Heteroexcitonic molecule

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In this letter we report the first observation of an excitonic molecule formed by an edge exciton and by an exciton bound to a deeper band state: a heteroexcitonic molecule.

We observed this new formation experimentally in the emission spectrum of a gallium selenide crystal subjected to intense laser excitation. The radiative recombination of the heteroexcitonic molecule can be described by the diagram

$$\text{Het. mol.} \begin{cases} \nearrow \text{edge exciton} + \hbar\omega_{\text{deep}} \\ \searrow \text{deep exciton} + \hbar\omega_{\text{edge}} \end{cases}.$$

In other words, two lines appear in the emission, shifted a distance equal to the binding energy of the heteroexcitonic molecule in the long-wave direction from the photoluminescence lines of the deep and edge excitons. It follows from an analysis of the kinetics of the process that there is a quadratic dependence on the pump intensity. The relative intensities of these lines are associated with the probability for the annihilation of the corresponding excitons. During the excitation of the crystal by light with a photon energy greater than the energy of a deep exciton, the recombination occurs as described above. At a lower photon energy, this recombination mechanism does not operate.

We studied the photoluminescence spectra of β-GaSe at 4.2 K during excitation by the second harmonic from a ruby laser (3.57 eV) with a maximum intensity of 2×10^{24} photons/(cm$^2\cdot$s) in a 40-ns pulse and by the second harmonic from a neodymium laser (2.34 eV), with a maximum intensity of 4×10^{24} photons/(cm$^2\cdot$s). The luminescence signal at the output of a DFS-12 spectrograph is recorded by a pulsed synchronous detection system.

Figure 1 shows some typical emission spectra for various pump intensities in the regions of the edge and deep excitons of GaSe (the ordinate scales are the same in the two parts of the spectrum). Figure 2 shows the intensity of the emission lines versus the pump intensity. During pumping by light with a photon energy of 3.57 eV, the photoluminescence spectrum at 4.2 K has, in addition to emission lines which have been observed previously [a free deep exciton A_{deep} (3.385 eV) and a free edge exciton A_{edge} (2.113 eV), which coincide with corresponding absorption lines of this crystal[1]; biexcitons, a deep biexciton M_{deep} (3.365 eV; Ref. 1) and an edge biexciton M_{edge} (2.108 eV; Ref. 2); and collections of deep excitons, P (3.325 eV), and biexcitons, P_b (3.345 eV; Ref. 1)], the following emission lines: lines of heteroexcitonic molecules, at 3.371 eV and 2.099 eV, shifted in the long-wave direction from the emission lines of the deep and edge excitons by 14 meV, which is the binding energy of the heteroexcitonic molecule.

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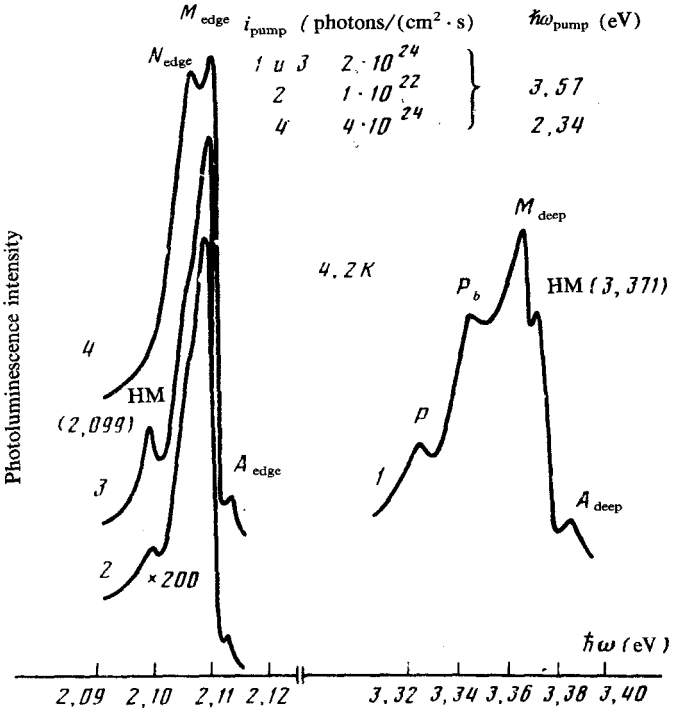

FIG. 1.

The intensities of these heteroexcitonic-molecule lines increase quadratically with the pump intensity.

During the excitation of photoluminescence by the second harmonic of a neodymium laser (2.34 eV), the heteroexcitonic-molecule line at 2.099 eV is not found in the

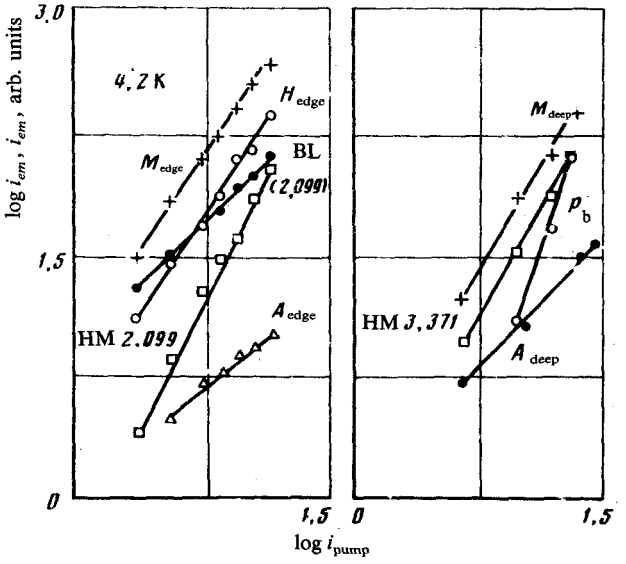

FIG. 2.

emission. The background level (BL) at this energy (2.099 eV) varies linearly with the pump intensity (Fig. 2). At the same time, the line H_{edge} (2.104 eV) begins to dominate the spectrum. In the emission spectra found during pumping with a photon energy of 3.57 eV, that line is visible only as a ledge. It is apparently due to an emission during exciton-electron collisions.[4]

In summary, it has been found possible for the first time in these experiments to observe an excitonic molecule formed by edge and deep excitons: a heteroexcitonic molecule. The emission of this molecule is one of the primary pathways for recombination under these excitation conditions.

I wish to thank V. K. Subashiev for useful discussions.

[1)]The edge and deep excitons are direct excitons and correspond to the center of the Brillouin zone, specifically, the Γ point; however, we do not rule out the possibility that the deep exciton belongs to the point M_0 (Ref. 3).

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Translated by Dave Parsons