PECULIARITIES OF EXCITON-PHONON INTERACTION IN LAYERED FERROELASTIC CRYSTALS ($Cs_3Bi_2I_9$)

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For the first time, we have found a new physical effect which is appeared as a change of the exciton-phonon interaction from a weak to strong one in the same sample with increase in temperature. We have explained this effect on the basis of the model which takes the reconstruction of the crystal lattice from a non-layered to layered one into account.

Many experimental and theoretical works were devoted to investigations of the exciton-phonon interaction in well-known molecular, alkali halide, and semiconductor substances. The data obtained are very valuable for understanding a lot of physical properties. In particular, they are necessary to explain the shape and shift of the exciton absorption and luminescence bands and the migration and localization of excitons. Concerning of the exciton-phonon interaction in a new numerous class of unique ferroelastic compounds, in which a spontaneous strain is brought about by a structural phase transition [1], it has been pooly studied else. As far as the authors know, there are only a few works [2, 3] in this area.

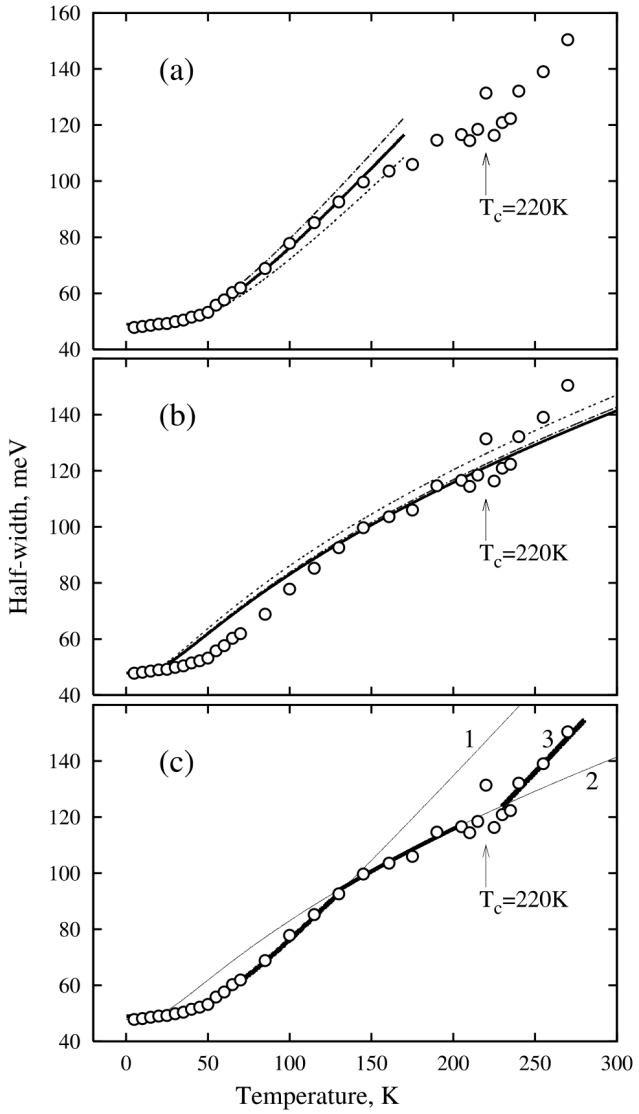
The scientific and applied interest in $Cs_3Bi_2I_9$ layered semiconductors is due to the appearance of a ferroelastic phase transition at $T_c = 220$ K [4–12], the search of an incommensurate phase at $T < 220$ K [5, 7, 8], the manifestation of a heterostructure region [9], the observation of a nontraditional temperature shift of the fundamental absorption edge [11, 12], the discovery of a giant thermodynamical optical effect near the ferroelastic phase transition [13], and a variety of possible applications in recording systems, pressure sensors, scintillation detectors of cosmic rays and high-energy particles, and acousto- and optoelectronics.

The present paper deals with a study of broadening the half-width of the exciton band (n=1) as a function of temperature with the aim to obtain information on the exciton-phonon interaction in $Cs_3Bi_2I_9$ layered ferroelastic crystals.

The crystals were grown by the Bridgman method. The reflection spectra of the samples with mirror-smooth surface in the polarization $\mathbf{E} \perp \mathbf{c}$ were recorded in the heating regime with an automated experimental setup [11]. The relative error of measurements of the reflection spectra did not exceed 3%. The temperature was stabilized with accuracy better than 0.1 K by a system "Utreks" worked out in the Institute of Physics of NASU.

The typical experimental temperature dependence of the half-width $H(T)$ (open circles) of the exciton band (n=1) of $Cs_3Bi_2I_9$ layered ferroelastic crystals is shown in Figure. It is necessary to note the following. When temperature increases from 5 to 150 K, the nonlinear broadening of exciton band is manifested. Then, with increase in temperature further up to $T < 220$ K, the broadening of the half-width begins to slow down, by forming a plateau in the transition region with a surge at the ferroelastic phase transition point $T_c = 220$ K. Finally, $H(T)$ increases again at $T > 220$ K. Thus, the data obtained can be considered independently in any of three temperature intervals indicated above.

For the explanation of such nontraditional temperature behaviour of the exciton band half-width, we made some efforts to analyze it on the basis of the



Temperature dependence of the half-width of the exciton absorption band (n=1) of $Cs_3Bi_2I_9$ layered ferroelastic crystals (open circles) and its fitting on the basis of formula (1) (5 K $\leq T \leq$150 K) with phonon frequencies of 114.8 (dotted line), 105.8 (solid line), and 99.8 cm^{-1} (dash-dotted line) (*a*), formula (2) (150 K $\leq T \leq$220 K) with phonon frequencies of 44.3 (dotted line), 47.9 (solid line), and 48.2 cm^{-1} (dash-dotted line) (*b*), and empirical relation (3) (220 K $\leq T \leq$300 K) K) (*c*). Curves *1* and *2* correspond to the final theoretical curve fitting with formula (1) ($\omega_{\rm ph}$=105.8 cm^{-1}) and formula (2) ($\omega_{\rm ph}$=47.9 cm^{-1}), respectively

Toyozawa theory [15]. In accordance with this theory, in the case of the weak or strong interaction of excitons with one sort of optical phonons $H(T)$ can be written as

$$H(T) = H(0) \cdot \mathrm{cth}\frac{\hbar\omega_{\rm ph}}{2kT} \quad (1)$$

or

$$H(T) = H(0) \cdot \sqrt{\mathrm{cth}\frac{\hbar\omega_{\rm ph}}{2kT}}, \quad (2)$$

respectively, where $H(0)$ is the exciton band half-width at $T = 0$ K, and $\hbar\omega_{\rm ph}$ is the energy of phonons interacting with excitons.

At temperatures 5–150 K, the exciton band half-width of $Cs_3Bi_2I_9$ layered ferroelastic crystals can be described by formula (1). The fitting curves are given in Figure,*a* for $H(0)$=47.82 meV and three sorts of phonons with frequencies of 99.8, 105.8, and 114.8 cm^{-1}, the first and third ones of which are real LO-phonons registered earlier in the Raman spectrum at 5 K [10]. The best fitting of the calculated curves to experimental results corresponds to the effective phonons with a frequency of 105.8 cm^{-1}. It should be noted that the observed temperature dependence of $H(T)$ differs from that of the basic classical layered semiconductor BiI_3 [16], in which the structure phase transitions are absent, and the strong exciton-phonon interaction takes place.

At temperatures 150–220 K, the experimental data can be described by formula (2). The fitting curves are depicted in Figure,*b* for $H(0)$=47.82 meV, two real *LO*-phonons at 44.3 and 48.2 cm^{-1} [10], and one effective phonon at 47.9 cm^{-1}. The best agreement of theory with experiment takes place for phonons with the least frequency.

Thus, the increase in temperature from 5 to 220 K is accompanied by the manifestation of a new physical effect observed as a change of the exciton-phonon interaction from a weak to strong one as temperature increases.

It stands to reason that the effect found may be caused by the formation of a heterostructure region between temperatures of 183 and 221 K [9] which consists of the regions of the polydomain ferroelastic phase and the regions of paraelastic one separated by the phase boundaries. It should be emphasized that the formation of twin domains and twin boundaries (the domain walls) was reliably established by optical investigations under polarized light in [6] and neutron-diffraction studies in [8]. Six types of the twin boundary orientation in (001) plane were observed in the monoclinic phase. Such domain walls may be thick [8] due to the absence of the mechanical compatibility between domains. The boundaries can affect considerably the physical

properties of the crystal [4], which can be caused by the "mobility" of twin boundaries under load and by the dependence of their concentration, in turn, on the specimen history. Apparently, the temperature range of the heterostructure appearance is more extended and coincides with the whole transition region from 150 to 220 K. As a result, what is very important, the frequency of the phonons interacting with excitons decreases considerably from 105.8 to 47.9 cm^{-1}, i.e., by more than two times. Thus, one can conclude that the $Cs_3Bi_2I_9$crystal lattice is reconstructed under heating from a non-layered to layered one, by supporting, in such a manner, the results obtained in [11–13]. It follows from Figure that the temperature T^*=150 K is a characteristic point, since $Cs_3Bi_2I_9$ crystals become layered (or non-layered) at higher (or lower) ones.

As is well known [8], the crystal remains to be a polydomain one below T=150 K, but it is already single-phase (monoclinic) and exhibits the C12/m1 structure. With decrease in temperature, the monoclinic angle β increases (from β=90° (T=220 K) up to β=90.608° at T=143 K) [4]. Therefore, one can expect an increase of the interaction between neighbouring layered sandwiches, because the distances between sandwiches are decreased. The lower the temperature, the more the interaction is. As a result, the crystal must lose its highly anisotropic properties (inherent in a layered crystal), because it becomes non-layered.

The following possible arguments supporting the above-considered lattice reconstruction were obtained from the Raman studies of $Cs_3Bi_2I_9$ layered ferroelastic crystals at $T < 150$ K [10]. First, the detection of low-frequency doublets in the region of translation vibrations due to the Davydov splitting (the lines 37.0, 45.0, 61.4, and 68.3 cm^{-1} caused by the dynamical interaction between $[Bi_2I_9]^{3-}$ molecular ions occupying two inequivalent positions in the crystal lattice) or the splitting of degenerate vibrations of the E-symmetry (the line at 97.4 cm^{-1} because of the removal of the degeneracy under a spontaneous strain which appears when the high-symmetry hexagonal crystal lattice becomes a low-symmetry monoclinic one by passing the phase transition point). Second, the more clear manifestation of doublets as the temperature further decreases down to 5 K. Third, the doublets of the Raman lines with higher frequencies appear later on than those with lower frequencies. Finally, the smaller values of doublet splitting for the Raman lines with higher frequencies that can be caused by a higher toughness of the intermolecular vibrations with higher frequencies. Moreover, it is necessary to point out also the absence of an anomaly in the temperature shift of the energy gap $E_g(T)$ of $Cs_3Bi_2I_9$ layered ferroelastic crystals [11, 12] described by the Varshni formula.

At last, at temperatures 220–300 K, $H(T)$ increases linearly (Figure,*c*) in accordance with the following empirical extrapolation:

$$H(T) = \alpha(T - 225K) + H_0. \quad (3)$$

Here, α=0.758 meV/K and H_0=116.3 meV. It should be noted that the extrapolation is in agreement with the linear dependence obtained by Schreiber and Toyozawa ($H(T) \sim T$) [17] within the renormalized perturbation theory for a two-dimensional lattice.

Thus, we have found the variation of the exciton-phonon interaction from a weak to strong one for the same ferroelastic sample in the heating mode. The temperature T^*=150 K can be considered as a characteristic one, below which a crystal losses the nature of layered substance. The effect is explained on the basis of a model taking the reconstruction of the crystal lattice from a non-layered to layered one into account.

The effect found gives the possibility to apply the powerful optical methods to studying the exciton-phonon interaction in ferroelastics and has both scientific and practical interests. In particular, it can be used for the development of the theory of ferroelastic compounds, as well as be taken into account when developing and manufacturing the arrangements with "phase" memory, precise temperature and pressure sensors, devices for acoustics and optoelectronics, etc.

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ОСОБЛИВОСТІ ЕКСИТОН-ФОНОННОЇ ВЗАЄМОДІЇ В ШАРУВАТИХ СЕГНЕТОЕЛАСТИЧНИХ КРИСТАЛАХ ($Cs_3Bi_2I_9$)

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Р е з ю м е

Вперше ми виявили новий фізичний ефект – зміну екситон-фононної взаємодії від слабкої до сильної в одному і тому ж зразку з підвищенням температури. Ми пояснили цей ефект на основі моделі, що враховує перебудову кристалічної ґратки від нешаруватої до шаруватої.