Radiation of an electron-hole drop in the layered semiconductor PbI_2

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By investigating its low-temperature (4.2 K) photoluminescence spectra under laser excitation, we have obtained, for the first time, indications that an electron-hole drop is produced in the layered crystal PbI_2.

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For the condensation of an exciton gas of high density into an electron-hole drop (EHD)[1] there must exist between the excitons attraction forces which are larger the greater the difference between the total exchange and correlation energy, on the one hand, and the Fermi energy of the electrons and holes, on the other. Therefore, the lower the Fermi level of the semiconductor, the more probable and more stable the multiexciton formation, as is evidenced by the observation of EHD in Ge[2] and Si,[3] in which the Fermi level is strongly depressed because of the multivalley character of the energy bands in these crystals. A low Fermi energy is possessed also by substances having large effective carrier masses, such as layered semiconductors. In addition, the strong anisotropy of the effective masses of such crystals leads to an increase of the binding energy of the EHD,[4] making layered semiconductors a suitable object for observation of such an exciton formation. We present below the first experimental indications of the appearance of EHD in a layered crystal. They were obtained with the compound PbI_2, polytype $2H$, by investigating its low-temperature photoluminescence spectra at high excitation levels.

All the investigated samples had high-quality cleavage-plane and end-plane surfaces, and this enabled us to measure, for the first time, the photoluminescence spectra at different experimental geometries (indicated in the insert of Fig. 1). The photoluminescence was excited by a mercury lamp or a nitrogen laser. The maximum exciton concentration following excitation with a focused laser beam was 10^{18} cm^{-3}. The spectral width of the gap in all the measurements did not exceed 0.3 meV.

Figure 1 shows the photoluminescence spectrum measured under ordinary and laser excitation at 4.2 K. Here A_1, A_2, and A_3 are the free-exciton emission lines for the different geometries of the experiment, I is the bound-exciton emission line, and K_1, K_2, and K_3 are emission lines of impurity origin. The main feature of the presented spectra at ordinary excitation levels is the polarization splitting of the exciton band by an amount $\Delta E_{A_1A_2} = 4.5$ meV, which was revealed previously by reflection spectra,[5] and the difference in the position of the component $\mathbf{E} \perp \mathbf{C}$ for different directions of the light.

In the case of laser excitation, as follows from the same figure, a new line appears, with half-width ~ 10 meV and with a faster-than-linear dependence on the excitation intensity: $J_L = J_{exc}^{(1.8-2.1)}$. Its position ($\lambda = 4981 \pm 0.5$ Å) at 4.2 K is practically independent of the experimental geometry, and the character of the temperature shift of the maximum differs from that of the free-exciton emission-line shift (Fig. 2). In fact, whereas the position of the exciton A band changes nonmonotonically with increasing temperature (Fig. 2a), the temperature shift of the L band has a linear character (Fig. 2b).

A question arises concerning the nature of the L band. The superlinear character of the dependence of its intensity on the excitation intensity can be due to different interaction effects (exciton-exciton scattering, exciton-electron scattering, formation of an exciton molecule, and formation of an electron-hole drop) and is in itself insufficient to explain the L band. However, the aggregate of the other properties of the L band gives grounds for discarding the first three possibilities. Indeed, the

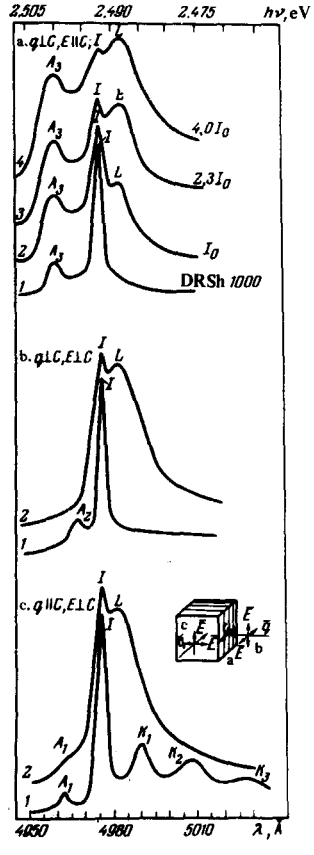

FIG. 1. Photoluminescence spectra of single crystals of PbI_2 for the experimental geometries a, b, c, following excitation by (1) a DRSh-1000 mercury lamp and (2) a nitrogen laser. For the experimental geometry with $\mathbf{q} \perp \mathbf{C}$ and $\mathbf{E} \parallel \mathbf{C}$, curves 2, 3, and 4 illustrate the photoluminescence spectra at different levels of excitation with a nitrogen laser.

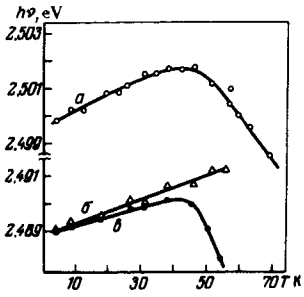

FIG. 2. Temperature dependence of the spectral positions of the free-exciton emission line (a), of the L line (b), and of the line corresponding to emission of an exciton molecule (c). All the curves correspond to the geometry with $\mathbf{q} \perp \mathbf{C}$ and $\mathbf{E} \parallel \mathbf{C}$.

spectral position of the line excludes its connection with an exciton Auger process, since the shortest-wavelength line due to this process should be observed at 5020 Å. The exciton-electron scattering line must shift with increasing temperature towards the red side of the spectrum, since $\mu^*_{exc} = m^*_e + m^*_h > m^*_e$,[6] whereas the L band has a temperature shift of opposite sign. Finally, in the case of formation of an exciton molecule (biexciton) the temperature dependence on its position should have the form shown in Fig. 2c. In addition, from the point of view of the biexciton is it possible to explain the spectral position of the L line and its large half-width. Thus, according to[7], at $\sigma = m^*_e/m_h = 0.7$ (this value of σ is obtained for PbI_2) the exciton binding energy should be ~ 5 meV. In fact, the distance between the L line and the free-exciton line, depending on the geometry of the experiment, changes from 9 to 12 meV. To explain the large half-width of the L band it would be necessary to assume that the effect of temperature of biexciton gas, if it has a Maxwellian velocity distribution, exceeds 100 K, which is not very likely.

All the revealed singularities of the L line can be explained by resorting to the EHD model. The main property of this formation is its large mobility, which is due to the low density of the effective mass of the drop and the decreased scattering of its electrons and holes by phonons. The very weak interaction of the drop with the phonons can be responsible for the difference in the temperature dependences of the spectral positions of the emission lines of the drop and of the free excitons. Thus, the dependence of the width of the forbidden band E_g on the temperature is determined by two factors: the temperature variation of the lattice parameters (which in different substances can lead to an energy shift of arbitrary sign) and electron-phonon interaction (which always decreases E_g). Owing to their influence, if the indicated two factors are of opposite signs the function $E_g(T)$ and consequently also $E_{exc}(T)$ can be complicated. In the case of EHD, owing to its weak interaction with the phonons, the temperature dependence of the position of the recombination line is determined only by the first factor and should be practically linear. Since it is precisely this picture observed in the experiment, it is most probable that the L line is connected with the EHD radiation. A confirmation of this identification is the appreciable half-width of the L line (~ 10 meV), which is close to the sum of the Fermi energies of the electrons of holes and the energy of their Coulomb interaction.

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[1]L. V. Keldysh, Materialy IX Mezhduhar. Konf. po fizike poluprovodnikov [Materials of 9th International Conference on Semiconductor Physics], Moscow, 1968, p. 1387.
[2]Ya. E. Pokrovskiĭ and K. I. Svistunova, Pis'ma Zh. Eksp. Teor. Fiz. 9, 435 (1969) [JETP Lett. 9, 261 (1969)].
[3]A. S. Kaminskiĭ and Ya. E. Pokrovskiĭ, Pis'ma Zh. Eksp. Teor. Fiz. 11, 381 (1970) [JETP Lett. 11, 255 (1970)].
[4]Y. Kuramoto and H. Kamimura, J. Phys. Soc. Jap. 37, 716 (1974).
[5]G. Harbeke and E. Tosatti, Phys. Rev. Lett. 28, 1567 (1972).
[6]A. Mercier and J. Voitchovsky, Phys. Rev. B11, No. 6 (1975).
[7]W. Huang, Phys. Status Solidi (b) 60, 309 (1973).