

# Tracing of the first-order phase transition in a layered $\text{PbI}_2$ semiconductor by the method of exciton spectroscopy

I. V. Blonskiĭ, V. A. Gubanov, L. V. Mizrukhnin, and V. V. Tishchenko  
*Institute of Physics, Ukrainian Academy of Sciences*

(Submitted 26 March 1979; resubmitted 28 April 1979)  
*Pis'ma Zh. Eksp. Teor. Fiz.* **29**, No. 12, 741–744 (20 June 1979)

By analyzing the spectra of the free and localized excitons in  $\text{PbI}_2$  we were able to trace the entire process of conversion of the  $2H$  polytype into the  $4H$  polytype: from the formation of the  $4H$ -polytype nucleation centers of angstrom size to the total conversion of the  $2H$  polytype into the  $4H$  polytype.

PACS numbers: 64.50.Ks, 71.35. + z

1. The kinetics of a first-order phase transition (transformation of one polytype into another) presupposes nucleations of the new phase in the initial stage. Their size and number can be so negligible that the conventional methods of detection are not always acceptable. In this communication, we show that the spectral measurements in the region of free and localized excitons are promising for this purpose.

The well-known property of the layer semiconductors-abundant polytypism-was the main criterion in selecting the test material. The polytypes in such structures can often be distinguished by the different number of translation-nonequivalent layers in the unit cell, which are bound by the weak van der Waals forces. Therefore, by heating such samples even at low temperatures we can easily convert one polytype into another and hence monitor the kinetics of the phase transition by the proposed method.

2. For this purpose we measured the low-temperature ( $T = 4.2$  K) reflection (RS) and photoluminescence (PL) spectra of single-crystal  $\text{PbI}_2$  samples, which were isothermally annealed for 5–6 hours at different temperatures in the temperature range 100 to 200 °C. The measurements were carried out using a setup described in Ref. 1. All the samples can be divided into three groups (group *a*, *b*, and *c*) on the basis of the effect of isothermal annealing of the samples on their exciton spectra. Figure 1 shows the RS and PL of these sample: *a*, original samples which belong (judging by the spectral location of the free-exciton lines  $A^{(1,2)}$ ) to the  $2H$  polytype; *b*, isothermally annealed samples at  $T_{\text{anneal.}} = 140$  °C (spectra 1) and  $T_{\text{anneal.}} = 160$  °C (spectra 2); *c*, isothermally annealed samples at  $T_{\text{anneal.}} = 180$  °C.

It can be seen in Fig. 1 that the original samples are almost perfect. The exciton part of the PL spectra of this group of samples has two lines corresponding to the radiation of a free exciton  $A$  and a localized exciton (1).

The characteristic property of the samples of group *b*, which were isothermally annealed at 140 °C, is the formation of a number of narrow gaps  $I_{2H}$ ,  $I_{2H}^1$ ,  $I_{2H}^2$ ,  $I_{2H}^3$ , and  $I_{2H}^4$  in the (max RS) region, which, in terms of the spectral location and intensity, correlate with the appearing emission lines in the PL spectrum. It follows from the reproducible results of the measurements that the number of lines in the additional structure, their spectral position and intensity depend on the time and temperature of

annealing. Thus, eight  $I^{1-4}$ -type lines, whose intensity is higher than that in the spectra of samples annealed at 140 °C, were observed in the reflection and photoluminescence spectra of samples annealed at 160 °C. Moreover, the spectra of free excitons in the samples annealed at 160 °C are a superposition of the spectra of 2H and 4H polytypes.<sup>(1,2)</sup> It should be noted that the line of the localized exciton 1, which is always present in the PL spectra of pure samples, also increased in intensity under the influence of annealing and became dominant in the PL spectrum.

In the samples of group *c*, which were annealed at 180 °C, the exciton reflection and photoluminescence spectra were shifted 10 meV to the shortwave region of the spectrum relative to the spectra of the original samples.

3. In evaluating the results of the experiment, first we determined the nature of the  $I^1 - I^4$  lines. The large intensity of these lines, which in the reflection spectrum are the same as the excitonic, indicates that the localized excitons are responsible for their occurrence. In fact, since the intensity of the absorption bands (reflection bands) is determined by the product of the concentration of the absorption centers per unit volume  $N_j$  and the oscillator strength of the transition  $f_j$ , the same order of intensity of the  $I$  and excitonic  $A$  lines indicates that the values of the corresponding products are close  $N_I f_I \approx N_A f_A$ . It can be seen that if this condition is satisfied in the presence of impurity or defects, then we obtain a concentration of the latter  $N \approx 10^{21} \text{ cm}^{-3}$ , in which case the observation of the excitonic states in the reflection and photoluminescence spectra is unlikely. Taking into account the giant oscillator strength ( $f_I \approx 10^4 f_A$ ) of the localized excitons,<sup>(3,4)</sup> a very small concentration of the centers that localize the excitons ( $N_D \approx 10^{16} - 10^{17} \text{ cm}^{-3}$ ) is necessary to produce to the corresponding complexes in the reflection spectra. Such complexes appear in the photoluminescence spectra at even lower concentrations of the localization centers.

On the basis of the known data for identification of the  $\text{PbI}_2$  polytype composition from its reflection<sup>(2)</sup> and photoluminescence<sup>(1)</sup> spectra and on the basis of the results of the measurements shown in Fig. 1, we can see that the conditions for annealing ( $T_{\text{anneal.}} = 180 \text{ }^\circ\text{C}$ , annealing time is 5–6 h) are those for which the total transition of the 2H crystal phase to 4H is accomplished. In view of this, the lowest annealing temperature (140 °C), at which the samples still belong to the original 2H polytype but whose low temperature spectra produce a number of lines of localized excitons, corresponds to the temperature of formation of the nucleation centers of the new phase, whose size is very small (smaller than the exciton radius  $a_{\text{exc}} = 18 \text{ \AA}$ ) and whose presence localizes the excitons. If the samples are annealed for the same length of time but at a higher temperature (160 °C), then the nucleation centers of the 4H polytype, after their formation, increase in size to macroscopic dimensions  $> a_{\text{exc}}$ . As a result, the RS and PL are a superposition of the spectra of the 2H and 4H polytypes. The formation of other lines of localized excitons ( $I_{4H}^1 - I_{4H}^4$  lines) are most likely attributable to the capture of excitons by the defects because of the presence of the boundary of two crystal phases.<sup>(1)</sup>

Thus, we can see from this study that, because of the giant oscillator strengths of the localized excitons, the method of exciton spectroscopy is very sensitive to minute structural rearrangements accompanying the phase transition. As a result, by using the method of exciton spectroscopy we were able to observe for the first time the 2H-

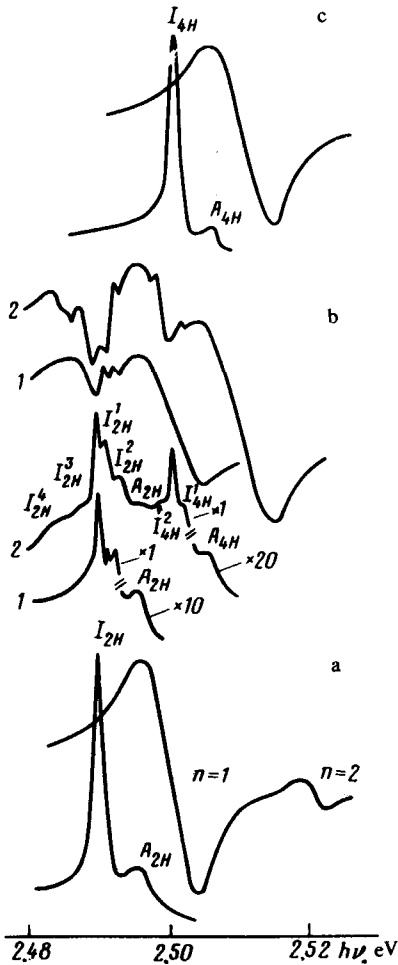


FIG. 1. The low-temperature ( $T = 4.2$  K) reflection and photoluminescence spectra of the three types of  $\text{PbI}_2$  samples: a, original samples belonging to the  $2H$  polytype; b, isothermally annealed samples at  $140^\circ\text{C}$  (spectra 1) and at  $160^\circ\text{C}$  (spectra 2); c, samples annealed at  $180^\circ\text{C}$ .

$4H$  polytype phase transition in  $\text{PbI}_2$  from the moment of formation of the nucleation centers of the new phase, whose size is equal to several  $A$ , to the total conversion of the  $2H$  polytype into the  $4H$  polytype.

We thank M.S. Brodin and S.M. Ryabchenko for useful remarks.

<sup>1</sup>It was pointed out in Ref. 5 that line  $I$  is formed by the exciton captured by a neutral impurity center. The given results show that such centers are formed because of the disorder of the crystal structure of the layer  $\text{PbI}_2$  semiconductor, which can occur even in the original samples.

<sup>1</sup>I.V. Blonskiĭ, I.S. Gorban', V.A. Gubanov, Ya.A. Lyuter, L.V. Poperenko, and M.I. Strashnikova, Fiz. Tverd. Tela **15**, 3664 (1973) [Sov. Phys. Solid State **15**, 2439 (1973)].

<sup>2</sup>Ch. Gähwiller and G. Harbeke, Phys. Rev. **185**, 1141 (1969).

<sup>3</sup>É.I. Rashba, Fiz. Tekh. Poluprovodn. **8**, 1241 (1974) [Sov. Phys. Semicond. **8**, 807 (1974)].

<sup>4</sup>V.I. Sugakov and V.N. Khotyaintsev, Fiz. Tverd. Tela **21**, 939 (1979) [Sov. Phys. Solid State **21**, 551 (1979)].

<sup>5</sup>R. Kleim and F. Raga, J. Phys. Chem. Sol. **30**, 2213 (1969).