

EXCITON DYNAMICS IN SYNTHETIC ONE DIMENSIONAL SEMICONDUCTOR



T. GOTO^{a,*}, N. OHSHIMA^a, G. A. MOUSDIS^b and
G. C. PAPAVALASSILOU^b

^a*Department of Physics, Graduate School of Science, Tohoku University,
Sendai 980-8578, Japan;* ^b*Theoretical and Physical Chemistry Institute,
National Hellenic Research Foundation, 48, Vassileos Constantinou Ave.,
Athens 116/35, Greece*

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We have measured polarized absorption and photoluminescence (PL) spectra of an organic–inorganic semiconductor single crystal, $\text{C}_{10}\text{H}_7\text{CH}_2\text{NH}_3\text{PbI}_3$, at low temperatures down to 5 K. The temperature and time dependences of the PL intensities have been measured. From these results, it is concluded that quasi-1D excitons are photogenerated in the PbI_3 chain, and some of them are transferred to a triplet exciton in the organic and the others are relaxed to a self-trapped exciton in the PbI_3 chain. The triplet exciton, however, is not transferred to the self-trapped exciton. The lifetimes of the triplet exciton and the self-trapped exciton are estimated to be 1.2 ms and 52 ns, respectively, at low temperature range, and the former and the latter thermal activation energies are obtained as 9.7 meV and 18 meV, respectively.

Keywords: Exciton dynamics; 1D semiconductors

A lead iodide perovskite crystal $\text{C}_{10}\text{H}_7\text{CH}_2\text{NH}_3\text{PbI}_3$ is one of organic–inorganic hybrid semiconductors based on the organic molecules. Such perovskite crystals are called natural quantum structures [1].

* Corresponding author. Organo-Optic Research Laboratory, 6-2-1 Seiwa-dai, Kita-ku, Kobe 651-1121, Japan

The crystal $C_{10}H_7CH_2NH_3PbI_3$ is a novel 1D crystal, where a quantum wire consisting of $[PbI_6]^{4-}$ octahedron twin chain are separated by naphthylmethylammonium ions from each other. A $[PbI_6]^{4-}$ octahedron is connected to its two neighbors by sharing the triangle faces.

Papavassiliou *et al.* [2] have measured absorption and photoluminescence (PL) spectra of $C_{10}H_7CH_2NH_3PbI_3$ and $C_{10}H_7CH_2NH_3I$ at room temperature, and an absorption band at 401 nm band and a broad band around 520 nm in $C_{10}H_7CH_2NH_3PbI_3$ have been found to be due to an exciton of the $[PbI_6]^{4-}$ octahedron wire and a triplet exciton of the organic compound, respectively.

No study, however, on the polarization and dynamics of the exciton in this single crystal has been made yet in spite of the quasi-1D crystal structure.

In this paper, we measured the polarized reflectance spectra and time response of the polarized luminescence spectra at various temperatures. On the basis of these results, we discuss the polarity, the lattice relaxation and the energy transfer of the exciton.

Small crystals with the size of about $3 \times 0.2 \times 0.02 \text{ mm}^3$ were used. The growth procedure of these crystals is reported in Ref. 2. The reflectance spectra were measured using a candescent lamp, a monochromator with the reciprocal dispersion 1.7 nm and a photodiode array. For the luminescence measurements, the sample was excited by light from an optical parametric oscillator of which the incident light was a third harmonic of a Q-switched Nd YAG laser. The photon energy, the repetition rate and the pulse width were 3.12 eV, 10 Hz and 10 ns, respectively. The backward luminescent light from the sample was analyzed by a monochromator with the dispersion of 5.5 nm and detected by a Princeton Instruments 576G/RB ICCD detector. The gate width of the ICCD detector was 15 ns. As the crystal was very small, an objective lens was used for the focus of the incident, reflected and luminescent lights. The spectral resolution was less than 1 meV for all the measurements.

The absorption spectra obtained by Kramers-Kronig analysis from the measured reflection spectra are shown in Figure 1, where solid and dotted lines represent the spectra for $E \parallel b$ and $E \perp b$, respectively. Large and small absorption bands are observed at 3.12 eV and 3.19 eV, respectively, for $E \parallel b$ and $E \perp b$, respectively, where the b axis is parallel to the PbI_3 chain. Appearance of the small absorption band for $E \perp b$ may be due to a quasi-1D crystal structure. Namely, the exciton wave function may spread over scarcely on the surface perpendicular to the b axis.

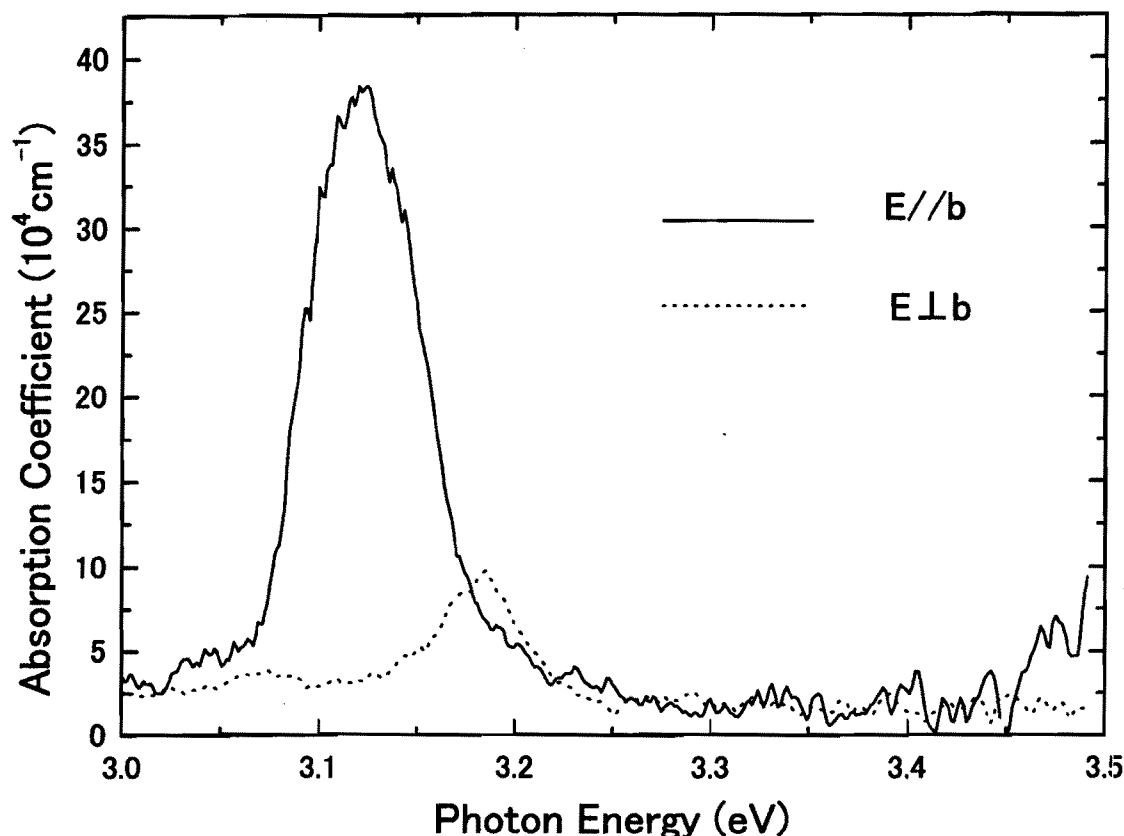


FIGURE 1 Absorption spectra obtained by Kramers-Kronig analysis from measured reflection spectra. Upper and lower curves are spectra for $E \parallel b$ and $E \perp b$ polarizations, respectively.

Figure 2 shows PL spectra for $E \parallel b$ at different temperatures for 3.12 eV light excitation. The exciting light energy coincides with the exciton energy for polarization $E \parallel b$. Namely, the quasi-1D exciton is resonantly excited by the 3.12 eV light. All the PL lines in the spectrum at 5 K are due to the triplet exciton in the organic [2]. This fact suggests that the photogenerated exciton in the PbI_3 chain transfers to the triplet exciton in the organic, as seen in some similar materials [3, 4]. In the lowest PL spectrum at 70 K, a broad band appears at 2.1 eV instead of the lines due to the organic molecules. This band shape is of Gaussian type, and the intensity is almost independent of the polarity. Moreover, the band shape does not depend on the delay time of the detected PL from the pulsed exciting light in the time resolved PL spectrum. From these results it is suggested that the broad band PL is caused by a self-trapped exciton in the chain. This suggestion is also supported from the quasi-one dimensionality of the free exciton. The decay time of this broad band PL is obtained as 52 ns at 77 K.

Figure 3 shows the intensity of the broad band PL as a function of the inverse temperature $1/T$. Closed and open circles represent the PL intensi-

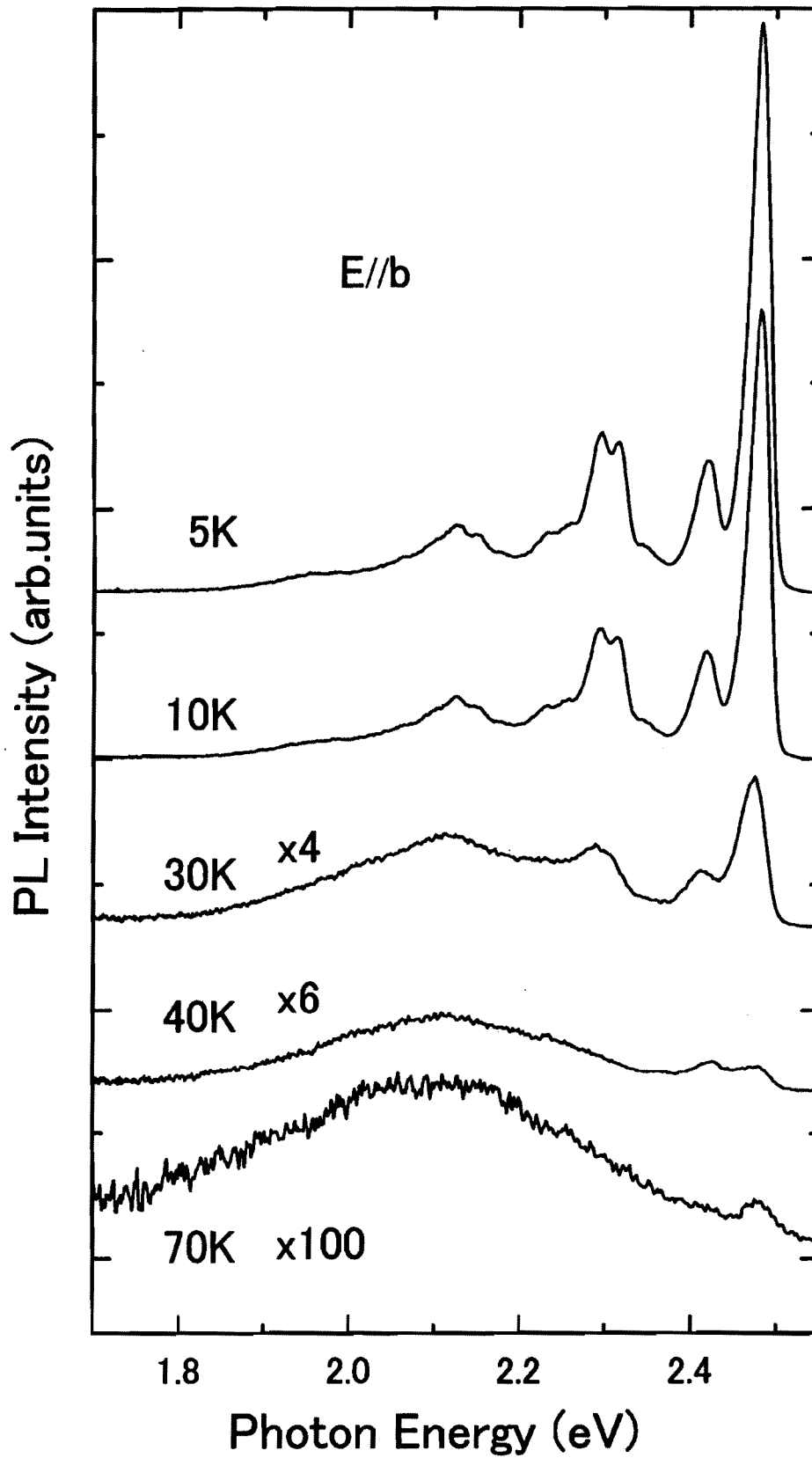


FIGURE 2 PL spectra for $E//b$ at different temperatures, when the exciton in the PbI_3 chain is directly photogenerated.

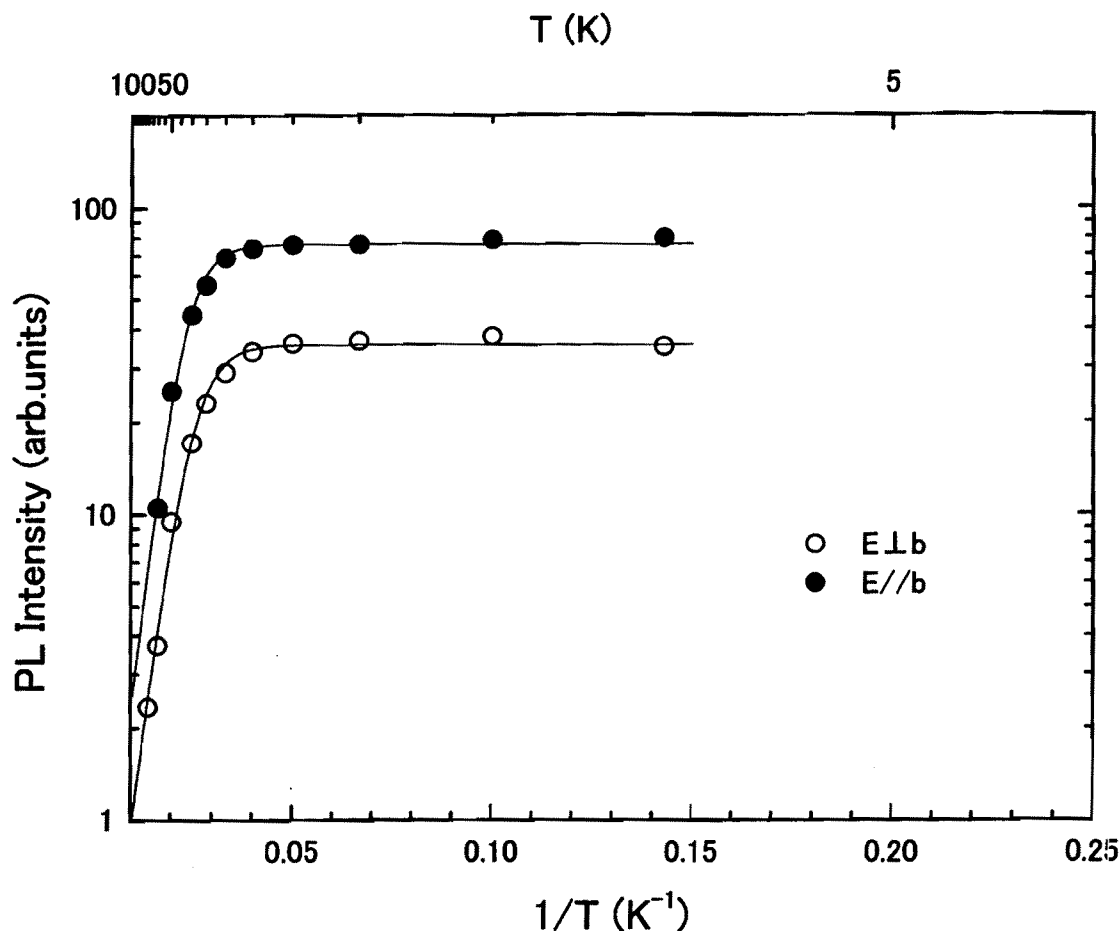


FIGURE 3 Temperature dependence of the broad band PL intensity. The PL intensity is represented in the logarithmic scale as a function of the inverse temperature. Closed and open circles show the PL intensities for polarizations $E \parallel b$ and $E \perp b$, respectively. Upper and lower solid curves are calculated ones by Eq. (1) with adjustable parameters $E_a = 18.8$ eV and 16.9 eV, respectively.

ties for $E \parallel b$ and $E \perp b$ polarizations, respectively. As seen in Figure 2, the triplet exciton PL lines mainly appear at low temperatures, and hence the broad band PL intensity is difficult to be estimated in the time integrated spectrum. In order to obtain the broad band PL intensity, we have measured the time resolved PL spectra, and estimated the integrated intensity of the broad band at zero delay time, because the decay time of the broad band PL is much shorter than that of the triplet exciton PL, resulting in appearance of only the broad band in the PL spectrum at zero delay time. The PL intensity, I , may follow Eq. (1), in the mechanism where the self-trapped exciton decays radiatively or non-radiatively through the thermal barrier E_a

$$I = \frac{1}{A + C \exp(-E_a/k_B T)} \quad (1)$$

where A and C are parameters, and k_B is the Boltzmann constant. An adjustable parameter, thermal activation energy E_a , is estimated to be 18.8 ± 1.2 meV and 16.9 eV ± 1.2 meV for $E \parallel b$ and $E \perp b$ polarizations, respectively.

Next, the lifetime of the triplet exciton is reported. The decay time of its PL intensity is obtained as 1.2 ms at 5 K. From the temperature dependence of the decay time, the thermal activation energy of the triplet exciton is estimated to be 9.7 ± 0.5 meV. The same energy is obtained also from the temperature dependence of the PL intensity.

From these results, we discuss the decay process of the photogenerated exciton in the PbI_3 chain. Some of the quasi-1D excitons transfer to the triplet exciton in the organic, and decays radiatively. The other are self-trapped with lattice relaxation inside the PbI_3 chain. Although the energy level of the triplet exciton in the organic is higher than that of the self-trapped exciton in the inorganic chain, the triplet exciton is not transferred to the self-trapped exciton, but decays radiatively or non-radiatively. It is because the broad band PL intensity does not increase with increasing temperature below 40 K in spite of the abrupt decrease in the organic PL intensity as seen in Figures 2 and 3.

In conclusion, quasi-1D excitons are formed in the PbI_3 chain. Some of them are relaxed to the self-trapped exciton with the lifetime of 52 ns at 77 K. The others are transferred to the triplet exciton in the organic with the very long lifetime more than 1 ms below 20 K, and decays without transferring to the self-trapped exciton.

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