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NEW QUEUES OF TIME-RESOLVED LUMINESCENCE LINES FROM EXCITONIC MOLECULES IN $AgCl_xBr_{1-x}$

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Two new queues of intrinsic lines supposed to be due to *"the partial recombination of the free excitonic molecules"* and *"the Auger process in the two-exciton system"* have been observed, for the first time, in the luminescence spectra of $AgCl_xBr_{1-x}$ mixed crystals at high density excitation by a time-resolved spectroscopy technique.

I. Introduction

An exciton in $AgCl_xBr_{1-x}$ mixed crystals is a stable elementary excitation in the free state in the range of $x<0.45$ as well as in pure AgBr, whereas it is self-trapped in the range of $0.45<x$ as well as in pure AgCl, as reported by Kanzaki et al. [1]. Typical recombination of a free exciton in $AgCl_xBr_{1-x}$ mixed crystals for $x<0.45$ takes place either in the process

$$\text{free exciton} \rightarrow \hbar\nu + \text{TO(L)} + n\text{LO}(\Gamma)\ , \qquad (n=0,1,2,\ldots) \qquad (1)$$

or

$$\text{free exciton} \rightarrow \hbar\nu + n\text{LO}(\Gamma)\ . \qquad (n=0,1,2,\ldots) \qquad (2)$$

Series in Process (1) denotes the indirect allowed transitions for an exciton with an assistance of 1-TO(L)-phonon emission for the momentum conservation and additional n-LO(Γ)-phonons. Series in Process (2) is characteristic to mixed crystals in which such a momentum conservation in recombination processes is not necessarily required because of the reduction of translational symmetry. Let us denote the luminescence lines in series (1) by FE^{TO+nLO}, and those in series (2) by FE^{NP+nLO}. These series are dominant components in luminescence spectra of mixed crystals at low density excitation. Then, how about similar situations of the excitons in mixed crystals at high density excitation? Here, we report our first observation of two new queues of intrinsic lines with x in luminescence spectra of $AgCl_xBr_{1-x}$ mixed crystals at high density excitations.

II. Experimental Method

Mixed crystals of $AgCl_xBr_{1-x}$ were grown by the Bridgeman technique from melt of pure powder (6-9s) in Cl_2 atmosphere. Samples were prepared carefully with a special attention on surfaces and immersed in pumped liquid He (1.9K). A CW light out of a high-pressurized Hg lamp filtered at 360 nm was used for low levels of excitation below $4W/cm^2$. An N_2-pulsed laser was used for high levels of excitation up to $1MW/cm^2$. At low levels of excitation, luminescence signals were detected by the normal lock-in method. At high levels of excitation, the photo-signals were sample-held,

averaged by a Boxcar integrator (with a gate width =5nsec), and then displayed on a chart recorder. For faster signals, a Sampling oscilloscope (with a gate width ≈300psec) was used. The stoichiometry x of each specimen of $AgCl_xBr_{1-x}$ mixed crystal was estimated approximately by observing the position of the optical absorption edge.

III. Experimental Results

Figure (1) illustrates typical luminescence spectra of $AgCl_xBr_{1-x}$ over the range of $0 \leqq x \leqq 0.5$ at high levels of excitation and similar data at low levels of excitation together with the optical density spectra all at 1.9K. At high levels of excitations, a new queue of peaks denoted by M were observed, as x becomes finite, together with the FE-lines with series (1) and (2). Another peculiar feature for finite $x \neq 0$ is an emergence of a second new queue of broad lines denoted by FE^{*NP} in the spectra for $AgCl_xBr_{1-x}$ with $x \lesssim 0.2$ at high levels of excitation. Over the range of $x \gtrsim 0.5$, so far no effect at high density excitation has been found including the case of pure AgCl.

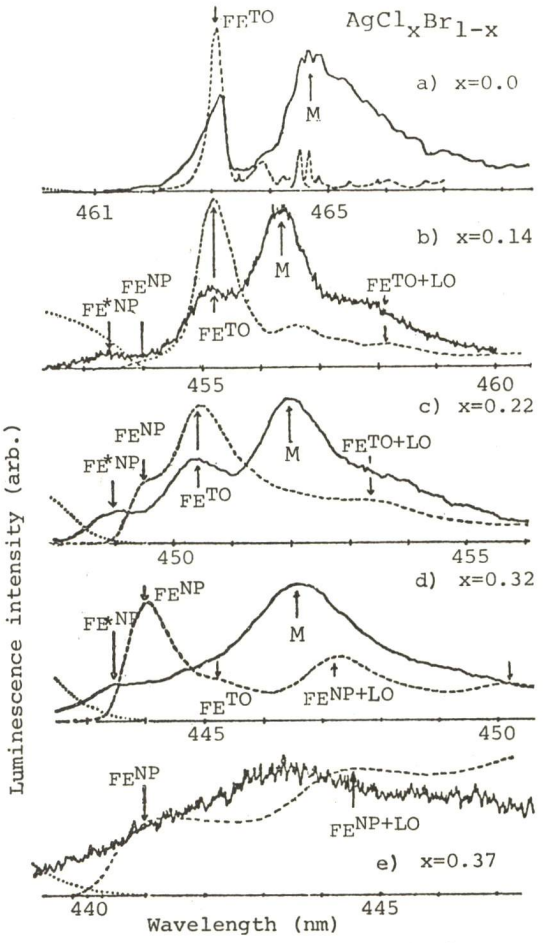

Fig.(1) Typical spectra of luminescence and absorption spectra of mixed crystal $AgCl_xBr_{1-x}$ at 1.9K
solid line → N_2 laser excitation
broken line → Hg lamp excitation
dotted line → optical density

As the excitation power P increases, the intensity of M-line and FE^*-line increases in proportion to $P^{1.5}$ and $P^{1.1}$, respectively, for a mixed crystal with x=0.14 as plotted in Fig.(2), whereas the intensity of FE^{TO}-lines is proportional to $P^{1.0}$. The line width of M-line increases as P increases. In the case of mixed crystals, the M-line sometimes becomes overlapped with the series of free exciton lines, so that it is rather difficult to analyze the shape of M-line. Nevertheless, no definite LO-phonon side band can be perceived for the queue of M-lines.

Typical time-resolved luminescence spectra of $AgCl_xBr_{1-x}$ are shown in Fig.(3) for the case of x=0.14. Here, the luminescence spectra at the highest levels of excitation obtained immediately after excitation were observed to change gradually to turn to the spectra similar to those at low levels of excitation. Even the M-line at high levels of excitation close to the FE^{NP+LO}-line at low levels of excitation in the case of $AgCl_{0.32}Br_{0.68}$ (Fig.1-d) can be clearly time-resolved each other with an accuracy better than the resolution power in wavelength. This technique assures the new

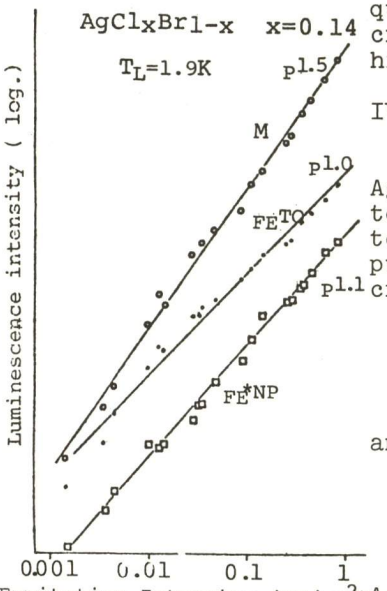

Fig.(2) Dependence of the intensity of M-, FE^{TO}- and FE^{*NP}-lines on the intensity P for $AgCl_{0.14}Br_{0.86}$
∘ M-line: · FE^{TO}-line:
▫ FE^{*NP}-line

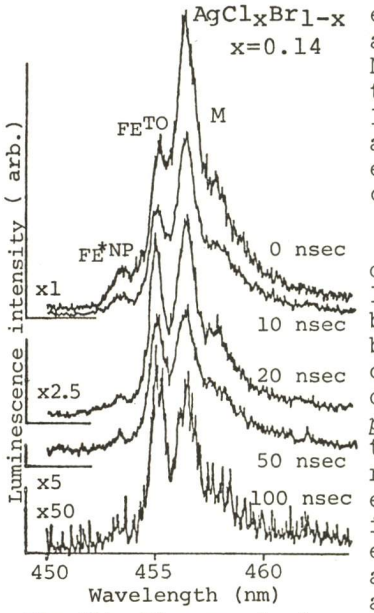

Fig.(3) Time-resolved luminescence spectra of $AgCl_{0.14}Br_{0.86}$ at 1.9K under an N_2 laser excitation (1MW/cm^2)

queues of M-line and FE^{*NP}-line in mixed crystals to be ascribed to the effect at high density excitation.

IV. Discussion

First, properties of the M(x)-line for $AgCl_xBr_{1-x}$ described above are quite similar to those of the M-line due to the free excitonic molecules for pure AgBr [2], [3]. In pure AgBr(x=0), an excitonic molecule is created in the process

$$\text{exciton(L)} + \text{exciton(L)} \rightarrow \text{excitonic molecule}(\Gamma \text{ or } x), \quad (3)$$

and annihilates in the process

$$\text{free excitonic molecule}(\Gamma \text{ or } x) \rightarrow \text{exciton(L)} + \hbar\nu + \text{TO(L)}. \quad (4)$$

Actually, in the experiment for pure AgBr crystals by Baba and Masumi [2], the intensity of M-line from free excitonic molecules was proportional to $P^{1.6}$ and the line shape of M-line well fits the curve calculated by using the Cho theory [4].

Results for $x \neq 0$ in Figs.(1)~(3) indicate quite similar situations to those for x=0 except that the line shape of both M-line and FE-lines become Gaussian-like for $x \neq 0$. Nevertheless, one can readily recognize that the new queue of M(x)-line tends to the M-line for pure AgBr (x=0) as $x \rightarrow 0$. Thus, we ascribe the queue of M(x)-line to the free excitonic molecules in $AgCl_xBr_{1-x}$ mixed crystals.

Secondly, we have recognized another new queue of broad luminescence called the FE^{*NP}-line in Fig.(1). These lines have never been observed for pure AgBr (x=0) but can be observed *"in* $AgCl_xBr_{1-x}$ *mixed crystals"* only *"at high density excitation"*. The P-dependence of FE^{*NP}-line is definitely *"superlinear"*. Also Fig.(3) clearly illustrates that the FE^{*NP}-line can be time-resolved as a component at high density excitation. As the position of FE^{*NP}-line is located just at the indirect absorption edge, this is indeed a rather rare case that a high density excitation effect appears at an energy region higher than FE-lines. Also, the shape of broad line is characteristic to the Boltzmann distribution with temperatures above 30K and the high energy tail of FE^{*NP}-line even extends into the region of indirect absorption. These results suggest a possi-

bility of the existence of a new Auger-like process in the exciton system such as the inelastic collision either between hot exciton and hot exciton (5a) or between hot excitonic molecule and trapping center (5b). The first possibility is written as

$$\text{free hot exciton} + \text{free hot exciton} \rightarrow \text{exciton} + \hbar\nu^{*}. \qquad (5a)$$

Here, the sign * denotes an excess gain of energy. The process (5a) can be predominant in the case of high density excitation but so far rarely noticed perhaps for lack of relevant experimental data. The second possibility is conceived to be due to the process such that

$$\text{frustrated excitonic molecule} \rightarrow \text{trapped exciton} + \hbar\nu^{*}. \qquad (5b)$$

In the process (5b), the FE^{*NP}-line may be due to the radiative recombination of the free exciton with zero phonon in $AgCl_xBr_{1-x}$ each of which, once in the past, formed an excitonic molecule but unfortunately dissociated each other with an unfair energy distribution between its partner-exciton either self-trapped or trapped at Iodine impurity. *"A frustrated excitonic molecule"* we call this type of molecule.

Finally, the binding energy of a free excitonic molecule, $E^{b}_{em}(x)$, was studied as a function of x. A peculiar feature here is an unexpected decrease of $E^{b}_{em}(x)$ around $x \lesssim 0.1$ with increasing x and its recovery above $x>0.2$. The fact that M-line has no higher orders of LO-phonon side-band in Fig.(1) can be explained by the weaker LO-phonon coupling-intensity of an excitonic molecule with a quadrupole moment than that of an exciton with only a dipole moment. It may be conceivable that a free excitonic molecule is associated with TO(L)- or TA(L)-phonons besides the momentum conserving TO(L)-phonon rather than with other types of phonons such as LO(Γ).

Thus, we conclude that the new queues of intrinsic luminescence lines supposed to be due to *"the partial recombination of the free excitonic molecules"* and possibly due to *"the Auger process in the two-exciton system"* have been simultaneously observed, for the first time, in $AgCl_xBr_{1-x}$ mixed crystals.

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