Laser emission of CdS single crystals under single-photon excitation

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The nature of the laser emission produced by single-photon excitation of thin CdS single crystals is investigated at temperatures $T = 1.4$, 77, and 300°K. It is shown that lasing occurs in total internal reflection modes. The main optical transition responsible for spontaneous luminescence and lasing at all the above temperatures is radiative recombination due to exciton-exciton scattering, i.e., the *P* line.

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INTRODUCTION

A number of studies of laser emission in CdS single crystals has been made under electron-bombardment[1–3] and two-photon[4] excitation. In these investigations, the main results on the nature of the laser transition were obtained at low temperatures.

The question of creating an inverted population in the CdS crystal has received much attention in the literature, and it has been established that at low temperatures the lasing in such crystals is via exciton processes. Excitation of enough excitons in the crystals to obtain population inversion on free excitons is considered unfeasible for many reasons. However, as they move through the crystal, the excitons can interact with lattice vibrations, impurities, electrons, and with one another. Interaction of excitons with lattice vibrations leads to the annihilation of the excitons with the creation of phonons.[4] Inversion is attained comparatively easily for such transitions. At low temperatures, one of the possible mechanisms responsible for laser action in the Cds crystal has been shown in[5] to be emission by bound excitons, for which the condition for population inversion is the same as for two-level molecules.

One of the main forms of inter-exciton interaction is exciton-exciton scattering.[3] In this case, when an exciton with quasimomentum $\hbar\mathbf{K}$ is scattered by an exciton with quasimomentum $\hbar\mathbf{K}'$, one of the excitons goes over to the excited state $|K+K'\rangle$ of the nth exciton band, while the other is annihilated and emits a photon with an energy deficit equal to the spacing between the bands $n=1$ and $n=2, 3, \ldots$. More exactly, according to Hvam,[6] the frequency of the emitted photon (the *P* line) is given by:

$$\hbar\omega=E_g-E_{ex}-E_{ex}\left(1-\frac{1}{n^2}\right)-\frac{\hbar^2\mathbf{K}\mathbf{K}'}{M}, \tag{1}$$

where E_g is the semiconductor band gap, E_{ex} is the exciton binding energy, $n=1, 2, 3, \ldots$, and M is the exciton translational mass.

It should be noted that lasing via exciton-exciton scattering is a more likely mechanism that lasing via free excitons with participation of phonons. In the former case the gain on the *P* line is proportional to the square of the exciton density N_{ex}^2,[3,7] whereas for emission of an exciton with creation of an LO phonon the gain is proportional simply to the exciton density N_{ex}.[3]

Laser emission on transitions due to the exciton-exciton scattering process has been obtained at low temperatures in the crystals CdS,[3] GaAs,[8] and GaSe,[9] while spontaneous emission on these transitions is observed in the crystals CdSe,[10] ZnO,[6] and ZnTe.[11] This indicates that exciton-exciton scattering is a process common to a broad class of semiconductors. Accordingly, in crystals in which excitons are excited and the exciton-exciton scattering process is allowed, we can expect lasing mainly via exciton-exciton scattering.

The aim of the work reported here was to investigate, over a broad range of temperatures 1.4–300°K, the nature of the spontaneous and laser emission in thin CdS single crystals excited by single-photon pumping, and also to investigate the effect of resonator structure and excitation conditions on the spatial distribution of the lasing in such crystals.

EXPERIMENTS AND RESULTS

The experiments were carried out at temperatures $T=300$, 77, and 1.4°K on homogeneous plane-parallel platelets of single-crystal CdS of thickness $\sim(10-50)\cdot 10^{-4}$ cm. The crystals had a donor impurity concentration of $\sim 10^{15}$ cm^{-3}. There was no green edge emission in these crystals at low temperatures. A resonator of length $l\approx 0.1$ cm was produced between the planes of the end faces by cleaving the platelets along the optic axis *C* of the crystal (Fig. 1a).

The surface of the crystal was excited by 3-kW nitrogen-laser light pulses (repetition frequency 100 Hz, pulse width 10^{-8} sec). The rate of generation of electron-hole pairs on the surface of the crystal reached approximately 10^{29} cm^{-1}. The emission from the sample was photographed with the aid of a DFS-13 spectrometer (dispersion 4 Å/mm).

Microscope investigations showed that laser emission emerged from all four edges of the crystal in the pumping region (Fig. 1a). The edges shone uniformly along the optic axis of the crystal over the height of the excited region. The laser emission emerged in the form of separate lobes, which formed, in a plane perpendicular to the *C* axis, angles from 0 to 90° with the planes of the end faces of the crystal (see Fig. 1b). The

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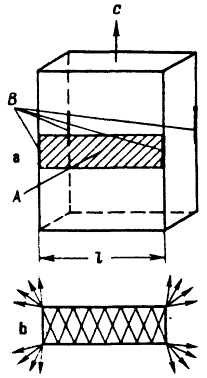

FIG. 1. Schematic representation of crystal: a—investigated CdS single crystal (C is crystal optic axis, l is length of crystal, A is direction of excitation, B denotes regions of emergence of laser emission, the part of the crystal shown cross-hatched is the region of excitation). b—Scheme of development of laser emission in plane perpendicular to crystal optic axis.

divergence of the light flux in an individual lobe amounted to 3–8° in this plane (the divergence increases with crystal thickness and with the length of the pumped region l) and was 8–15° in a plane parallel to the C axis. We note that the divergence of the lobes is independent of the angle at which the radiation propagates relative to the end face of the crystal and is the same for all lobes. At large sample thicknesses (50 μm), the number of lobes emerging from a single edge is quite small (3 to 5) and the emission intensity falls sharply with increasing lobe order number (the first lobe emerges almost perpendicular to the end face of the crystal). For small crystal thicknesses (up to 10 μm) and uniform excitation of the entire surface of the excited region, up to 30 lobes of approximately equal intensity are observed in the emission pattern of a single edge. The intensities of the first lobes increase with the length of the pumped region, and at large resonator lengths with no illumination of the end faces of the crystal, i.e., when the length of the excited region is less than the length of the crystal l, the emission goes over to lasing with a planar Fabry-Perot resonator, where the end faces of the crystal serve as the mirrors.

Lasing in the form of lobes ceases if the perfection of any of the planes of the crystal is disturbed, say by chemically etching the crystal surface. When crystals were selected in which the spontaneous emission due to exciton-exciton scattering had the same intensity at room temperature as in samples which lased but in which the faces were not plane-parallel, no lobe lasing was found to occur. Furthermore, in a CdS crystal lasing in separate lobes, the radiation density produced was such that the excited face and the one opposite to it were destroyed with time, which also led to the cessation of lasing. At room temperature, the best samples lase for 100 h and more at maximum pump level. At 77°K such crystals lase for a much longer time, and with decreasing temperature this time increases.

We can conclude from the manner in which the radiation emerges from the crystal and from its spatial distribution that lasing occurs in total internal reflection modes, which are developed in the crystal at definite angles and which can emerge from the crystal only in regions where total internal reflection is violated, i.e., in the edge region, when the wave vector of the light wave is perpendicular to the edge (Fig. 1b).

The high contrast $\gamma = 0.81$ in the interference pattern of the radiation of a single lobe, obtained with the aid of a Fresnel biprism, testifies to the high spatial coherence of the laser emission.

We investigated the dependence of the emission intensity (I_L) on the excitation intensity (I_P). The investigations showed that in the region below threshold, when the emission emerges uniformly from the excited region of the crystal, the plot of I_L vs. I_P is nonlinear: $I_L \propto I_P^{1.8}$ (Fig. 2, curve 2). The nature of the emission changes sharply when the pump intensity exceeds threshold: the above-described lobe structure is observed, and the dependence of I_L on I_P becomes more nonlinear (Fig. 2, curve 1). A similar behavior is observed at all investigated temperatures, 300, 77, and 1.4°K.

Spectral investigations showed that at $T = 300$°K the luminescence spectrum from the excited region of the single crystal contains, up to laser threshold, a single broad band ($\lambda_0 = 5070$ Å) with an extended long-wave edge of the order of 230 Å (856 cm^{-1}) (Figs. 3a, b). The short-wave edge of this band is shifted from the A-exciton line by an amount approximately equal to the exciton binding energy ~ 240 cm^{-1}. The energy position of this band, the spectral shape, and the dependence on pumping energy (see Fig. 2, curve 2) allow it to be ascribed to exciton-exciton scattering processes.[3] The extended long-wavelength edge of the P band is due to the kinetic energy of the free A-exciton (see the last term in Eq. (1)). The existence of excitons in the CdS crystal at $T = 300$°K was first reported by the authors of Refs. 12–14, who observed A- and B-exciton bands in the reflection and luminescence spectra.

With increasing pumping intensity, lines of laser emission are observed in the spectrum on the long-wave edge of the P band. The spectral composition of the emission varies from lobe to lobe; this can be due, according to Shaklee,[8] to the dependence of the lasing wavelength on the amgain length and the pumping level, i.e., the greater the amgain length and the pumping level, the more long-wave the laser line. In our case, total internal reflection modes with different amgain

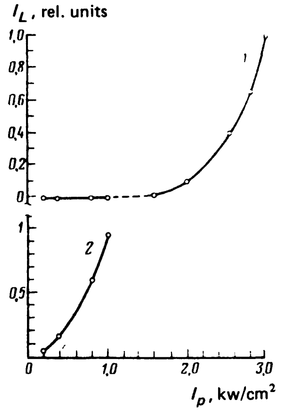

FIG. 2. Dependence on excitation intensity of: 1—laser emission (above threshold); 2—spontaneous emission.

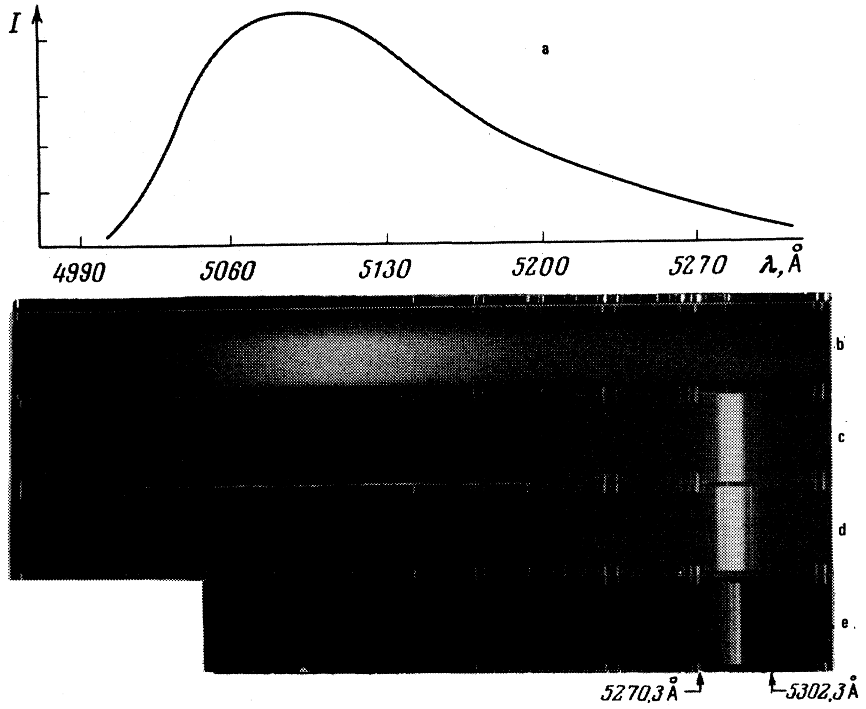

FIG. 3. Emission spectra of CdS crystal at $T = 300\,^\circ$K: a and b show a microphotograph and the spectrum of the spontaneous emission: c, d, and e show laser emission spectra of the three first lobes.

lengths in the different lobes begin to oscillate, and the laser emission spectrum varies in a nonmonotonic manner with increasing lobe order number. For the wave regime of lasing, the spectral composition of the emission also depends on the angle of propagation.[15]

The spacing between axial modes in the case of a dispersive resonator in which standing waves are formed is:

$$\Delta\nu\approx 1\Big/2l^*\left(n-\lambda\frac{dn}{d\lambda}\right), \qquad (2)$$

where l^* is the effective length of the resonator; n is the refractive index of light in the medium, which depends on the wavelength λ; and the value of $n-\lambda dn/d\lambda = 3.5$ for our crystals is obtained by measurement via the interference pattern in the reflection spectrum of a thin plane-parallel platelet. The calculated maximum value of $\Delta\nu$ (for $l^* = 0.1$ cm) amounts to 1.4 cm^{-1}. We were unable to determine experimentally the halfwidth of an individual axial mode because of the fluctuating power of the nitrogen laser pulses; accordingly, the laser emission spectrum contains individual lines of different halfwidths (Fig. 3, c to e) consisting of many modes and covering the spectral range from 5300 to 5280 Å.

Since the measured absorption coefficient at the lasing frequency in the CdS platelet at $T = 300\,^\circ$K amounts to ~ 80 cm^{-1}, the fact that identical emission was observed from all edges indicates that population inversion apparently occurs over the entire volume of the crystal, although only a surface layer of the crystal of thickness ~10^{-5} cm was excited. An exciton distribution of this sort can be achieved by diffusion, due to the high concentration gradient, of excitons from the high-density region.

At $T = 77\,^\circ$K the laser emission is also located on the long-wave edge of the P band (Fig. 4, curve 1). The P band has an edge extended in the long-wave direction (Fig. 4, curve 2). The position of the short-wave edge (the point where the curve falls) corresponds to a separation from the A-exciton equal to the free-exciton binding energy. The laser emission spectrum varies from lobe to lobe.

At $T = 1.4\,^\circ$K at small excitation levels, lines I_1 and I_2 due to bound-exciton annihilation[16] begin to oscillate. At higher pumping levels lasing at the P-line frequency is observed (Fig. 4, curve 3), as well as the M and P_M bands, which were ascribed in Ref. 17 to excitonic molecules (the M line) and to scattering of such molecules (the P_M line). The spectrum of the laser emission on the P line consists of three peaks, connected with scattering induced transitions of excitons to states $n = 2$, 3 and $n = \infty$ and not with resonator modes, since the quan-

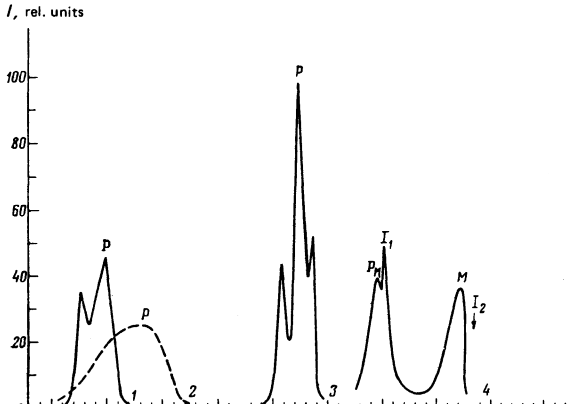

FIG. 4. Emission spectra of CdS crystal: 1, 2 correspond to $T = 77\,^\circ$K; 3, 4 to $T = 1.4\,^\circ$K.

tity $n - \lambda dn/d\lambda$ reaches a value of ~20 in the corresponding range of frequencies.[18] The different spectral positions of these peaks and their unequal spacing are probably due to different gains on different lines.

In individual crystals, M and P_M emission is observed in the form of broad bands (Fig. 4, curve 4) or in the form of narrow laser lines shifted towards the red from band center. When the lines I_1 and I_2 are not observed in the spectrum, the M band starts to oscillate. This behavior of lines I_1 and I_2 can be attributed to the increase in exciton density accompanying an increase in excitation level, as a result of which the number of exciton-exciton collisions increases, i.e., the free-exciton lifetime is reduced. In this manner, at certain exciton densities all excitons will collide, i.e., their lifetime becomes less than the time for which excitons are bound to neutral or ionized impurities. The presence in the luminescence spectrum at high excitation levels of M and P_M lines indicates that these lines are not associated with the decay of bound excitons with creation of acoustical phonons but are due to exciton-exciton interaction. Thus, at 1.4 °K lasing occurs on the bound-exciton lines I_1 and I_2, on the P line, and also on the M and P_M lines.

At 77 °K the laser threshold was reached at an excitation level four to five times less than at 300 °K. The threshold at 1.4 °K for the P line is lower by an order of magnitude than at room temperature. For the M and P_M lines it is almost the same as for the P line at $T = 300$ °K.

CONCLUSION

It follows from the above that the main laser transition in CdS single crystals in the temperature interval 1.4–300 °K is due to exciton-exciton scattering (the P band). Lasing due to the annihilation of a free exciton with creation of an LO phonon does not occur, probably because the light gain is insufficient to overcome absorption at the frequency $\omega_A - \omega_{\text{LO}}$, where ω_A is the resonance frequency of the free A-exciton, and ω_{LO} is the LO phonon frequency. At $T = 1.4$ °K the bands due to exciton-exciton scattering and to emission involving the creation of an LO phonon do not overlap in the spontaneous emission spectrum;[10] also, the value of the absorption coefficient at frequency $\omega_A - \omega_{\text{LO}}$ in the CdS crystal is approximately equal to 20 cm^{-1} and is at its smallest at $T = 1.4$ °K, being greater at higher temperatures at this same frequency. It is thus difficult to expect lasing at temperatures 77 and 300 °K on the transition due to annihilation of a free exciton with creation of an optical phonon, as is indeed confirmed experimentally.

Emission on the P-band frequency at low temperatures has recently been ascribed to: emission from an electron-hole plasma,[19] emission from an electron-hole drop,[20] and radiative recombination of excitonic molecules.[21] However, as the binding energies of excitonic molecules and electron-hole drops are respectively ~ 3 MeV and ~ 13 MeV, and the P band is also observed at $T = 300$ °K, it is not possible to ascribe the P band to emission from an electron-hole drop or radiative recombination of excitonic molecules.

The P band cannot be ascribed to electron-hole plasma emission for the following reasons: firstly, the intensity of the spontaneous emission in this band has an almost quadratic dependence on excitation intensity, whereas the intensity of the spontaneous emission of an electron-hole plasma should depend linearly on excitation intensity; secondly, the P band, as shown in Ref. 10, has at low temperatures a fine structure associated with the transition of excitons to states $n = 2$, 3, 4 and $n = \infty$, whereas electron-hole plasma emission is unlikely to have this sort of structure; thirdly, the P band is shifted towards shorter wavelengths with increasing pumping level, the shift being twice as large as the shift of the free-exciton line, a feature which cannot be explained on the basis of electron-hole plasma emission; and finally, the emission band of an electron-hole plasma should have an extended short-wave edge and a sharp long-wave edge, whereas in the present case the P band has a strongly drawn out long-wave edge.

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Mechanism of collisional dissociation of polyatomic molecules

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Recent experimental data are used as a basis for an analysis of the process of collisionless dissociation of molecules in a laser field. Some specific features of the vibrational-rotational spectrum of polyatomic molecules are established. The departure of molecules from the vibrational ground state independently of the rotational quantum number J is explained. A distribution is obtained for the density of vibrational states over the band for large vibrational numbers, and this is used to explain the large red shift of the optimum laser interaction during the dissociation stage of the process.

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1. Collisionless dissociation of polyatomic molecules in an infrared laser field has attracted considerable attention (a number of review articles has been published[1]). The subdivision of the vibrational excitation of polyatomic molecules into two stages[2] is now generally accepted. These two stages are: (1) traversal of several low-lying levels and (2) subsequent excitation in the so-called quasicontinuum, where the density of vibrational states is very high. It was originally assumed that the traversal of several low-lying vibrational levels occurred as a result of field broadening whereas the accumulation of energy in the quasicontinuum is definitely due to the high density of vibrational states and consequently, the resonant character of the process. Subsequent studies of the excitation of high-lying vibrational states showed that the resonant character of the transitions in the quasicontinuum is not in itself sufficient because these transitions occur with a considerable change in the vibrational quantum numbers and are, therefore, highly forbidden.

It has been shown[3] that, for symmetric molecules, intramode anharmonism, which removes the degeneracy of high-lying vibrational states of a degenerate mode, leads to the formation of bands of levels. Interband anharmonism ensures that band formation involves the states of other modes (Fermi resonance). The result of this is that bands of relatively well allowed transitions appear in the quasicontinuum, and the only forbidden transitions are those forbidden on the grounds of symmetry. The band structure of the quasicontinuum has, in fact, been confirmed experimentally.[4]

Recent experimental work suggest that the excitation of low-lying vibrational levels requires a more careful analysis. For example, Ambartsumyan *et al.*[5] have shown that the traversal of the low-lying levels in the case of the SF_6 molecule occurs in fields of moderate intensity (of the order of 100 kW/cm^2). Ambartsumyan *et al.* suggest vibrational compensation of anharmonism due to successive P, Q, and R transitions as the mechansim for the traversal of low-lying vibrational levels. However, this model is too schematic for a polyatomic molecule. We draw attention to the theoretical work of Larsen and Blombergen,[6] who pay considerable attention to the possibility of two- and three-photon resonances during the traversal of the low-lying vibrational levels.

However, the models mentioned above were based on the assumption that only particles in a narrow range of values of the rotational quantum numbers J participated in the excitation process. Recently, it was found experimentally[7] that the molecules could be removed from the vibrational ground state independently of their initial rotational state. It was shown that, in moderate fields of exciting radiation, beginning with $I = 300$ kW/cm^2, and for pulse lengths $\tau_p = 100$ nsec, the SF_6 and SiF_4 molecules can leave the vibrational ground state practically independently of J under conditions including rotational relaxation of the gas. This result is well outside the usual framework of the "bottleneck" effect.[8]

In this paper, we consider the mechansim responsible for the trapping of many rotational states during the vibrational excitation of molecules in a strong infrared field. We shall show that this trapping cannot be explained within the framework of the main vibrational transition alone, but is a consequence of the complicated structure of several low-lying vibrational levels as well as the presence of the quasicontinuum in the case of the polyatomic molecules. Even a considerable de-