the concentration was much lower, so that inclusion of only the first term is perfectly justified. The second term can be taken into account in[11], if at all, only at the highest excitation levels.

To analyze the solution of the balance equation (35) and (36), we assume that $\tau_R(\varepsilon) \sim \varepsilon^r$. Substituting in (37) the distribution (10), we obtain from (36)

$$n = G_0 \bar{\tau}_R u^r, \qquad (43)$$

where $\bar{\tau}_R$ is a certain constant with the dimension of time, and $u \equiv T_e/\hbar\Omega_0$. Using (41), we can express the balance equation (35) at $T_e \gg T$ in the form

$$\frac{1}{\bar{\tau}_A}(pu^{-1/2} + du^{-3/2}) + \frac{1}{\bar{\tau}_{ee}} u^{1/2} e^{-u} = \frac{G_0}{n}\left[\Delta y + y_0 \frac{n}{n_c} \right], \qquad (44)$$

where

$$\bar{\tau}_A^{-1} = \tau_{PA}^{-1} + \tau_{DA}^{-1}, \quad p = \tau_{PA}^{-1}/\bar{\tau}_A^{-1}, \quad d = \tau_{DA}^{-1}/\bar{\tau}_A^{-1},$$
$$\Delta y = (\varepsilon_{k0} - \hbar\Omega_0)/\hbar\Omega_0 < 1, \quad y_0 = \varepsilon_0/\hbar\Omega_0.$$

For GaAs we have $\bar{\tau}_A^{-1} = 1.94 \times 10^8$ sec^{-1}, $p = 0.29$, and $d = 0.71$. From (43) and (44) we see that at low concentration, when the term $y_0 n/n_c$ can be neglected, the quantity G_0 drops out of (44), i.e., T_e should not depend on the excitation level. This is not observed in experiment. On the other hand if the term $y_0 n/n_c$ predominates, then the concentration n drops out of (44) and we can obtain the dependence of T_e on G_0, i.e., on I. The energy relaxation mechanisms become comparable at $u = 14.6$, i.e., $T_e = 29\,°K$. At $T_e > 29\,°K$ the electron-electron relaxation mechanism predominates, and (44) leads to an exponential dependence of T_e^{-1} on

G_0. At $T_e < 29\,°K$, T_e^{-1} is a power-law function of G_0, i.e., $T_e^{-1} \sim G_0^{-2}$ (the term with the coefficient d makes practically no contribution). The temperature $T = 29\,°K$ at which the change of mechanisms takes place corresponds according to (44) to $G_0 \approx 10^{24}$ cm^{-3} sec^{-1}, i.e., $I \approx 10$ W/cm^2. A similar picture was indeed observed in experiment, [11] where noticeable deviations from an exponential dependence set in near 30 °K at intensities close to 100 W/cm^2. It is not clear, however, why such a fair agreement takes place, for at the concentrations that obtain in the experiment an important role is played not only by the term $y_0 n/n_c$, but also by the term Δy.

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Anti-Stokes resonant Raman scattering of light by excitons in CdS crystals

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A new mechanism for Raman scattering of light, due to the interaction between bound and free excitons in the intermediate state is suggested. We have observed and investigated the continuous stimulated light emission due to recombination of bound excitons following excitation by light from a mercury lamp, as well as the Raman scattering stimulated by this emission at the free-exciton frequency in the CdS crystal.

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1. It is known that the direct radiative recombination of free excitions in semiconductors usually leads to a relatively weak radiation. This is due primarily to three causes: 1) owing to the large absorption coefficient K at the free-excition frequency ($K = 2 \times 10^5$ cm^{-1} [11]) the observed radiation emerges mainly from a layer of thickness $\approx K^{-1}$; 2) the intensity of the radiation

depends to a great degree on the state of the semiconductor surface, which determines the lifetime of the exciton in the near-surface region[2,3]; 3) for most free excitons direct radiative recombination is forbidden: the law of momentum conservation can be satisfied when they recombine either as a result of interaction with the lattice, with impurities, or with the surface of the crys-
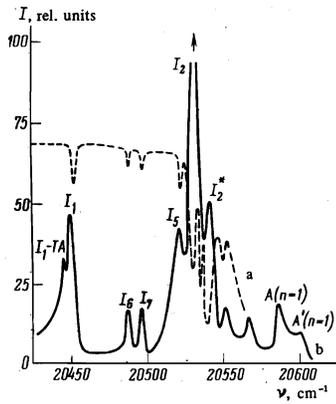
FIG. 1. Absorption spectra (a) and luminescence spectra from excited surface (b) at $E \perp c$.

FIG. 3. Change of the exponent of the power-law dependence of the radiation at the frequencies of the bound I_2 exciton (×) and and the free $A(n = 1)$ exciton (o) as functions of the logarithm of the external-excitation flux density.

tal. For the purest and most perfect CdS crystals (when the bound-exciton lines are weak) the exciton luminescence from the state $A(n = 1)$ is exceedingly weak. The concentration of the free excitons is then high enough, since strong radiation is observed from states ascribed to biexcitons.[4] The excitonic luminescence from $A(n = 1)$ is most strongly pronounced in crystals characterized by the strong bound-exciton lines I_1 and I_2.[5] However, even in such crystals the observed radiation flux due to the luminescence of the A excitons corresponds at free-exciton concentrations $n_{ex} \approx 10^{16}$ cm^{-3} to the probability of photon absorption (in one mode per unit time) and production of one A excitons larger four or five times than the probability of the inverse process (production of a photon with annihilation of an exciton). Thus, stimulated emission due to luminescence at the free-exciton frequency is impossible up to the concentrations n_{ex} at which the exciton states cease to exist.

The difficulty connected with the need of overcoming so strong a reabsorption, which is characteristic of exciton lines is no longer encountered in the case of various indirect transitions (e. g., with participation of optical phonons or free excitons), as well as in the case of phototransitions at bound-exciton frequencies. The requirements with respect to the quality of the crystal surface are also less stringent, since volume excitation is used. An experimental proof of lasing induced by pulsed two-photon photoexcitation of a CdS crystal was obtained by Kulevskii and Prokhorov,[6] and in the case of CdS$_x$Se$_{1-x}$ crystals in[7]. In those cases, the laser emission was at a frequency lower than that of
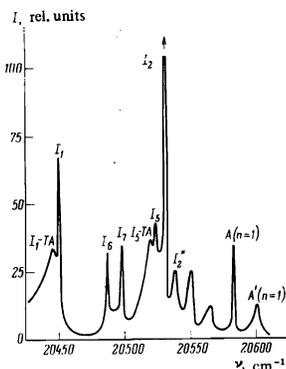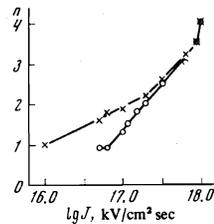
the free $A(n = 1)$ exciton by an amount approximately equal to the frequency of the longitudinal optical phonon; there was no emission at the frequency of the free exciton. At low temperatures, the main channel of lasing in the CdS crystal should be, as shown by Thomas and Hopfield,[3] the emission of the bound excitons, for which the condition of inverted population is the same as for two-level molecules. Up to now, however, laser emission was observed at frequencies of bound excitons only following pulsed excitation.

2. We proceed to describe our experimental results. The experiment was carried out in the following manner. A plane-parallel plate of an undoped CdS crystal with dimensions $5 \times 10^{-3} \times 0.4 \times 0.4$ cm was excited with light from a DRSH-500 mercury lamp at $T = 1.4$ °K. The luminescence was photographed both from the illuminated surface and from ends of the crystal (Figs. 1 and 2). With increasing excitation level, starting with a flux density $J_0 \approx 10^{17}$ kV/cm^{2}sec, the intensity at the center of the emission line, due to the annihilation of the bound exciton (I_1, I_2[5]) has a faster than linear dependence on the excitation level (Fig. 3). At the maximum excitation level ($J_0 \approx 10^{19}$ kV/cm^{2}sec) the emission flux density from the end is $\approx 10^{22}$ kV/cm^{2}sec, which is larger than the flux density from the excited surface by a factor $\sim 10^4$.

The emission at the frequency of the free excitons behaves similarly, but the faster-than-linear growth of the emission intensity begins with $J_0 \approx 7 \times 10^{17}$ kV/cm^{2}sec.

The half-widths of the lines of both the bound (I_1 and I_2) and free $A(n = 1)$ excitons at maximal excitations turn out to be less than 0.6 cm^{-1} (the measurements were performed with the aid of Fabry–Perot interferometer in conjunction with a DFS-13 spectrograph), which is approximately smaller by one order of magnitude than the half-width of the free exciton at a weak excitation level.

Using masks on the crystal surface, we obtained an exponential dependence of the emission intensity from the end of the crystal on the length l of the illuminated region of the surface (Fig. 4). The maximum gain obtained in this manner is 16 cm^{-1} at the free-exciton frequency and 9 cm^{-1} at the frequency of the bound excitons I_2.

All this points to a stimulated character of the emission at the frequencies of the free and bound excitons.

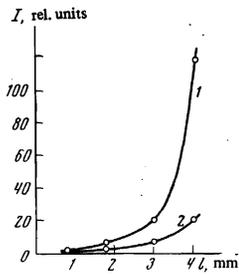FIG. 2. Luminescence spectrum from end face.

I, rel. units

FIG. 4. Emission intensity of free (curve 1) and bound (curve 2) excitons.

The gain was effected in the regime of one pass along the luminated surface, inasmuch as the darkened edges of the surface in a band of width 200 μ led to a complete vanishing of the free-exciton line in the emission from the given end, but did not influence noticeably the emission from the opposite end. The attenuation of the radiation at the bound-exciton frequency corresponded approximately to the coefficient of absorption on the I_2 line, measured when the crystal was not excited and amounting to $K_b \approx 50$ cm^{-1}.

We note that both the spontaneous and stimulated emission of the free exciton are characterized by maxima that are shifted to the long-wave side by ~ 8 cm^{-1} relative to the center of the corresponding line in the absorption spectrum (Fig. 1). The line of the bound exciton I_2^* is shifted relative to the line of the bound exciton I_2 also by $\delta \approx 8$ cm^{-1}. In what follows it is very important that the stimulated emission at the I_2^* line is absent, but the absorption at the I_2^* greatly exceeds the absorption at the I_2 line.

The emission at lines I_1 and I_2 from the unilluminated (rear) surface is close in intensity to the emission from the illuminated surface, i.e., the entire crystal is quite uniformly filled with light. This circumstance is favorable for Raman scattering of this light. There is no free-exciton emission from the unilluminated surface. This indicates that the diffusion length of the free excitons is much less than 50 μ (the crystal thickness).

3. Proceeding to the theoretical analysis, we consider first the conditions for inverted population at the frequency of the bound exciton I_2. Since it is impossible to "land" more than one free exciton on one impurity center, the condition for population inversion means that more than half of the impurity centers (in our case—neutral donors) is populated by excitons.[3] All the crystals in which stimulated emission was observed were of the low-resistance type. From measurements of the conductivity at room temperature it follows that the concentration of the neutral donors amounts to 10^{15}-10^{16} cm^{-3}. It must also be borne in mind that the donor concentration can be uneven over the depth, since, as shown in[4], the CdS crystal growth goes through two stages. The first stage corresponds to growth without deviation from stoichiometry, so that there are no bound-exciton lines in thin crystals. For this reason it can be assumed that near one of the surfaces there is a region with a lower donor concentration, in which population inversion is reached earlier than in other regions. Since the lifetime of the bound exciton is $\sim 10^{-8}$

sec, an inverted population $\sim 10^{15}$ cm^{-3} can be produced at an excitation density $\sim 10^{18}$ kV/cm^{2}sec, in which case the gain should not exceed 50 cm^{-1}, i.e., the value of K_b.

We consider now a Raman light scattering mechanism of the electronic type, in which the role of the pump is played by radiation at the frequency ω_1 of the bound excitons. To explain the situation, we first carry out a somewhat simplified analysis. At low exciton concentrations, the phototransitions at the frequencies of the free and bound excitons take place independently of one another. At sufficiently high exciton concentrations ($n_{ex} \approx 10^{16}$ cm^{-3}) an important role is assumed by exchange interaction between the free and bound excitons,[8] allowance for which makes it possible to "couple" with one another the optical matrix elements corresponding to photon absorption with production of a bound exciton (M_{01}) and emission of a photon upon annihilation of a free exciton (M_{20}). Thus, the composite matrix element of the considered Raman scattering process is

$$M = \frac{M_{01}M_{12}M_{20}}{(\hbar\omega_1 - E_1')(\hbar\omega_1 - E_1' + \hbar^2 k^2/2m_{ex})}, \qquad (1)$$

where M_{12} is the matrix element of the energy of the exchange interaction between the bound and free excitons, leading to the scattering of the free exciton from the state $|k \neq 0\rangle$ to the state $|k = 0\rangle$, E_1 is the energy of the bound exciton corresponding to the I_2 line, $\omega_1 = E_1\hbar^{-1}$, E_1' is the bound-exciton energy corresponding to the I_2^* line, and m_{ex} is the exciton effective mass.

As a result of the scattering event, the frequency of the photon is increased, since one free exciton turns out to be bound. The frequency of the scatter photon is

$$\omega_2 = E_2\hbar^{-1} - \delta = \omega_1 + \hbar^{-1}(E_2 - E_1'), \qquad (2)$$

where E_2 is the energy of the free exciton (we have neglected here the energy of the translational motion of the exciton). The scheme of the corresponding transitions is shown in Fig. 5a.

In addition to the considered variant of almost resonant Raman scattering of light, a somewhat different variant corresponding to resonant scattering can be realized. In this case the vanishing of the photon with frequency ω_1 leads to production of a bound exciton on one of the empty local levels with energy E_1, and this
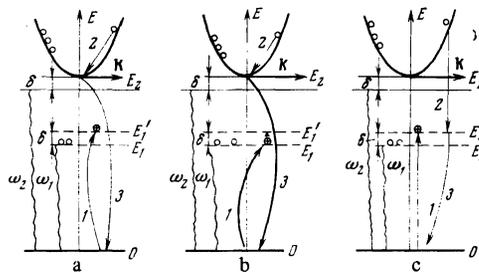

FIG. 5. Transition scheme and energy levels: 1, 2, 3—sequence of transitions.

exciton, after colliding with a free exciton, goes over into a higher state with energy E'_1. During the last stage, a photon is emitted with a frequency determined in (2). This variant, the transition scheme for which is shown in Fig. 5b, corresponds to the largest scattering cross section, but in contrast to the preceding one it can be realized only when the levels E_1 and E'_1 pertain to one and the same impurity center, and not to different centers that are separated in space.

The third variant (Fig. 5c) corresponds to emission of a free exciton via the state of bound excitons.

In each variant, the final state has an energy E'_1 and its population can be neglected (see Sec. 2). It is possible to disregard here the inverse Raman scattering of light.

4. In this section we discuss several general premises pertaining to the absorption and luminescence in the exciton region, from a point of view that differs in a number of respects substantially from the customary one. We consider first the ratio of the coefficients of light absorption due to interband transitions in the quasi-continuous spectrum and for the discrete exciton state. We represent the coefficient K_b of absorption due to the interband transition, in the form

$$K_b = Cf\rho(\hbar\omega), \qquad (3)$$

where C is a constant, f is the oscillator strength, $\rho(\hbar\omega)$ is the density of states of a transition with energy $\hbar\omega$ per unit volume, and ω is the photon frequency. Expression (3) agrees quantitatively with experiment, although it does not contain a dependence on the damping Γ of the Bloch states. Let us see what happens when the damping is taken into account. Assuming a Lorentz shape of the broadening of the individual state, we replace the δ-function by the quantity Γ^{-1}. Now the absorption of a photon with frequency ω will receive contributions from all the states with energies belonging to the interval ~ Γ near the energy $\hbar\omega$. Each such state corresponds to electron-hole pairs with total momentum equal to the photon momentum. Thus, in place of (3) we have

$$K_b = C\Gamma^{-1}fS(\omega), \qquad (4)$$

where $S(\omega) = \rho(\hbar\omega)\Gamma$ is the number of states participating in the considered transition per unit volume. Consequently, expression (3) describes the absorption also without allowance for the damping. At $S(\omega) = 10^{19}$ cm^{-3} we have $K_b \approx 10^5$ cm^{-1}.

The absorption coefficient at the frequency of the free $A(n=1)$ exciton is equal to

$$K_{ex} = C\Gamma^{-1}f(\pi a_0^3)^{-1} \equiv C\Gamma^{-1}fS_{ex}. \qquad (5)$$

which follows directly from the results of[9]. Here a_0 is the Bohr radius of the exciton, and the remaining factors are the same as in (3) and (4). The quantity S_{ex} is roughly speaking the concentration of the exciton "spheres" when they are mutually tangent to one another. This quantity plays the role of the density of states for

the excitonic absorption. Inasmuch as $S_{ex} \approx 10^{19}$ cm^{-3} for CdS, it is now clear why absorption at the exciton frequency is also characterized by $K_{ex} \approx 10^5$ cm^{-1}. Usually, without carrying out the absorption calculations to conclusion, one includes in the definition of the oscillator strength of the excitonic transition per molecule of the crystal a factor containing the volume of the exciton:

$$f_{ex}|_{1 mol} = f\Omega/\pi a_0^3 n^3,$$

where Ω is the volume of the unit cell and n is the number of excitonic subband. However, it follows even from this that the oscillator strength of a transition with exciton production is equal to $f \approx 1$, inasmuch as the sphere of the wave function of the relative motion of the electron and hole encloses precisely $\pi a_0^3 \Omega^{-1}$ molecules. In our approach, the decrease of the absorption coefficient with increasing n is due to a decrease of the volume density of the states $S_{ex}^{(n)}$. It is important to note that in the derivation of expression (5) the exciton is characterized by a definite wave vector. The appearance of the quantity S_{ex} reflects the circumstance that the photon can be absorbed at any point of the crystal, i.e., all the crystal molecules are capable eventually of taking part in the absorption of the photon. The fact that in the interaction with the light the exciton acts like an object with radius a_0 does not contradict the uncertainty relation, since the place of the absorption is not defined. Real excitons in crystals are characterized by wave packets that describe the position and motion of the center of gravity of the exciton.[10] The excitons are localized, e.g., as a result of the interexciton interaction. The exciton can then be approximately characterized by a wave vector k and by a position whose dimensions correspond to the uncertainty of the coordinate of the center of gravity.

From the equivalence of the representations of the localized functions and the Bloch states it follows that the probabilities of photon emission in one mode are independent of the dimension of the wave packet of the recombining excitons. Indeed, in a representation with exact localization of the center of gravity, at an exciton concentration of 1 cm^{-3}, the probability of photon emission in one mode with annihilation of an exciton is smaller by 19 orders of magnitude than the probability of absorption of such a photon with production of an exciton, inasmuch as 10^{19} electron-hole pairs per cm^3 take part in the absorption, and one electron-hole pair radiates. In the Bloch-wave representation, excitation with a definite value of k covers all the molecules, but the weight factor corresponding to the contribution of the individual molecules is inversely proportional to the square root of the number of molecules. Thus, the widely held view that the photon emission probability in annihilation of one exciton is of the same order as the absorption probability (see, e.g.,[11]) is in error. The probability W_a of absorbing a photon per unit time is $K_{ex}\bar{c}$, where $\bar{c}$ is the speed of light in the crystal. In our case $W_a \approx 10^{15}$ sec^{-1}, and even upon condensation of excitons at a concentration 10^{16} cm^{-3} in a state with the wave vector of the light wave, the probability of emis-

sion of one photon is only 10^{12} sec^{-1}. In the photon mode connected with the exciton condensate, there will be only $\lesssim 10^{-3}$ photons.

The scattering of free excitons, for example, by bound excitons, lifts the selection rule with respect to **k**, making it possible for all the excitons to take part in the recombination with emission of photons in all the 10^{12} cm^{-3} photon modes that fall in the luminescence band, but it is likewise impossible to obtain stimulated amplification of light as a result of such a recombination.

5. We consider now the discussed mechanism of Raman scattering of light in greater detail. The kinetic equation for the number of photons q_2 in one mode of scattered radiation will be written in the form

$$\frac{dq_2}{dt} = \frac{2\pi}{\hbar} \sum_{i,k} |M_{01}|^2 (1 - \bar{n}_i) |M_{12}|^2_{ij;k0} n_k^j \left[\left(\sum_l n_{k=0}^l \right) + 1 \right]$$

$$\times (1 - n_{k=0}^j) |M_{20}|^2_{k=0;j} q_1 (q_2 + 1) \delta \left(\hbar\omega_2 - \hbar\omega_1 - E_2 - \frac{\hbar^2 k^2}{2m_{ex}} + E_1' \right) (\hbar\omega_1 - E_1')^{-1}$$

$$- \frac{2\pi}{\hbar} \sum_{ij,k} |M_{02}|^2_{k=0;j} \left[\left(\sum_l n_{k=0}^l \right) + 1 \right] (1 - n_{k=0}^j) |M_{21}|^2_{ji;0k}$$

$$\times \left[\left(\sum_l n_{k'}^j \right) + 1 \right] (1 - n_k^j) |M_{10}|^2 \bar{n}_i q_2 (q_1 + 1) \delta \left(\hbar\omega_2 - \hbar\omega_1 - E_2 \right.$$

$$\left. - \frac{\hbar^2 k^2}{2m_{ex}} + E_1' \right) (\hbar\omega_1 - E_1')^{-1} - W_0 q_2 - \gamma q_2. \quad (6)$$

where $\bar{n}_i$ is the occupation number of the state of the bound exciton in position i, n_k^j is the occupation number of the state of the free exciton with momentum $\hbar$**k** in the position j, q_1 is the number of photons in the generating mode at the frequency ω_1 of the bound exciton, and γ^{-1} is the lifetime of the photon in the resonator relative to processes that are not explicitly taken into account. In view of the smallness of $\bar{n}_i$, the second term in (6) can be discarded. Let us estimate numerically the first term of (6), i.e., the probability W_{sc} of scattering into one mode ($q_1 = 1$).

To estimate M_{12} we use the expression obtained in[8] for the case of two free excitons:

$$M_{12}(\rho) = \frac{e^2}{a_0} \frac{\rho}{a_0} 0.5 \exp\left(-1.1 \frac{\rho}{a_0}\right). \quad (7)$$

where ρ is the distance between the excitons. This expression is valid at $\rho > 2.5\, a_0$. At the level of excitation from a mercury lamp $\sim 10^{19}$ kV/cm^{2}sec, assuming the lifetime of the $A(n=1)$ exciton to be 10^{-8} sec,[12] we obtain $n_{ex} \approx 10^{16}$ cm^{-3}. This lifetime is typical of excitons near the surface, and should be larger for volume excitons. It should be noted that with increasing excitation level the lifetime decreases. We have shown earlier[13] that when a CdS crystal is excited by a nitrogen laser ($J_0 \approx 10^{23}$ kV/cm^{2}sec) the lifetime of the $A(n=1)$ exciton decreases by three orders of magnitude in comparison with the case of excitation with a mercury lamp.

At $n_{ex} = 10^{16}$ cm^{-3}, the average distance between the excitons in CdS is $\sim 20 a_0$; it can be assumed that the average distance between the free and bound excitons is equal to half the indicated quantity. Using (7) we obtain here

$$|M_{12}|^2 (\hbar\delta)^{-2} \approx 2.5 \cdot 10^{-3}.$$

It is convenient to estimate the expression for W_{sc} in individual blocks. We consider the collision of each bound exciton with only one nearest free exciton, and then $|M_{12}|$ is in fact proportional to δ_{ij}, and the double sum over ij is replaced by a single sum. The quantity $|M_{01}|^2 N_n$, where N_n is the number of donors not populated by excitons, was determined by measuring the absorption coefficient K_{abs} and the width of the absorption line (~ 4 cm^{-1}). Then

$$|M_{01}|^2 N_n \approx 2.4 \cdot 10^{-2} (\hbar\delta)^2.$$

The remaining block is simply the probability of emission of one photon per unit time by any of the 10^{15} excitons in 1 cm^3 from states with **k** = 0, which is equal to 10^{11} sec^{-1} (see Sec. 4). Thus, the probability of Raman scattering of light into one mode is $\sim 6 \times 10^6$ sec^{-1}.

The criterion for the applicability of perturbation theory in the interaction between the excitons in accordance with (8) is satisfied, and in terms of the interaction with the radiation at the frequency of the bound exciton it takes the form

$$|M_{01}|^2 q_1 < (\hbar\delta)^2.$$

In our case it is well satisfied.

The cross section of the considered Raman scattering of light per mode is

$$\sigma = W_{sc} V / \bar{c} \approx 5 \cdot 10^{-7}\ \text{cm}^2,$$

where V is the volume of the crystal. Finally, let us find the gain β, using the experimental value of the photon density q_1/V on the line I_2, which is equal to $\sim 10^{12}$ cm^{-3}:

$$\beta = \sigma q_1 / V \approx 5 \cdot 10^3\ \text{cm}^{-1},$$

which is sufficient to compensate for the absorption in the region of the $A(n=1)$ exciton line, which at the maximum of the line amounts to 2×10^5 cm^{-1}.[11] We note also that since the true gain (which takes into account the reabsorption) turns out to be ~ 16 cm^{-1}, the use of the expansion of the field in the modes (which is equivalent to the geometrical-optics approximation) is legitimate.

The final proof of our interpretation of the emission mechanism at the frequency of the free exciton can be obtained apparently by using modulation of the intensity of the radiation at the frequency of the bound excitons, e.g., at a frequency larger than the reciprocal lifetime of the excitons. In this case only the Raman scattering lines turn out to be modulated in intensity.

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Optical spectra of phonons bound to impurity centers

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A method proposed earlier for determining the energy spectrum of phonons bound to an electron impurity center is generalized to the calculation of the intensities of the lattice absorption and of the Raman scattering of light by bound phonons. Simple closed formulas are obtained for the intensities of both these processes. The behavior of the wavefunction of a bound phonon is also investigated. In conclusion, equations determining the vibrational spectrum of Jahn–Teller centers with an arbitrary structure of the electron spectrum are presented.

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1. INTRODUCTION

Under certain conditions, states which can be regarded as bound states of a phonon with a polaron, magnetopolaron, exciton or impurity electron arise in the energy spectrum of the electron-phonon system in semiconductors and ionic crystals. The spectrum of such states depends on the strength of the electron-phonon interaction and on a number of other parameters. A review of the experimental and theoretical work is contained in[1,2].

In the first theoretical papers[3−5] on the theory of bound states of phonons with electron centers (phonon-impurity complexes), the spectrum of the electron subsystem was described in a two-level approximation. This makes it possible to investigate the principal qualitative relationships sufficiently fully, but in the majority of cases—in particular, as applied to hydrogen-like centers of large radius—it cannot give a quantitative description.

It was shown previously by the author[6,7] that, when the dispersion of the phonons can be neglected and the electron-phonon coupling is weak in a certain sense, for an arbitrary spectrum of the electron subsystem the determination of the bound states of the phonons reduces

to solving the equation[1)]

$$\lambda \{(\lambda + H - \varepsilon_0)^2 - \omega_0^2\} \varphi = 2(\lambda + H - \varepsilon_0) A \varphi, \tag{1}$$

where $\lambda = \omega_0 - \omega$ are the eigenvalues defining the binding energy of the phonons and φ is related to the phonon wavefunction (see below). Here ω_0 is the phonon frequency in the ideal crystal, H is the Hamiltonian of the electron at the impurity center, and A is an integral operator with the kernel

$$A(\mathbf{r}, \mathbf{r}') = \psi_0(\mathbf{r}) V(\mathbf{r} - \mathbf{r}') \psi_0(\mathbf{r}'). \tag{2}$$

The operator

$$V(\mathbf{r}) = \sum_{\mathbf{q}} \gamma_{\mathbf{q}}^2 e^{i\mathbf{q}\mathbf{r}} \tag{3}$$

is entirely determined by the coefficients $\gamma_{\mathbf{q}}$ in the electron-phonon interaction Hamiltonian; ψ_0 and ε_0 are the wavefunction and energy corresponding to the lowest level (which is assumed to be nondegenerate) of the Hamiltonian H.

In[9] it was shown that the one-particle electron Green function can be expressed in terms of the functions φ,