Comment on “Inverse exciton series in the optical decay of an excitonic molecule”

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Tokunaga et al. [Phys. Rev. B 59, R7837 (1999)] claim the first successful observation of the inverse exciton M series in the emission spectrum of excitonic molecules. We assert that actually such a series was observed as early as 1989 in the β-ZnP₂ crystal. We show that the objections of Tokunaga et al. against the biexciton nature of the inverse exciton series in β-ZnP₂ are ungrounded. In particular, their estimations for the ratio of the intensities of M2 and M1 emission lines in this crystal give two orders smaller value because they do not take into account the reabsorption of the M1 line photons. We report the observation of additional inverse exciton M’ series in the emission spectrum of excitonic molecules in β-ZnP₂.

To our knowledge the first observation of the emission M series caused by two-electron radiative transitions in a biexciton was reported by some authors of the present Comment ten years ago.

In the recent publication Tokunaga et al. have reported an observation of the inverse exciton M series in the emission spectrum of excitonic molecules in CuCl crystal. They claim that their experiment is the first successful observation of such a series in semiconductors. The aim of our Comment is to show that the above claim is not actual.

Our first argument is that the ratio of the intensities of M2 and M1 lines of the series in β-ZnP₂ is too large for the biexciton M series: $I_2/I_1 \sim 10^{-1}$. We would like to point an attention of the authors of Ref. 2 to the following. Indeed, an experimental value of $I_2/I_1$ is $1.1 \times 10^{-1}$. Proceeding from the assumption of biexciton nature of the inverse exciton series in β-ZnP₂, we obtained theoretically in Ref. 5 $I_2/I_1 = 1.1 \times 10^{-2}$. Numerical estimations of the authors of Ref. 2 give $\sim 10^{-3}$ for $I_2/I_1$ in this material. However, as we have pointed out in Ref. 5, this disagreement between theory and experiment is clear enough. At high excitation of the sample by powerful pulse N₂ laser (excitation intensities $\sim 10^6 W/cm^2$) the concentration of 1S excitons is high enough. In addition to this, in β-ZnP₂ the lowest exciton state is the forbidden state of orthoexciton that could raise the concentration of excitons in 1S state. Transitions from the 1S state of exciton into the molecule ground state cause reabsorption of M1 line photons ($h\nu_{1S} + h\nu_{M1} \rightarrow h\nu_{2G}$) and corresponding decrease of this line intensity. Concentration of excitons in the 2S, 3S, ... states does not increase considerably because of their fast relaxation to the 1S state, and there is no saturation of the lines M2, M3 and M∞. This our argument is based on the results of experimental study of the dependences of the intensities of inverse series lines on the excitation intensity $I_{exc}$ (fig. 2). The second power increase of the M1 line intensity with $I_{exc}$ slows done at high excitation levels, and this effect becomes stronger with increase of the excitation intensity. Such saturation effect is not observed for other lines of the series. Let us extrapolate the M1 line intensity dependence on excitation intensity to the values of $I_{exc}$ at which an experimental value of $I_2/I_1 = 1.1 \times 10^{-1}$ (fig. 3). Consequently, we obtain the value of $I_2/I_1$ in the case of the absence of reabsorption of M1 line photons and the respective absence of this line saturation. An extrapolation gives $I_2/I_2 = 4.3 \times 10^{-3}$. This value agrees with Ref. 5 estimations ($\sim 10^{-3}$) which do not consider the reabsorption effect. Some disagreement between the value obtained from the extrapolation and our estimations made in Ref. 5 ($1.1 \times 10^{-2}$) is possibly due to rough wave function of biexciton that we have used in Ref. 5. For other lines of the inverse series in β-ZnP₂ good agreement between experimental and theoretical values of the ratios of intensities takes place: $(I_3/I_2)_{exp} = 1.4 \times 10^{-1}$ and $(I_3/I_2)_{th} = 1.3 \times 10^{-1}$; $(I_\infty/I_3)_{exp} = 4.3 \times 10^{-1}$ and $(I_\infty/I_3)_{th} = 3.9 \times 10^{-1}$, where $I_\infty = \sum_{n=4}^{\infty} I_n$ is the total intensity of M4, M5, ... lines which merge into the total M∞ line. In CuCl the lowest exciton state is allowed. Biexcitons in Ref. 5 were resonantly created by two-photon absorption method and, therefore, excitons would be created only at the optical decay of biexcitons. Due to these two facts, the concentration of excitons would be insufficient for reabsorption of M1 line photons, and this line would not be saturated, i.e. an agreement between experiment and theory would not be perfect for all lines of the inverse series in CuCl. Such an agreement was reported in Ref. 5. 
$M$ series in $\beta-ZnP_2$ is observed at considerably higher temperatures too (fig. 1). This fact confirms high binding energy of the biexciton in $\beta-ZnP_2$ and rejects any possible impurity interpretation. $\beta-ZnP_2$ is very remarkable in the following. If the direction of the wavevector of emitted photon $k$ is parallel to axis $b$ of crystal ($k \parallel b$) and photon polarization is $E \parallel a$, another inverse exciton $M'$ series is observed in emission spectrum of this crystal (fig. 3). This additional series is symmetric to $A$ series of the free $S$ orthoexciton which is observed in absorption spectrum at $E \parallel a$ and $k \parallel b$. Thus, $M'$ series is due to the radiative transitions from the excitonic molecule ground state to the $S$ states of orthoexciton. Main $M$ series is symmetric to $C$ series of the free $S$ paraexciton which is observed in absorption and emission spectrum at $E \parallel c$. Respectively, $M$ series is due to the radiative transitions from the biexciton ground state to the $S$ states of paraexciton.

Authors of Ref. [4] see the cause that the previous attempts of biexciton $M$ series observation were unsuccessful in fact that “the $M_{n \geq 2}$ lines are extremely weak in intensity, requiring for their observation a highly sensitive detection technique and a high-quality sample free from impurity emissions”. However, the fact of extremely weak intensities of $M$ series lines in $CuCl$ does not prove the impossibility of that in other materials these intensities can be considerably higher. Indeed, in $CuCl$ intensities of $M_{n \geq 2}$ lines are extremely small, since in this material: $I_2/I_1 = 1.4 \times 10^{-4}$; $I_4/I_1 = 4.0 \times 10^{-5}$; $I_6/I_1 = 1.5 \times 10^{-5}$. In $\beta-ZnP_2$ we have more than one order higher values: $I_2/I_1 = 4.3 \times 10^{-3}$; $I_6/I_1 = 6.0 \times 10^{-4}$; $I_4/I_1 = 2.6 \times 10^{-4}$. This fact simplifies the observation of $M$ series in $\beta-ZnP_2$. And finally, authors of Ref. [4] asserted that our experimental data were not confirmed in a similar experiment by K. Kondo (K. Kondo, M.S. thesis, Okayama University, 1998). However, they have answered by themselves on this point having written that the high-quality samples are required for biexciton $M$ series observation. Most likely, K. Kondo just did not have the samples of the required quality.

The authors of Ref. [4] determined the components $C_n$ of the excited states $n = 2, 3, 4$ in the biexciton wave function in $CuCl$ from the relative intensities of $M1, M2, M3, M4$ lines. This allowed them to reconstruct the internal molecule wave function. However, they did not say that this idea was proposed in Ref. [4]. Only the reabsorption of $M1$ line photons and the respective saturation of this line did not allow us to reconstruct the biexciton wave function in $\beta-ZnP_2$. However, taking for $I_2/I_1$ the extrapolation value obtained above, we can estimate the components $C_n$ of the excited states in the biexciton wave function in $\beta-ZnP_2$ as following: $|C_2/C_1|^2 = I_2/I_1 = 4.3 \times 10^{-3}$; $|C_3/C_1|^2 = I_3/I_1 = 6.0 \times 10^{-4}$; $|C_4/C_1|^2 = I_4/I_1 = 2.6 \times 10^{-4}$.

In conclusion, we assert that the inverse exciton $M$ series in the emission spectrum of excitonic molecules was observed for the first time in $\beta-ZnP_2$ crystal in 1989. Besides this series, we have observed in this crystal an additional inverse exciton $M'$ emission series which is due to the radiative transitions from the biexciton ground state to the $S$ states of orthoexciton.

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**FIG. 1.** (a) Biexciton $M$ series in emission spectrum of the $\beta-ZnP_2$ at excitation intensity $\sim 10^6 W/cm^2$ (pulse $N_2$ laser) and temperature $2K$. (b) $S$ paraexciton $C$ series in emission spectrum of the $\beta-ZnP_2$. Photon polarization: $E \parallel c$. The inset presents the scheme of radiative transitions in biexciton causing the $M$ series.

**FIG. 2.** Dependences of $M1$ and $M2$ line intensities on excitation intensity.

**FIG. 3.** Emission $M$ series in $\beta-ZnP_2$ at excitation intensity $\sim 10^6 W/cm^2$ and temperature $77K$. Photon polarization: $E \parallel c$.

**FIG. 4.** Main biexciton $M$ series and additional biexciton $M'$ series in emission spectrum of the $\beta-ZnP_2$ at $I_{exc} \sim 10^6 W/cm^2$ and $T = 2K$. $k \parallel b$, $E \parallel a$. 
\( \beta - \text{ZnP}_2 \)

\[ T = 2 \text{ K} \]

\[ \mathbf{E} \parallel \mathbf{c} \]
\[(I_2 / I_1)_{\text{extrapol}} = 4.3 \times 10^{-3}\]
$\beta - \text{ZnP}_2$

$T = 77 \text{ K}$

$E \parallel c$

Intensity

$\text{Energy (eV)}$

1.5144

1.5268

1.5392

1.5516

M1

M2
$\beta - \text{ZnP}_2$

$T = 2 \, \text{K}$

$k \parallel b; E \parallel a$

$E \parallel a$

$M_1 L$

$M_1'$

$M_1 T$

$M_2$

$M_2'$

Intensity

Energy (eV)

1.5144

1.5268

1.5392

1.5516