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Photoluminescence of the inorganic-organic layered semiconductor $(C_6H_5C_2H_4NH_3)_2PbI_4$: Observation of triexciton formation

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By mean of subpicosecond pulsed excitation of excitons, we have measured the photoluminescence spectra of $(C_6H_5C_2H_4NH_3)_2PbI_4$ under a high-excitation regime up to 4×10^{14} photons/cm^2. At 10 K, two additional lines are observed below the exciton energy by 55 and 75 meV for excitation greater than 2×10^{13} photons/cm^2. The former is assigned to the amplified spontaneous emission of the excitonic molecule. The latter is presumed to be the emission of a triexciton leaving two excitons behind, because the intensity is proportional to the 2.6 power of the excitation intensity. An elementary model of the triexciton is presented. The dissociation energy of a triexciton is estimated to be 14 meV from the temperature dependence.

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I. INTRODUCTION

High-excitation effects in semiconductors have been studied extensively.[1] By increasing the excitation power, one observes not only excitons but also stable biexcitons (excitonic molecules).[2,3] On the other, the band gap energy is renormalized owing to the screening of the Coulomb interaction by photogenerated species. It is intriguing whether it is possible to observe a three-exciton complex (a triexciton) bound by the Coulomb interaction in unconfined systems.[4] In most semiconductors under high excitation, the system causes a transition to the electron-hole-plasma phase where excitons are not stable yet, before a triexciton becomes observable. In quantum dots and nanocrystals, triply excited states, called triexcitons, have been observed,[5,6] but the constituent excitons are not bound by the Coulomb interaction but confined together by the geometric condition.

In order to explore a triexciton, we consider two factors. One is to adopt a system with effectively strong Coulomb interaction between photoexcited carriers. The exciton system is stabilized. Moreover, because an exciton hardly dissociates, the system may be free from the strong screening by free carriers, if excitons are resonantly excited. The other factor is to adopt a low-dimensional system, such as a quantum well, where screening by other excited species is not effective.[7] Because an exciton in a quantum well is open to the barrier part which is unchanged even under high excitation, the dynamic screening has only a limited effect.

Along this line, an inorganic-organic layered semiconductor $(C_6H_5C_2H_4NH_3)_2PbI_4$ (PhE-PbI$_4$) is quite a suitable test case. A crystal of PhE-PbI$_4$ consists of PbI-based inorganic layers and organic layers of phenethylammonium.[8] The inorganic layer is made of $[PbI_6]^{4-}$ octahedra whose four vertices are shared with one another. The thickness of the inorganic layer is ca. 1 nm. Since the band gap energy of the inorganic part (1.7 eV) is much lower than that of the organic part (6 eV), an exciton is confined in the thin inorganic layer. The effective Coulomb interaction between photogenerated carriers in inorganic layers is rather strong, because it is influenced by the lower dielectric constant (3.3) in the organic part rather than that (6.1) in the inorganic part. By virtue of this dielectric confinement, the exciton binding energy is 220 meV.[9,10] In short, PhE-PbI$_4$ is expected to have both the benefits of strong Coulomb interaction and weak dynamic screening.

In the inorganic-organic layered semiconductors, high-excitation effects have not been well studied. A stable excitonic molecule is known to exist with a binding energy of 50 meV in PhE-PbI$_4$.[11,12] In a very similar substance, $(C_6H_{13}NH_3)_2PbI_4$ (C6-PbI$_4$), photoluminescence (PL) spectra were measured with nanosecond pulsed excitation up to 2×10^2 kW/cm^2.[13] It was reported that the PL intensities of the exciton and the excitonic molecule are proportional to I_{exc}^1 and I_{exc}^2, respectively, for $I_{\mathrm{exc}} < 0.1$ kW/cm^2 but to $I_{\mathrm{exc}}^{0.5}$ and I_{exc}^1, respectively, for $I_{\mathrm{exc}} > 1$ kW/cm^2. By mounting it in a cavity, lasing by the excitonic molecule was also demonstrated at more than 20 kW/cm^2. To date, for a series of inorganic-organic layered semiconductors, neither band gap renormalization nor electron-hole plasma has been reported, while a triexciton has not been observed.

In this paper, we report PL spectra of PhE-PbI$_4$ under the high-excitation regime up to 4×10^{14} photons/cm^2. Two PL lines which have not been reported are observed. One is observed below the exciton line by 55 meV and assigned to the amplified spontaneous emission of the excitonic molecule leaving an exciton behind. The other is observed below the exciton line by 75 meV, and examined as a signature of a stable triexciton. The latter line shows superquadratic dependence on the excitation light power. To further examine the possibility of a triexciton, the temperature dependence of the photoluminescence is tested.

II. EXPERIMENT

PhE-PbI$_4$ was prepared by a chemical synthetic method, as described elsewhere.[8,9] The specimens for measurements were spin-coated films from an acetonitrile solution on glass substrates. Thicknesses were estimated to be 10–20 nm. It is known that the films are polycrystalline but the *c* axis of each crystal domain is highly oriented to be perpendicular to the substrate.[14] The sample was placed on a cold finger of a closed-cycle He-circulation-type cryostat. Temperature was monitored by a silicon diode sensor.

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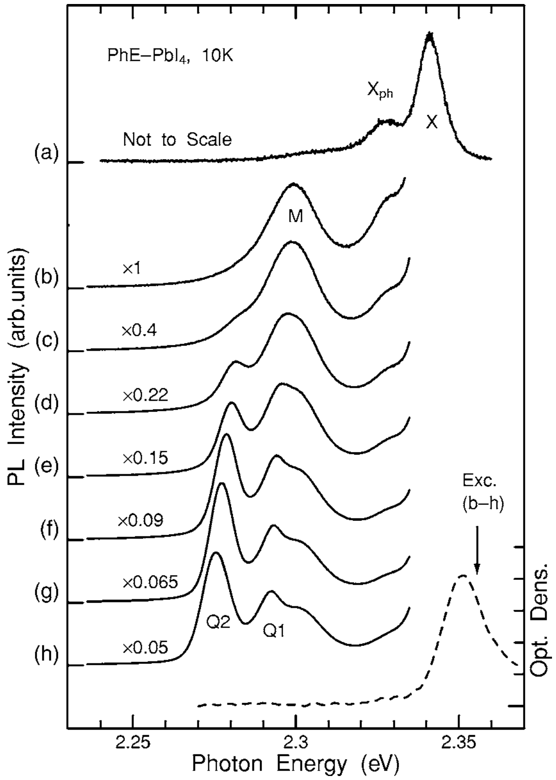

FIG. 1. PL spectra under various excitation intensities: (a) 4.6×10^{10}, (b) 4.6×10^{12}, (c) 1.4×10^{13}, (d) 2.8×10^{13}, (e) 4.6×10^{13}, (f) 9.2×10^{14}, (g) 1.6×10^{14}, and (h) 3.2×10^{14} photons/cm^2. While spectra (b)–(h) were excited by 2.355 eV photons, the spectrum (a) was excited by 2.58 eV photons. The dotted curve shows the optical density spectrum.

As excitation light, the output of an optical parametric amplifier (OPA) was used, which was excited by a subpicosecond 1 kHz regenerative amplifier. The wavelength of the OPA output was tunable. The pulse had a duration of about 100 fs when best recompressed by a prism pair. Polarization and power were controlled by a zero-order λ plate and a variable neutral density filter, respectively. The excitation light was loosely focused on the sample. The spot size was measured by means of a pinhole fixed on a translational stage.

Luminescence from the sample was collected by a lens and guided to a spectrometer. The detector was a liquid-nitrogen-cooled charge-coupled device. While a series of data was retrieved, the degradation of the sample was negligible.

III. RESULTS AND DISCUSSION

A. Excitation power dependence

Figure 1 shows PL spectra at 10 K under various excitation powers. Excitation photon densities were 0.046 (a), 4.6 (b), 14 (c), 28 (d), 46 (e), 92 (f), 160 (g), and 320 (h) $\times10^{12}$ photons/cm^2. In order to show the exciton line under low excitation, only (a) was excited at 2.58 eV. For (b)–(h), the exciton was resonantly excited at 2.355 eV, so that the PL profile of the exciton was not observable due to the scattered excitation light. The linear absorption spectrum is shown at the bottom for reference. The peak of exciton absorption is seen at 2.35 eV.

In (a), the peak (X) at 2.342 eV is assigned to the emission by exciton recombination. The peak (X_{ph}) at 2.325 eV is most probably assigned to a phonon sideband of X, while the related phonon mode is not yet identified. When the excitation power increases (b), a broad emission line (M) is observed, which is already assigned to the radiative decay of an excitonic molecule leaving an exciton behind.[11] For more excitation (c)–(h), two lines are additionally observed at ca. 2.295 and 2.275 eV. The latter line slightly redshifts as the excitation power increases. To discuss the sources of these two lines, we shall temporarily give notations of $Q1$ and $Q2$ to these lines.

The PL spectra were independent of whether the excitation light was linearly or circularly polarized. On the other hand, when free electron-hole pairs were excited by 2.58 eV photons, neither $Q1$ nor $Q2$ was observed in the same excitation regime.

In order to obtain intensities of luminescence lines, spectra were analyzed by the deconvolution technique. Lorentzian line shapes were assumed for all the X_{ph}, M, $Q1$, and $Q2$ lines. While thermal distribution of excitonic molecules is sometimes important, it was not taken into account for simplicity, because thermal energy is considered to be much smaller than the linewidth at 10 K. In practice, spectra were fitted rather well on these assumptions. Examples of the fit are shown in Fig. 2.

It is noted that the authors tried to fit the spectra not only with Lorentzian line shapes but also with Gaussian line shapes. Consequently, the presented analysis with Lorentzian line shapes was adopted for the better fit. However, the results obtained (the exponent of each line's dependence on the excitation power, examined just below) were almost independent of assumed line shapes, except for $Q1$ for less than 5×10^{13} photons/cm^2.

Figure 3 shows the excitation power dependence of intensities of X_{ph}, M, $Q1$, and $Q2$ at 10 K, obtained by the deconvolution.[15] Solid lines shows exponents on the excitation power for X_{ph}, M, and $Q2$. For $Q1$, no fitting line is given, because errors for $Q1$ intensities (not shown in Fig. 3) for less than 5×10^{13} photons/cm^2 were too large to discuss its exponents on the excitation power. This uncertainty occurs because of the large spectral overlap of $Q1$ and M. It is noted that in spite of this uncertainty, errors in M intensities are negligibly small relative to their absolute intensities, because M is much more intense than $Q1$.

The intensity of X_{ph}, which is expected to be in proportion to X, is proportional to $I_{\text{exc}}^{0.3}$ in all the range between 4×10^{12} and 4×10^{14} photons/cm^2. On the other hand, the intensity of M is approximately proportional to $I_{\text{exc}}^{0.9}$ for the lowest power range of this experiment, below 2×10^{13} photons/cm^2. These intensity behaviors suggest that intensities of these lines are saturated even in this excitation regime in our measurement. The saturation can be explained for two reasons. One, which is considered to be the main reason, is that nonlinear nonradiative decay processes, such as bimolecular annihilation, will occur. The second reason is

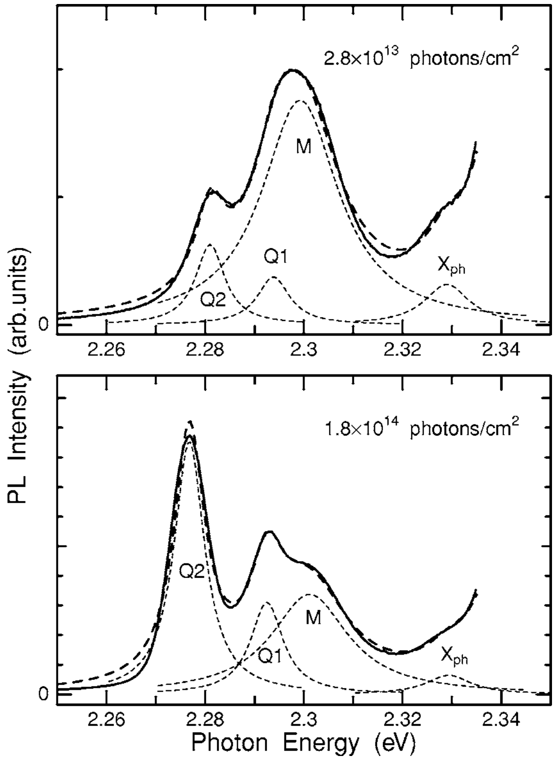

FIG. 2. Examples of spectral deconvolution. Solid and dashed curves show experimental results and fitting curves, respectively. Thin solid curves represent deconvoluted components.

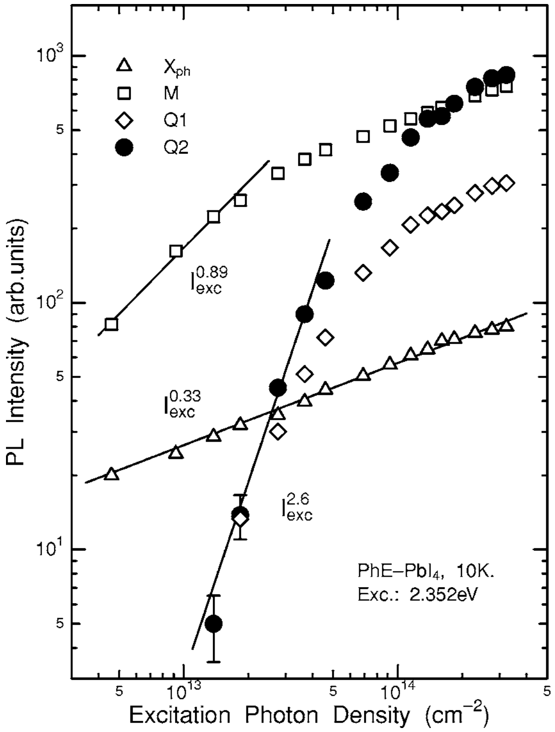

FIG. 3. Excitation power dependence of PL intensity at 10 K. Errors for $Q1$ are shown with vertical bars.

the excitation-induced transient decrease of the absorption coefficient at the excitation photon energy. Because of the ac Stark effect caused by the subpicosecond pulsed photon field of the excitation, the exciton absorption band is supposed to be bleached and blueshifted. It is noted that the excitation power dependence of X_{ph} and M in this excitation regime seems to be comparable to that of the exciton and the excitonic molecule observed in C6-PbI$_4$ under the nanosecond pulsed excitation of more than 1 kW/cm^2.[13] There is a slight difference that the exponents for X (or X_{ph}) and M are slightly smaller in our experiment with the subpicosecond excitation than those for C6-PbI$_4$ with nanosecond pulsed excitation. It is likely that the transient absorption change is not important with the nanosecond pulsed excitation.

Beyond 2×10^{13} photons/cm^2, the intensity of M becomes more strongly saturated. Since $Q1$ and $Q2$ become intense in this excitation regime, the saturation of M is explained as due to the consumption of excitons by $Q1$ and $Q2$.

$Q1$, which appears above 2×10^{13} photons/cm^2, is assigned to the amplified spontaneous emission of M, the radiative recombination of an excitonic molecule leaving an exciton behind. There are three reasons. One reason is that $Q1$ is located in the bandwidth of M. The second reason is the spectral similarity to the lasing by the excitonic molecule observed in the cavity-equipped C6-PbI$_4$ in Ref. 13. As mentioned just above, our lowest-excitation regime and the high-excitation regime in Ref. 13 seem to correspond. The third reason is that population inversion between the excitonic molecule and the exciton is likely in PhE-PbI$_4$, because the oscillator strength for the decay of an excitonic molecule to an exciton is smaller than that for the exciton decay to the ground state.[16,17]

The intensity of $Q2$ is proportional to $I_{\mathrm{exc}}^{2.6\pm0.3}$ for $I_{\mathrm{exc}} < 4\times10^{13}$ photons/cm^2, while it saturates for higher excitation intensity. In contrast to $Q1$, $Q2$ can be well resolved, because $Q2$ is spectrally well separated from other lines.

Because the exponent for $Q2$ clearly exceeds 2, it is expected that a three-exciton process is involved for $Q2$. On the other hand, $Q2$ cannot be a coherent transient for two reasons. One is that spectra were independent of the excitation pulse duration for 100–500 fs. Considering that the phase relaxation time[18] ($\approx$300 fs) of an exciton is comparable to the excitation pulse duration, the amplitude of a coherent transient should be strongly dependent on the duration, while the insensitiveness to the duration suggests that the signal depends on the accumulated number of generated excitons, regardless of the coherence. The other reason is that there is no polarization anisotropy even when the specimen is excited by polarized light, while a coherent transient is expected to have some memory of the excitation polarization. Thus, the emission of $Q2$ photons should occur after some relaxation process. In conclusion, the authors consider a stable three-exciton complex, i.e., a triexciton, as the source of $Q2$.

B. Temperature dependence

Suppose a triexciton emits a $Q2$ photon, the intensity of $Q2$ is expected to be weakened as temperature rises, because a triexciton will dissociate to an excitonic molecule and an exciton. Figure 4 shows the temperature dependence of PL

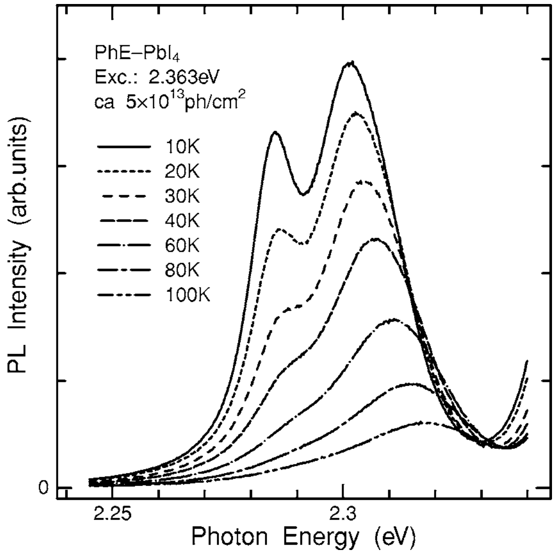

FIG. 4. Temperature dependence of PL spectra. The excitation photon energy is 2.363 eV.

spectra. The excitation photon energy was 2.363 eV, approximately resonant with the exciton. The excitation power was 50 nJ/pulse. Although the excitation spot size was not precisely under control in this measurement, the photon density is presumed to be about 5×10^{13} photons/cm^2 in comparison to the measurement displayed in Fig. 1. M and $Q1$ were not well resolved in this measurement, though the spectral shape around 2.3 eV suggests the presence of $Q1$ at 10 K. As temperature rises, both M and $Q2$ blueshift. These shifts are explained to be due to the shift of the band gap energy.[14,19] The intensity of $Q2$ decreases more rapidly than that of M. $Q2$ is almost undetectable at 100 K.

Figure 5 plots the intensity of $Q2$ as a function of temperature. Here, the intensity of $Q2$ was determined manually.[20] For examining triexciton dissociation, the data were analyzed with the model

$$\gamma(T) = \gamma_0 + \nu \exp\left(-\frac{\epsilon_{\rm diss}}{k_{\rm B}T}\right), \tag{1}$$

where γ, γ_0, ν, and $\epsilon_{\rm diss}$ represent the triexciton decay rate, that at $T=0$, the frequency factor, and the thermal energy required for triexciton dissociation. As a result, $\epsilon_{\rm diss} = 14 \pm 1$ meV is estimated. The fit is shown by the solid curve.

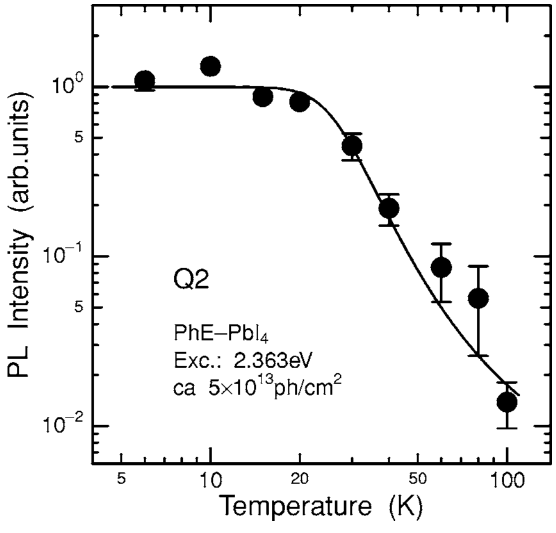

FIG. 5. Temperature dependence of $Q2$ intensity.

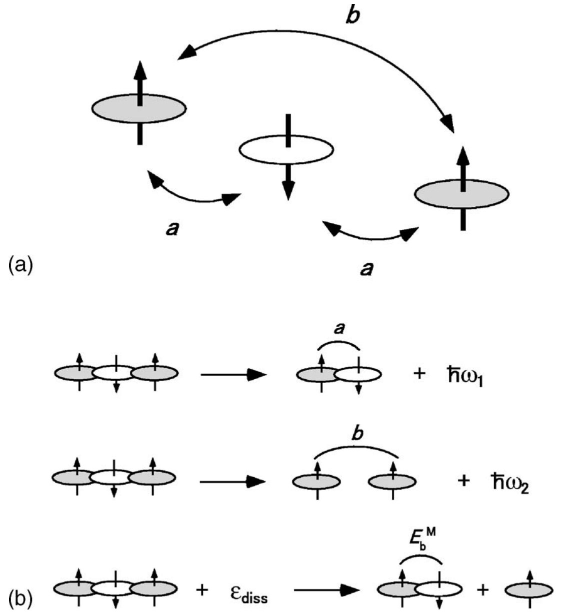

FIG. 6. (a) Triexciton model. (b) Emission and dissociation. Disks with up and down arrows represent excitons with $J_z=+1$ and $J_z=-1$, respectively.

C. Possibility of a triexciton

On the assumption that the exciton system is stable under the excitation regime, the authors consider a triexciton as a bound complex of three spin-singlet excitons. Constituent excitons are assumed to consist mainly of the 1s exciton component, although slight inclusion of higher (other than 1s) components is required for attractive interaction, as examined for an excitonic molecule.[21]

Figure 6(a) shows a schematic drawing of the triexciton model. Although three excitons are considered to locate in the inorganic layer in PhE-PbI$_4$, the model is applicable to general systems with more than one-dimensional freedom. We consider a triexciton, which consists of two excitons with $J_z=1$ ($X_\uparrow$) and an exciton with $J_z=-1$ ($X_\downarrow$), where J_z represents the total angular momentum of the exciton. The quantization axis is arbitrary. We shall write the effective interaction energy between $X_\uparrow$ and $X_\downarrow$ and that between two $X_\uparrow$'s as a (<0) and b (>0), respectively. Owing to the Pauli exclusion principle between constituent electrons and holes, two $X_\uparrow$'s, which share the same phase space, will avoid each other and tend to locate symmetrically around $X_\downarrow$. If this is the case, $|a| > |b|$ is expected. Anyway, the total energy of a triexciton is written as

$$E_T = 3E_X + 2a + b, \tag{2}$$

where the exciton energy is denoted by E_X.

For a triexciton, two radiative processes are likely. See Fig. 6(b). One is that one of two $X_\uparrow$'s recombines leaving behind two excitons attracting each other. The energy of the emitted photon will be

$$\hbar\omega_1 = (E_X - E_b^M) + a + b + E_b^M, \tag{3}$$

where E_b^M (>0) represents the binding energy of an excitonic molecule. The other process is that the $X_\downarrow$ recombines, leaving two excitons repelling each other. In this case, the emitted photon energy will be

$$\hbar\omega_2 = (E_X - E_b^M) + 2a + E_b^M. \tag{4}$$

Between the two processes, $Q2$ can be assigned solely to $\hbar\omega_2$ but not to $\hbar\omega_1$, because $Q2$ is observed below M. Considering that two $X_\uparrow$'s are attracted to one $X_\downarrow$, $|a| < E_b^M$ is expected. Thus, $a+b+E_b^M > 0$.

The thermal energy required for the dissociation of a triexciton to an excitonic molecule and an exciton is considered to be

$$\epsilon_{\mathrm{diss}} = -E_b^M - 2a - b. \tag{5}$$

Adopting $\epsilon_{\mathrm{diss}} = 14$ meV from the temperature dependence and $\hbar\omega_2 = E_X - 75$ meV from the spectra, we obtain $a = -37.5$ meV and $b = 11$ meV by use of Eqs. (4) and (5). One can see that these quantities are convincing, in comparison with $E_b^M = 50$ meV.

There is a question why the other emission line $\hbar\omega_1 = (E_X - E_b^M) + 23.5$ meV has not been observed. For this fact, the authors have no account at present.

The problem of a triexciton has been theoretically examined by Rebane.[22] He discussed the instability of a triexciton in a homogeneous three-dimensional system, based on the absence of a H_3 molecule and the virial theory for the Coulomb potential. In the case of PhE-PbI_4, however, there are two factors to be considered. One is that the kinetic freedom of electrons and holes is limited to the two-dimensional plane of the inorganic layer. The other factor is the dielectric confinement effect.[9,10] As mentioned in Sec. I, the dielectric constant of the organic part is much smaller than that of the inorganic part. Under this circumstance, the effective Coulomb potential between confined carriers is not simply $1/r$, but takes a "logarithmic" form which is longer ranged.[23] Rebane's theory nor our preliminary model considers these two factors. It is probable that these factors contribute to stabilizing a triexciton in PhE-PbI_4.

D. Other possibilities for $Q2$

In this section, other possibilities for explaining $Q2$ are examined, and ruled out.

Impurity-related phenomena are unlikely. Considering the density of impurity-related states, they must easily saturate in the high-excitation regime.

One may expect photon emission subsequent to exciton-exciton scattering, by which one exciton is excited to a higher state (such as a longitudinal exciton and higher exciton states) and the other is scattered to a low-energy photon-like branch of polariton bands. However, the intensity of such a line should be subquadratic in the excitation power, because the process is bimolecular.

Since $Q2$ is below M, the electron-hole plasma (EHP) state is considered. However, this assignment is not reasonable for two reasons. One is that the linewidth of $Q2$ is narrower than that of M. The linewidth of the EHP is expected to be much wider than that of M. The other reason is that X_{ph} and M still have comparable amplitudes to $Q2$ in the excitation regime where the intensity of $Q2$ saturates. The exciton system seems to be still stable in the high-excitation regime, while excitons should dissociate under the EHP phase.

IV. SUMMARY

Two luminescence lines have been observed below the exciton by 55 and 75 meV, under high excitation beyond 2×10^{13} photons/cm^2 at 10 K. The former is assigned to amplified spontaneous emission by the excitonic molecule. The latter is presumed to be the emission of a triexciton leaving two excitons behind, because the intensity depends on the excitation power superquadratically. A preliminary model of the triexciton was presented. The triexciton dissociation energy is estimated to be 14±1 meV from the temperature dependence. The possibilities of some other interpretations were examined and ruled out.

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