Excitonic molecule bound to a neutral acceptor in a hexagonal CdS crystal

B. S. Razbirin and D. K. Nel'son
A. F. Ioffe Physicotechnical Institute, Russian Academy of Sciences, 194021, St. Petersburg, Russia

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A new emission line has been found in the luminescence spectrum of an intensely excited CdS crystal. This line is interpreted as resulting from the radiative decay of an excitonic molecule bound to a neutral acceptor.

Under certain conditions the interaction between excitons in a dense exciton gas results in the formation of an excitonic molecule: a biexciton. There is now convincing proof that these entities exist in numerous direct-gap crystals, including CdS. Biexcitons bound to impurity centers may also arise in an intensely excited semiconductor, and many-exciton impurity complexes may form. Complexes of this sort have been observed in indirect semiconductors, e.g., germanium and silicon.[1] The existence of many-exciton impurity complexes in the case of direct-gap semiconductors, on the other hand, remains an open question.

According to the Pauli principle, the electrons (or holes) which are part of a many-exciton impurity complex cannot be in the same quantum state. For direct-gap semiconductors with nondegenerate bands, only one pair of electrons (or holes) can thus be in the lowest energy state. For indirect semiconductors such as Ge and Si, this restriction is lifted, because there are several valleys in the conduction band. The electrons in a complex are thus in the lowest energy state, but they lie in different valleys. For direct-gap semiconductors, the restrictions imposed by the Pauli principle have the consequence that the third, fourth, etc., electron (or hole) which goes into a many-exciton impurity complex must be in an excited state. The energy stability of such complexes requires further analysis.

We consider a structure of exciton-impurity complexes in hexagonal II–VI crystals. The D^0X-exciton complex bound at a neutron donor is a positively charged center near which there are two electrons and one hole. This complex is shown schematically by diagram (1) in Fig. 1. It was shown in Ref. 2 that a hole taking part in a complex in the hexagonal CdS crystal may be in not only the $1S$ ground state but also the $2P$ or $3D$ excited state (we have in mind excited states of the hole, not excited states of the overall exciton). Since the activation energy of these states is on the order of a few meV, these states are stable at low temperatures. For an A^0X-exciton complex bound at a neutral acceptor, there are a negatively charged immobile center, two holes, and one electron [diagram (2) Fig. 1]. If we now imagine that we connect one more exciton to this complex, we find the complex shown by diagram (3) in Fig. 1. The part of the complex enclosed by the dashed line may be thought of as an immobile, positively charged center. The overall complex can thus be assumed to be analogous to an exciton bound at a neutral donor, with the one distinction that only two holes can be

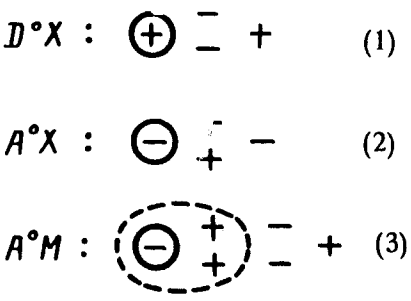

FIG. 1. Schematic structures of exciton-impurity complexes.

in the $1S$ ground state; the third must be in a $2P$ or $3D$ excited state, as mentioned above. On the other hand, this complex constitutes a biexciton bound to a neutral acceptor; we accordingly denote it by A^0M.

We now consider the radiative transition

$$A^0M \rightarrow A^0X + h\nu,$$

and we wish to calculate the energy of the corresponding photon. The annihilation of one of the excitons in the complex releases an energy

$$h\nu = E_g - R - E_b - \Delta E,$$

where E_g is the band gap, R is the exciton rydberg, E_b is the binding energy of the exciton with the impurity center, and ΔE is the energy distance between the $2P$ (or $3D$) and $1S$ states of the hole. If we assume that, in accordance with the analogy mentioned above, the binding energy of an exciton connected to the A^0X complex is roughly equal to the binding energy of an exciton with a neutral donor ($\approx$6–7meV for CdS), and when we note that ΔE is on the order of several meV, as mentioned above, we might expect a line corresponding to the transition $A^0M \rightarrow A^0X + h\nu$ to appear in the luminescence spectrum, near the familiar I_2 line. In this letter we are reporting the observation of a new emission line in the luminescence spectrum of an intensely excited CdS crystal. This new line can be interpreted as resulting from the radiative decay of a biexciton bound to a neutral acceptor.

We studied the luminescence spectra of pure (i.e., not deliberately doped) CdS single crystals. The test samples were crystalline platelets with a thickness on the order of 10 μm, with c axis lying in the plane of the platelet. The beams from a nitrogen laser ($\lambda = 337.1$ nm) and an argon laser ($\lambda = 476.5$ nm) were used to excite the luminescence. The measurements were carried out at a liquid-helium temperature ($T = 2$ K).

Figure 2 shows the luminescence spectra of one of the test samples, during excitation by the nitrogen laser. We see from this figure that, as the excitation intensity is raised, a new emission line — not found in the spectra in the case of weak excitation — appears in the luminescence. Its wavelength is $\lambda \approx 486.8$ nm. This line can be seen clearly in the spectrum at excitation intensities $P \approx 10^2$–10^4 W/cm^2. As the excitation intensity is raised further, this line becomes difficult to distinguish against the background of the familiar M band.[3]

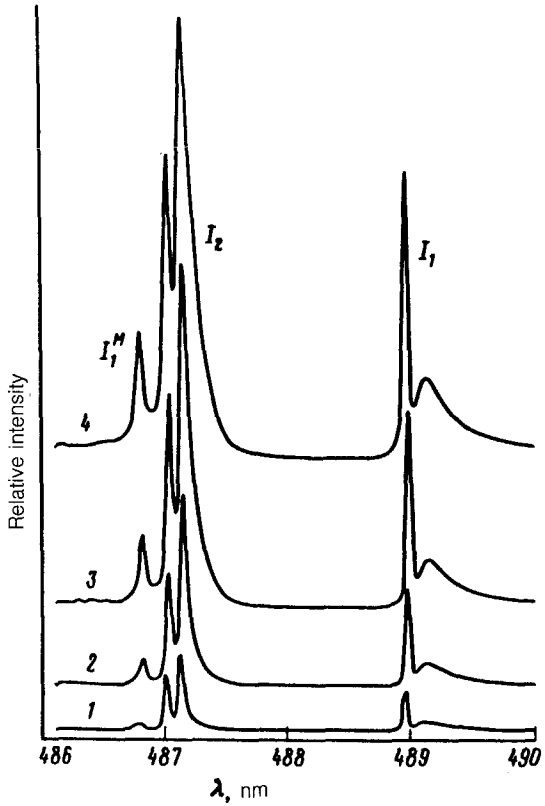

FIG. 2. Luminescence spectra of a CdS crystal. Excitation intensity, W/cm^2: 1—200; 2—500; 3—1000; 4—2000.

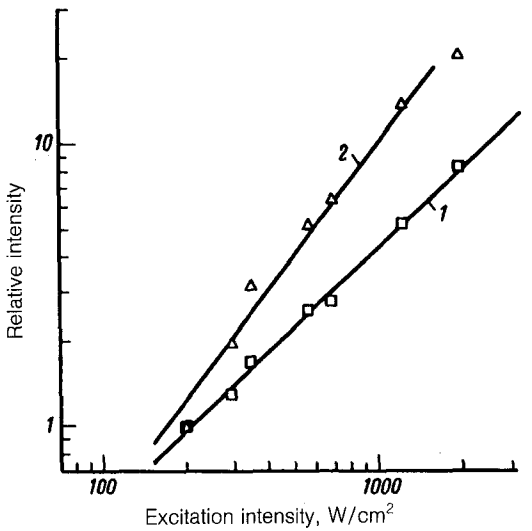

FIG. 3. Intensity of the luminescence lines of a CdS crystal versus the excitation intensity. 1—The line I_1; 2—the line I_1^M.

Interestingly, the intensity of this new line (which we call I_1^M) is correlated with the intensity of line I_1, which is due to the radiative decay of an exciton bound to a neutral acceptor. For example, the line I_1^M can be clearly seen in samples which have an intense line I_1, while in samples for which I_1 is missing we cannot see I_1^M. The line I_1^M is thus indeed associated with the presence of acceptor centers in the crystal.

The fact that the intensity of I_1^M increases faster than linearly with the excitation intensity is strong evidence that this line is due to exciton–exciton interactions in the intensely excited crystal. Figure 3 shows the intensity of line I_1 and of the new line I_1^M versus the excitation intensity in logarithmic scale. We see that over the range of excitation intensities considered here the intensity of line I_1 increases essentially linearly with excitation intensity, while the intensity of I_1^M clearly increases faster than linearly. The fact that I_1^M appears only in the case of intense excitation, the fact that its intensity increases at a faster than linear pace with the excitation intensity, and the fact that the spectral position of this line is close to what we would expect support the interpretation that this line is a consequence of the radiative decay of an excitonic molecule bound to a neutral acceptor.

[1] V. D. Kulakovskiĭ, G. E. Pikus, and V. B. Timofeev, Usp. Fiz. Nauk **135**, 237 (1991) [Sov. Phys. Usp. **24**, 815 (1991)].
[2] J. Puls, F. Henneberger, and J. Voigt, Phys. Status Solidi B **119**, 291 (1983).
[3] C. Klingshirn and H. Haug, Phys. Rep. **70**, 315 (1981).

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