Biexcitons in II–VI crystals

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The existence of biexciton states at high excitation intensities has been experimentally established in crystals CdS and CdSe with binding energies 2.5 meV (CdS) and 1.2 meV (CdSe).

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1. It is believed, as a result of a number of investigations by Shionoya's group, that biexcitons in hexagonal II—VI crystals are the cause of the M emission band[1] produced at high excitation intensities and situated on the low-energy side of the well known line I_2, which is due to excitons bound by neutral donors. There are serious objections to this interpretation in[2,4], where the M band is not attributed to biexciton emission and is explained as being due to other mechanisms. The main arguments against the biexciton interpretation are the excessively large binding energy[1] in comparison with the theoretically predicted value,[5] the presence of a chemical shift[2,3] (dependence on the spectral position of the I_2 line), and the possibility of a different interpretation of the phenomenon.[3,4] Thus, the question of the biexciton state in II—VI crystals must be reviewed anew.

2. We prove in this paper the existence of biexcitons in II—VI compounds and show that their radiative decay corresponds to a different spectral singularity, the so called P line previously attributed to Auger recombination of two free excitons.[1]

Figure 1 shows the emission spectrum of a CdS crystal excited by an LGI-21

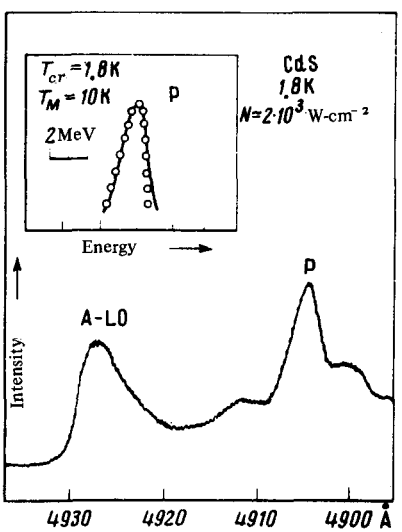

FIG. 1. Emission spectrum of CdS crystal at high excitation intensity. The insert shows a comparison of the experimental contour of the P line (solid line) with the Maxwellian-distribution contour (points).

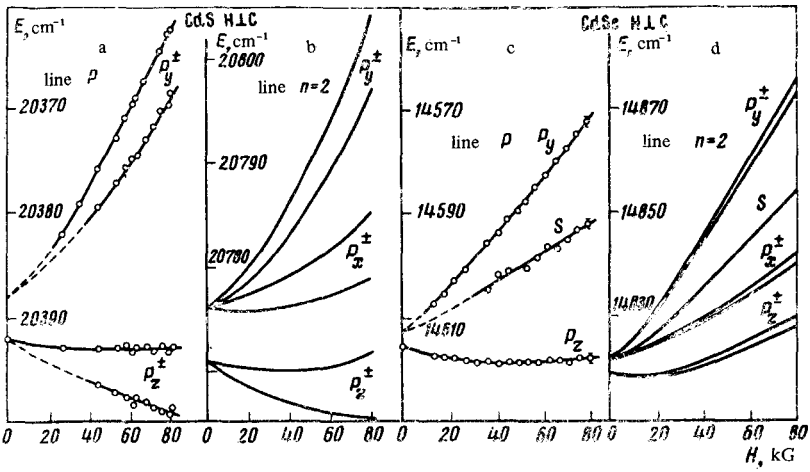

FIG. 2. Energy positions of the P lines (a, c) and of the $n=2$ lines of the free excition (b, d) vs the magnetic field ($H \perp c$) for the crystals CdS (a, b) and CdSe (c, d).

nitrogen laser. A detailed analysis of the spectral position of the line $P(\lambda = 4904.5$ Å) has shown that it can be attributed to biexciton radiative decay with transition of the remaining exciton to an excited state $A, n=2$. An analogous line $P(\lambda = 6842$ Å) was observed by us in the CdSe crystal. The contours of the P lines are characterized by a reciporcal Maxwellian distribution, corresponding to a biexciton temperature ~10 K (CdS) or ~20 K (CdSe). The binding energies of the biexcitons, determined from the spectral shifts of the P lines relative to the exciton level $A_T(\Gamma_5)$, are equal to 2.5 meV (CdS) and 1.2 meV (CdSe). These quantities are close to the theoretically expected[5] 2.6 meV (CdS) and 1.3 meV (CdSe), and agree with the rapid temperature vanishing of the P lines. The intensity of these lines increases superlinearly with increasing excitation intensity.

3. A magneto-optical investigation was carried out to confirm the hypothesis based on the aforementioned experimental facts, that the P lines are of biexciton origin. We have observed a complex splitting of these lines (CdS, CdSe) in a magnetic field (see Fig. 2). Comparison of the pictures of the Zeeman splitting of the P line and of the absorption line $n=2$[1)] for both orientations of the magnetic fields, $H \perp c$ and $H \| c$, has made it possible to interpret unambiguously the observed terms and to prove that the final state at which the transition terminates is indeed the level $n=2$ of the free exciton. The symbols for the smooth components on Fig. 2 pertain to the terms of the level $n=2$ to which the transitions take place. As seen from Fig. 3, the P lines are split with exactly the same g factors as the $n=2$ line. This fact denies the possibility of attributing the P line to Auger recombination of the bound excitons,[8] which is characterized by an entirely different picture of the Zeeman splitting.

The identification of the final state ($n=2$ of the free electron) in the P transition has enabled us to determine the behavior of the initial (biexciton) state in a magnetic field. No splitting of the biexciton level was observed, but a strong

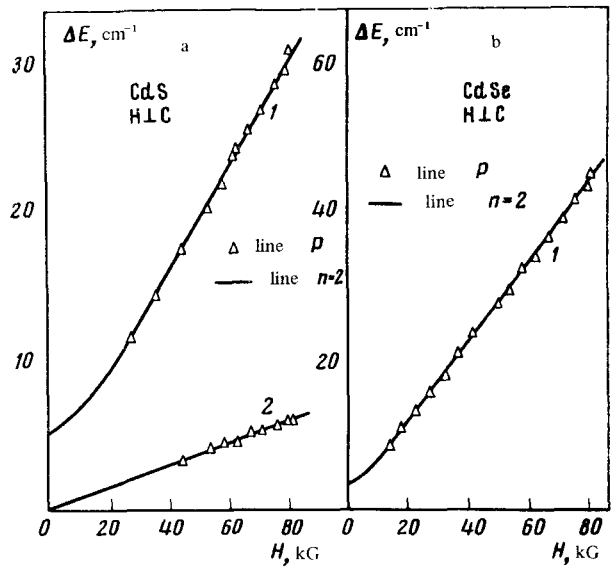

FIG. 3. Comparison of the orbital (1) and spin (2) splittings of the Zeeman components of the P lines (triangles) and $n=2$ lines (solid): a—CdS, b—CdSe.

diamagnetic shift has been established, which was determined by substracting the quadratic shift of the corresponding components of the state $n=2$ from the experimentally established shift of the Zeeman components of the P line. The diamagnetic shift turns out to be substantially anisotropic (for CdS: $d_\perp = 6 \times 10^{-10}$ and $d_\parallel = 9.4 \times 10^{-10}$ cm^{-1} G^{-2}), as expected of hexagonal crystals in which the wave function of the biexcitons should be flattened in the direction of the c axis. The diamagnetic shift itself is much larger than double the diamagnetic shift of the exciton level $n=1$, and consequently the P line cannot be attributed to collision of two free excitons. Thus, the magneto-optical experiments enable us to establish that the P line is indeed due to radiative decay of a biexciton with a transfer of the remaining exciton into the excited state $n=2$.

4. In principle, the radiative decay of a biexciton with formation of an exciton in various quantum states could lead to observation of an inverted series of emission lines ($M \to n=1, 2, 3, \cdots \infty$), shifted to the low-energy side of the exciton level $n=1$ by an amount equal to the binding energy of the molecule. However, as follows from Buttner's work[9] the intensity of the transitions to excited states ($n>1$) decreases rapidly with increasing quantum number. Indeed, in our experiments one observes distinctly the transition $M \to n=2$, while the transition $M \to n=3$ is hardly noticable. An important experimental fact is the absence, at high excitation intensities, of noticable emission lines, which might be interpreted as $M \to n=1$. transitions. This may be caused by two effects. The probability of the process $M \to n=1$ is proportional to the square of the modulus of the Fourier component of the wave function of the relative motion of the excitons in the biexciton[10]

$$W(Q) \sim |\psi_m(\frac{Q}{2})|^2 ,$$

where Q is the wave vector of the biexciton. The calculation of $W(Q)$ using the wave function of the biexciton from[5] reveals a sharp decrease of $W(Q)$ with increasing Q, and this leads to a decrease of the probability of the $M \to n=1$ transitions. On the other hand, in the region of low values of Q one should expect a decrease of the probability of the $M \to n=1$ transition, owing to the optical-exciton interaction in the states $n=1$.[11,12]

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[1)]An analysis for magnetic fields up to 35 kG was also carried out on the basis of perturbation theory in[6,7].

[1]H. Saito, S. Shionoya, and E. Hanamura, Solid State Commun. **12**, 227 (1973); S. Shionoya, Proc. Twelfth Intern. Conf. on Physics of Semiconductors, Stuttgart, 1974, p. 113; H. Saito, A. Kuroiwa, S. Kuribayashi, Y. Aogaki, and S. Shionoya, J. Luminescence **12/13**, 575 (1976).
[2]C. Klingshirn, Phys. Status Solidi [b] **71**, 547 (1975).
[3]A. F. Dite, V. I. Revenko, V. B. Timofeev, and P. D. Altukhov, Pis'ma Zh. Eksp. Teor. Fiz. **18**, 579 (1973) [JETP Lett. **18**, 341 (1973)].
[4]V. G. Lysenko, V. I. Revenko, and V. B. Timofeev, Pis'ma Zh. Eksp. Teor. Fiz. **24**, 157 (1976) [JETP Lett. **24**, 136 (1976)].
[5]O. Akimoto and E. Hanamura, Solid State Commun. **10**, 253 (1972); J. Phys. Soc. Jap. **33**, 1537 (1972).
[6]J. J. Hopfield and D. G. Thomas, Phys. Rev. **122**, 35 (1961).
[7]R. G. Wheeler and J. O. Dimmock, Phys. Rev. **125**, 1805 (1962).
[8]D. C. Reynolds, C. W. Litton, and T. C. Collins, Phys. Rev. **140**, A1726 (1965).
[9]H. Buttner, Phys. Status Solidi **42**, 775 (1970).
[10]É. I. Rashba, Fiz. Tekh. Poluprovodn. **8**, 1241 (1974) [Sov. Phys. Semicond. **8**, 807 (1975)].
[11]A. A. Gogolin, Fiz. Tverd. Tela (Leningrad) **15**, 2746 (1973) [Sov. Phys. Solid State **15**, 1824 (1974)].
[12]F. Heneberger and J. Voigt, Phys. Status Solidi [b] **76**, 313 (1976).