

Two-electron transitions involving a biexciton

N. M. Belyĭ, I. S. Gorban', V. A. Gubanov, and I. N. Dmitruk
T. G. Shevchenko State University, Kiev

(Submitted 6 June 1989)

Pis'ma Zh. Eksp. Teor. Fiz. **50**, No. 2, 75-77 (25 July 1989)

The luminescence spectrum of a highly excited β -ZnP₂ crystal revealed the presence of an inverse hydrogen-like series of bands which are interpreted as radiative transitions from the state of an exciton molecule to the ground state and the excited state of an exciton.

We have studied the photoluminescence of β -ZnP₂ single crystals upon exciting them with argon, copper, and nitrogen lasers over a broad range of power densities ($P = 10^1 - 10^6$ W/cm²). Figure 1 (curve *a*) shows the photoluminescence spectrum of the test crystal upon exciting it with an argon laser ($P = 50$ W/cm²). In this spectrum we see emission bands with an upper and lower polariton branch and some narrow lines which are apparently attributable to the radiative transitions from the localized-exciton states. An increase in the power density of the laser ($P = 60$ kW/cm² for a copper laser, curve *b*; $P = 1$ MW/cm² for a nitrogen laser, curve *c*) changes the spectrum fundamentally: There are virtually no localized-exciton emission lines because of the saturation of the corresponding recombination channels, and several intense broad photoluminescence bands form. These bands produce an inverse hydrogen-like series (IHS) which converges toward longer wavelengths. The IHS bands and the exciton energy levels are symmetric with respect to the point $E^* = 12\,539$ cm⁻¹. The spectral position of the IHS bands and the appearance of IHS at high excitation levels of the crystal lead us to assume that it is produced as a result of radiative transitions from the ground state of the exciton molecule to the exciton levels with $n = 1, 2, 3, \dots \infty$. To test our assumption of the nature of the IHS bands, we analyzed the intensities of the photoluminescence bands versus the power density of the exciting light. This dependence turned out to be a power function with an exponent of nearly 2, in complete agreement with the assumption that this series of photoluminescence bands belongs to the exciton molecule emission spectrum.

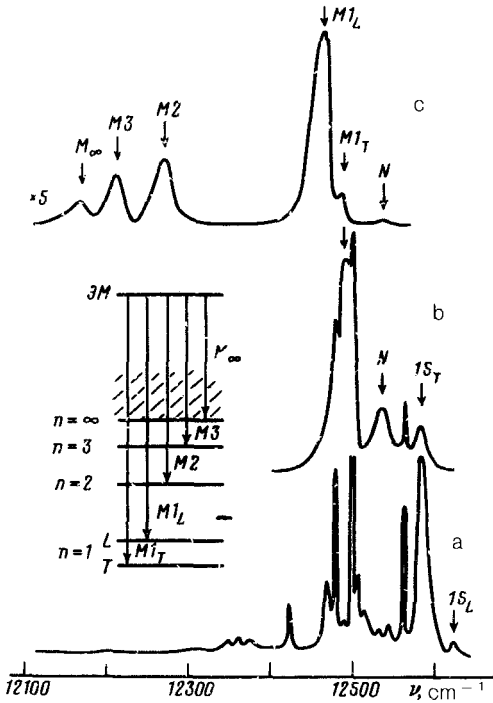


FIG. 1. Photoluminescence spectra of a monoclinic zinc diphosphide crystal at $T = 2$ K and various pumping levels. Schematic diagram of the transitions which form an inverse hydrogen-like series.

The validity of this interpretation of the nature of IHS bands has also been confirmed by a group-theory analysis of the symmetry of the exciton molecule. This analysis was carried out with allowance for the Pauli principle which imposes on the biexciton wave function the requirement that it be antisymmetric with respect to the interchange of electrons and holes and with respect to the assumption that the envelope function of the ground state of the exciton molecule is totally symmetric. Taking into account the different parities of the states in the valence band and in the conduction band of the test crystal [one of them is described by representation $(E')^+$ and the other by $(E')^-$, as follows from the allowed transitions of excitons to the S states observed in Ref. 1], we can describe the symmetry of the exciton molecule by

$$\begin{aligned} \Gamma_{EM} &= [\Gamma_v \times \Gamma_v]_- \times [\Gamma_c \times \Gamma_c]_- \times \Gamma_{env} \\ &= [(E')^+ \times (E')^+]_- \times [(E')^- \times (E')^-]_- \times A^+ = A^+, \end{aligned}$$

The biexcitons in β -ZnP₂ are thus identical in symmetry to the ground state of the crystal and have no fine structure, while the photodisintegration of an exciton molecule must include exciton states, the transitions to which are allowed in the absorption, reflection, and photoluminescence spectra. Despite the fact that the fine structure of an exciton molecule is assumed to be absent, the spectra of its radiative recombination may exhibit a fine structure of the exciton states to which the transition occurs:

$$\Gamma(nS)_{ex} = \Gamma(nS)_{env} \times \Gamma_v \times \Gamma_c = A^+ \times (E')^+ \times (E')^- = 2A^- + 2B^-.$$

These spectra may also exhibit a polariton splitting of the exciton states. Such a structure has been observed in an $M1$ band (curve c). The distance between its two main components, $M1_L$ and $M1_T$, corresponds to the longitudinal-transverse splitting of the $1S$ exciton. This splitting can be interpreted as the result of transitions from the ground state of the exciton molecule to the levels of the upper and lower polariton branches of the exciton ground state (see Fig. 1).² Less pronounced singularities of the fine structure of the $M1$ band are apparently attributable to the fine structure of the energy states of the $1S$ exciton, to which the transition occurs. Interesting results were obtained in the study of the fine structure of the $M1$ band over a broad interval of intensities of the laser pumping of the crystal. At $P = 10^3 - 10^4$ W/cm² (curve b) the dominant transitions were those to the lower polariton branch of $M1_T$. Upon increasing the excitation level, the rate of increase of the intensity of the $M1_T$ band decreased (probably because of the increase in the number of excitons in the $1S_T$ state and because of the overabsorption of the photons of the $M1_T$ band as a result of the transitions $1S_T \rightarrow$ exciton molecule), while the intensity of the $M1_L$ band increased. At $P = 10^5 - 10^6$ W/cm² the $M1_L$ band became the dominant band of the spectrum. The amplitude "pumping" of the $M1_L$ band can apparently be explained in terms of the slight increase of the upper polariton branch population due to the fast relaxation of the excitons to the lower polariton branch. At $P = 10^4$ W/cm² an N band, whose intensity increases ultralinearly but slower than that of an exciton-molecule band, appears in the photoluminescence spectra of β -ZnP₂. It is assumed that the N band forms during the inelastic polariton-polariton scattering $1S_T + 1S_T \rightarrow 1S_L + \hbar\omega_N$ or as a result of annihilation in the three-particle complex which consists of an exciton and a free carrier.

Working from the value of E^* , we can determine the binding energy of an exciton molecule

$$E_{\text{bEM}} = 2 [E(1S)_{ex} - E^*] = 120 \text{ cm}^{-1}.$$

An inordinately large value of the binding energy (~ 0.3 of an exciton rydberg) can be attributed to either the appreciable difference in the effective masses of the electron and hole in β -ZnP₂ or to a large deviation in the energy position of the $1S$ exciton from its calculated value (a similar situation has been observed in a ZnO crystal²).

In summary, we have observed for the first time in β -ZnP₂ crystals at a laser excitation power density $P = 10^5 - 10^6$ W/cm² an inverse hydrogen-like series of bands which are caused by the transitions from the ground state of an exciton molecule to the excited ($M2$ and $M3$) states and the ionized (M_∞) state of an exciton.

¹I. S. Gorban' *et al.*, Dokl. Akad. Nauk Ukr. SSR, series A No. 4, 48 (1988).

²C. Klingshirn and H. Haug, Phys. Rep. 70, 315 (1981).

Translated by S. J. Amoretty