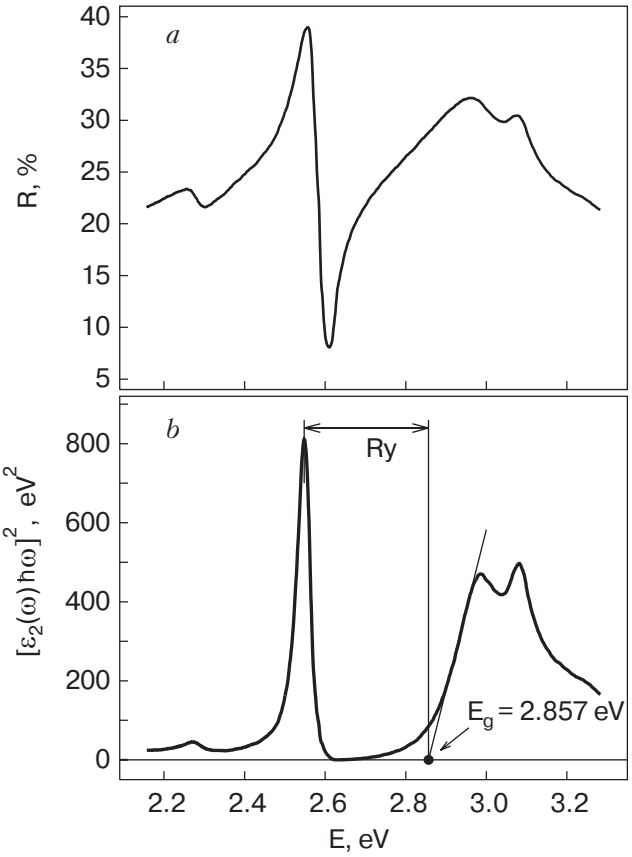

Fig. 1. Reflection spectrum (T = 4.2 K, $\mathbf{E} \perp \mathbf{c}$ (*a*) and $[\varepsilon_2(\omega)\hbar\omega]^2$ (*b*)) of $Cs_3Bi_2I_9$ layered crystals.

* The optical functions of a system of two noninteracting classical oscillators were simulated taking into account the traditional extrapolations by the Philipp–Taft and Yahoda methods. It was found that the functions are in good agreement with the model functions only in the second case.

The temperature shift of the energy gap $E_g(T)$ and the temperature dependence of the half-width $H(T)$ of the exciton absorption band of $Cs_3Bi_2I_9$ crystals are shown in Fig. 2. In Fig. 2,*a* the points are experimental data for $E_g(T)$ and the continuous curve represents $E_g(T)$ as obtained from the computation by the Varshni formula [28]

$$E_g(T) = E_g(0) + \frac{\alpha T^2}{T + \theta}, \qquad (1)$$

where $E_g(0) = 2.857$ eV, $\alpha = -7 \cdot 10^{-4}$ eV/K and $\theta = 258.654$ K. We would like to stress a few points: 1) the experimental results are described very well by this formula; 2) the energy position of the energy gap does not change at $T < 45$ K and shifts to the long-wavelength side with increase of temperature up to 300 K without any anomalies at $T_c = 220$ K. Such behavior of $E_g(T)$ is not peculiar to layered semiconductors but is typical for the majority of the well-studied ones, for example Ge, Si, SiC, A_2B_6, and A_3B_5. It can therefore be explained in the following manner. First, at low temperatures the mechanisms caused by the interaction of electrons and holes with acoustic and optical phonons are included and then at higher temperature the other mechanisms connected with the thermal expansion of the crystal lattice take place. It is very important that all mechanisms contribute with the minus sign.

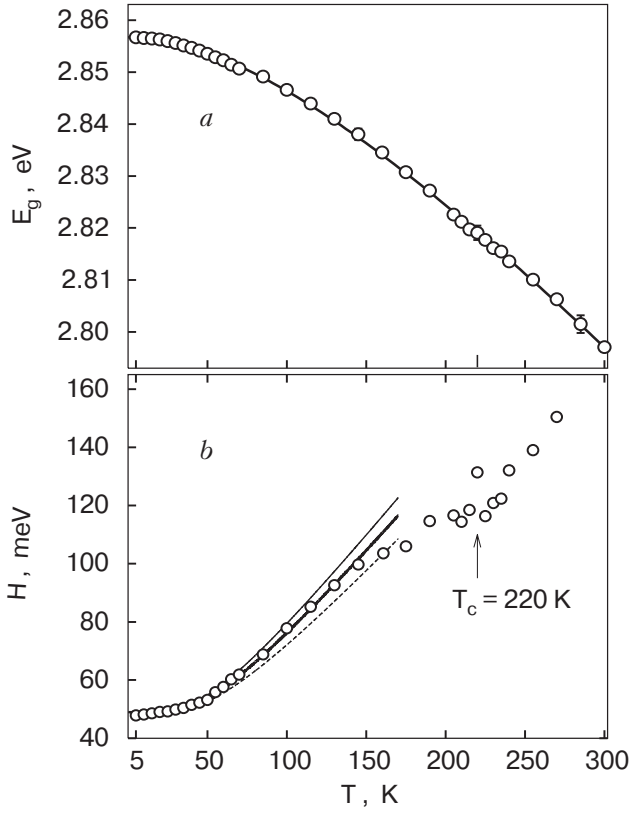

Fig. 2. Temperature shift of the energy gap $E_g(T)$ (*a*) and broadening of half-width $H(T)$ (*b*) of the exciton band of $Cs_3Bi_2I_9$ layered crystals.

The absence of an anomaly in the temperature shift of $E_g(T)$ allow us to suppose that the anisotropy of the optical properties in the monoclinic structure is not high. This conclusion correlates very well with the low intensities of the low-frequency doublets (33.4, 38.3), (44.3, 48.2) cm^{-1} in the Raman spectra at 4.2 K. Therefore $Cs_3Bi_2I_9$ crystals are not typical layered compounds. These crystals can be considered as layered semiconductors in the hexagonal phase and normal ones in the monoclinic phase.

Thus $Cs_3Bi_2I_9$ crystals demonstrate nontraditional temperature behavior of $E_g(T)$ for layered substances.

The experimental temperature dependence of the half-width $H(T)$ (points) of the exciton band of $Cs_3Bi_2I_9$ crystals is depicted in Fig. 2,*b*. With increasing temperature from 4.2 to 150 K the half-width increases nonlinearly from 48.9 to 99.7 meV. Then $H(T)$ begins to rise less sharply, forming a plateau (the transition region) up to $T < 220$ K with a surge at $T = 220$ K. After that $H(T)$ returns almost to the starting point at $T = 225$ K and increases linearly ($H(T) = k(T - 225\ \text{K}) + H_0$, where $k = 0.758$ meV/K and $H_0 = 116.3$ meV) in the temperature range $225\ \text{K} \le T \le 300$ K.

We made an effort to model the temperature dependence of the half-width of the exciton band. It was found that the half-width can be described at $T \le 150$ K by the following equation:

$$H(T) = H(0) \coth\left[\frac{\hbar\omega_{ph}}{2kT}\right], \qquad (2)$$

obtained by Toyozawa [29] for weak exciton–phonon interaction. Here $H(0)$ is the half-width at absolute zero temperature and $\hbar\omega_{ph}$ is the energy of the interacting phonon. The results of the modeling are given in Fig. 2,*b* for $H(0) = 48.92$ meV and two real optical phonons which were registered in Raman spectra [8] at 4.2 K. The calculated curves are localized above ($\omega_{ph} = 99.8\ cm^{-1}$) and under ($\omega_{ph} = 114.8\ cm^{-1}$) the experimental dependence. The best correlation between experiment and theory exists for an effective phonon with frequency 105.8 cm^{-1} (thick curve). Established dependence is essentially differed from $H(T)$ dependence of exciton band of BiI_3 classical layered semiconductor in which the phase transitions are absent and high exciton–phonon interaction takes place [14,24].

The deviation of experimental dependence $H(T)$ from the theoretical (2) and appearance of the transition region indicates the reconstruction of the monoclinic crystal lattice between 150 and 220 K. As

was shown in Ref. 30, the region 183–221 K corresponds to a heterophase structure where ferroelastic and paraelastic phases coexist. Therefore the whole transition region may be identified with the heterophase structure.

The appearance of a surge at $T = 220$ K is probably due to the ferroelastic phase transition (as $T = T_c$ [2–4]).

Thus the half-width of the exciton band may be used as a highly sensitive nondestructive probe for revealing a phase transition.

4. Conclusions

We have presented analyses of the effect of temperature variation on the exciton reflection spectra of $Cs_3Bi_2I_9$ layered crystals. It was found that these crystals are not typical layered ones. These crystals are layered semiconductors in the hexagonal phase and behave like conventional semiconductors in the monoclinic phase. We have registered the transition region in the temperature broadening of the half-width of the exciton band in temperature interval of 150–220 K and the surge at $T = 220$ K. Our analyses suggest that both phenomena are caused by the formation of the heterophase structure region and the ferroelastic phase transition, respectively.

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