

## Many-body and hot-phonon effects in the radiative emission spectrum of CdS under high excitation intensities

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We present here experimental results concerning the photoluminescence spectrum of CdS under high excitation intensities. With increasing excitation intensity the single emission band observed at 77 °K shows a peak displacement towards lower energies, an enhancement of its low-energy side as well as of its high-energy side. These effects increase with excitation intensity. We develop a complete model that can account for the above behavior and the emission band shape. The broadening is mainly due to nonequilibrium distribution of LO phonons, though contributions to the high-energy side from hot electrons is quite significant. Self-energy corrections account for the band reduction and consequently to the shift of the luminescence band peak towards lower energies.

### I. INTRODUCTION

The study of high-excitation effects in semiconductor behavior, such as metallic droplets, excitonic molecules, nonequilibrium distribution of electrons, phonons, excitons, etc., has become in recent years one of the dominant fields of interest both to experimentalists and theoreticians.<sup>1</sup> This paper is an attempt to consolidate our results, experimental and theoretical, by incorporating details which by necessity were left out of some earlier short communications reporting on the photoluminescence spectrum of CdS at temperatures above 77 °K and at high-excitation intensities.<sup>2-4</sup>

Our results have evidenced the participation of nonequilibrium distributions of optical phonons and conduction-band electrons, as well as the need for introduction of carriers self-energy to fully account for the luminescence behavior and shape dependence with excitation intensity.

The present research was motivated by analogy with highly doped, closely compensated semiconductors that have been shown to develop a "tail of states" penetrating into the forbidden energy band. These states affected the intrinsic radiative emission band in two ways, namely by a shift towards lower energies of its peak and by introducing an enhancement of its low-energy side. This is, both theoretically and experimentally, an abundantly studied phenomenon.<sup>5</sup>

Since these effects are mainly due to Coulomb interaction one should expect similar results when large densities of free charges are injected. Indeed band-peak shifts towards lower energies with excitation intensities were attributed to these effects when observed in GaAs.<sup>6</sup> However, these observations were not detailed enough to extract the related broadening of the low-energy side of the emission band. Under high-excitation intensities CdS displayed an emission spectrum very

much similar to those reported for compensated heavily doped GaAs. A theoretical calculation based on carriers self-energy corrections was able to account for large part of the shift of the emission-band peak towards lower energies but could not explain the observed large enhancement of the low-energy side.<sup>3</sup> Concomitantly, the broadening of the high-energy side of the emission spectrum was attributed to hot electrons.<sup>4</sup> Results from Raman spectroscopy under excitation conditions similar to the present case disclosed that in most semiconductors, nonequilibrium distributions of LO phonons were induced.<sup>7</sup> Due to the strong coupling between electrons and LO phonons we should expect that both low- and high-energy sides to reflect the LO-phonon population rather than the crystal temperature. The calculations to be presented here show that this is indeed the case. The entire behavior and shape of the photoluminescence emission spectrum of CdS under high excitation can only be properly accounted for by taking into consideration known effects that are unavoidable at high excitation, i.e., nonequilibrium populations of LO phonons and electrons and Coulomb interaction between carriers.

### II. EXPERIMENTAL NOTES

A diagram of the experimental arrangement used is shown in Fig. 1. The CdS samples were immersed in liquid N<sub>2</sub> in a Dewar with quartz windows. A pulsed nitrogen laser operating at  $\lambda = 3371 \text{ \AA}$  ( $h\nu = 3.68 \text{ eV}$ ) with pulse duration of nearly 10 nsec at 100-kW maximum power, was used as the excitation source. Focusing was obtained by a quartz lens or by a set of mirrors and maximum power density attained was nearly  $10^7 \text{ W cm}^{-2}$ . Variation on power was obtained by a series of glass plates introduced in the laser path that after calibration acted as attenuators. An Ebert 0.5-m monochromator was used together with an S-20 photomultiplier. A box-car integrator pre-

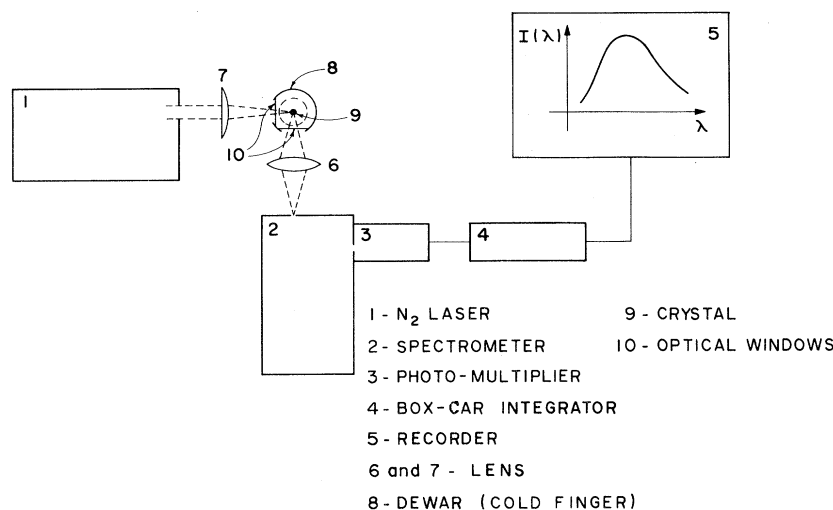


FIG. 1. Diagrammatic description of experimental setup.

ceded the strip chart recorder. The radiative lifetime was verified to be much shorter than the laser rise or decay times. For higher temperatures we have used a cold-finger Dewar capable of reaching temperatures as high as 400 °K by use of a heating resistor in the sample holder.

### III. EXPERIMENTAL RESULTS

At temperatures of liquid-helium typical radiative band-edge emission spectra of CdS are dominated by transitions involving shallow impurities. At temperatures above that of liquid H<sub>2</sub> however the spectrum is often dominated by the so-called *A* band attributed to the singlet exciton. This emission band increasingly involves band to band transitions as the temperature increases. Due to our specific interest in intrinsic processes, we have restricted our observations to temperatures above that of liquid N<sub>2</sub>.

Figure 2 gives the evolution of the radiative emission band with increasing excitation intensity for a CdS sample immersed in liquid N<sub>2</sub>. Note that the shift of the emission band towards lower energies is accompanied by a broadening of the low-energy side. If we characterize the low-energy side by an expression of the form  $I(h\nu) = Ae^{-h\nu/E_0}$ , where  $I(h\nu)$  is the observed emission intensity at the photon energy  $h\nu$ , we may express through the empirical characteristic energy  $E_0$  the induced broadening of the low-energy side of the emission band.

We ensured ourselves that sample heating was not significant by using different duty cycles in the excitation source. Though a temperature increase would not only shift the emission peak but also increase the bandwidth, effects observed here, we may be sure that this is not the case by simply comparing spectra at high excitations intensities, and low temperatures with spectra at low-excitation

intensities and higher temperatures. This is because when we match band-gap reduction  $\Delta E_g$  due to temperature with that due to high excitation the slopes of both sides of the spectra for which  $\Delta E_g$  was matched never coincided.

Figure 3 shows the dependence of the peak energy on the excitation intensity for three different temperatures. It is worth noticing that the slopes in Fig. 3 are the same for all temperatures.

Figure 4 gives the evolution of the emission spectrum for a CdS sample at room temperatures, 300 °K, with increasing excitation intensities. The same effects are noted here also. Due to an initial larger broadening the effects are not as readily noticeable as at 77 °K.

It is clear from the experimental results that  $E_g$  as well as  $E_0$  and the high-energy slope are monotonic functions of the excitation intensity. The excitation at these intensities introduces in the crystal not only free carriers but also a large population of longitudinal-optical phonons. These phonons must be important because from several experimental results we know that they participate in radiative transitions in CdS even when not in excess population.<sup>8</sup>

Therefore, any attempt to account for the radiative emission spectrum of CdS, and, in fact, in most direct-gap semiconductors, of these high intensities must take into consideration not only electron self-energy correction and Coulomb correlation but also electron interaction with an LO-phonon excess population. Next we consider the theoretical aspects of the subject.

### IV. THEORY

In this section we propose a phenomenological theory which attempts to describe the luminescence spectra in conditions of nonequilibrium distribution

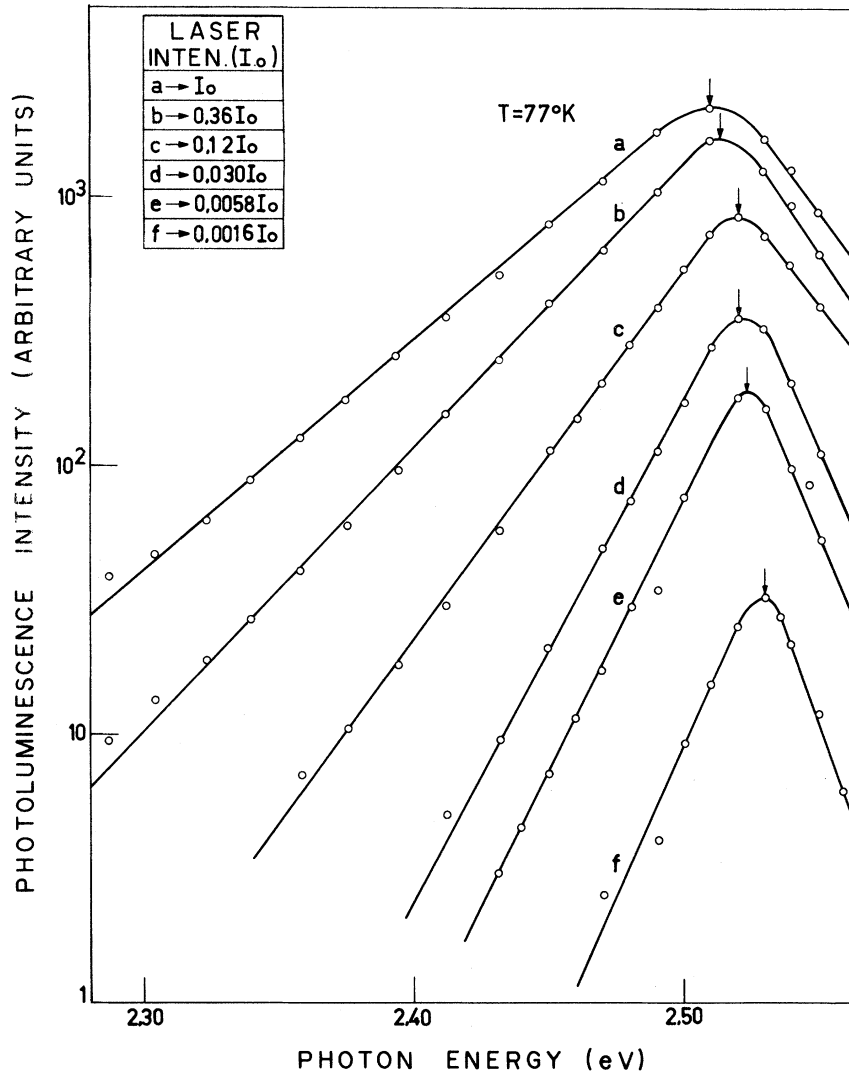


FIG. 2. Emission spectra of CdS at different excitation intensities. Thermal bath at 77°K.

of elementary excitations in direct-gap semiconductors.

In the conditions of the experiment under consideration it is expected that the saturation condition, when the rate of generation of electron-hole pairs equals the recombination rate,<sup>9</sup> is not achieved. Hence, with the intensity of the electromagnetic field not too high so that the probability of induced transitions are smaller than the probability for collisions between the elementary excitations we make the simplifying assumptions of introducing quasichemical potentials ( $\mu_\alpha$ ) and effective temperatures ( $T_\alpha$ ) for the subsystems of electrons, holes, and phonons in quasiequilibrium condition.<sup>10</sup> Figure 5 gives a pictorial description of the physical system we are considering and the relaxation mechanisms and transitions involved: (i) electron-hole pairs are created through intense laser excitation; (ii) these elec-

trons and holes decrease their energies by emission of LO phonons in times of the order of  $\tau_{ep}$  and  $\tau_{hp}$ , respectively, leaving a LO-phonon population in large excess of equilibrium value; (iii) quasiequilibrium distribution of all three systems is assumed to be established through collisions and multiple emission and absorption of optical and acoustic phonons, involving relaxation times  $\tau_{eL}$ ,  $\tau_{hL}$ , and  $\tau_{pL}$  ( $T_e$ ,  $T_h$ ,  $T^*$ , and  $\mu_c$  and  $\mu_v$  are the temperatures and chemical potentials that characterized the quasiequilibrium distributions); and finally (iv) radiative recombination occurs with the characteristic time  $\tau_r$ . Process (ii) is the fastest;  $\tau_{ep}$  and  $\tau_{hp}$  are much smaller than  $\tau_r$ . Thermodynamic equilibrium is not achieved in the interval  $\tau_r$  because all other  $\tau$  are of the order or larger than  $\tau_r$ , and recombination occurs in the nonequilibrium conditions (iii). It should be noted however that we are introducing a unique effective

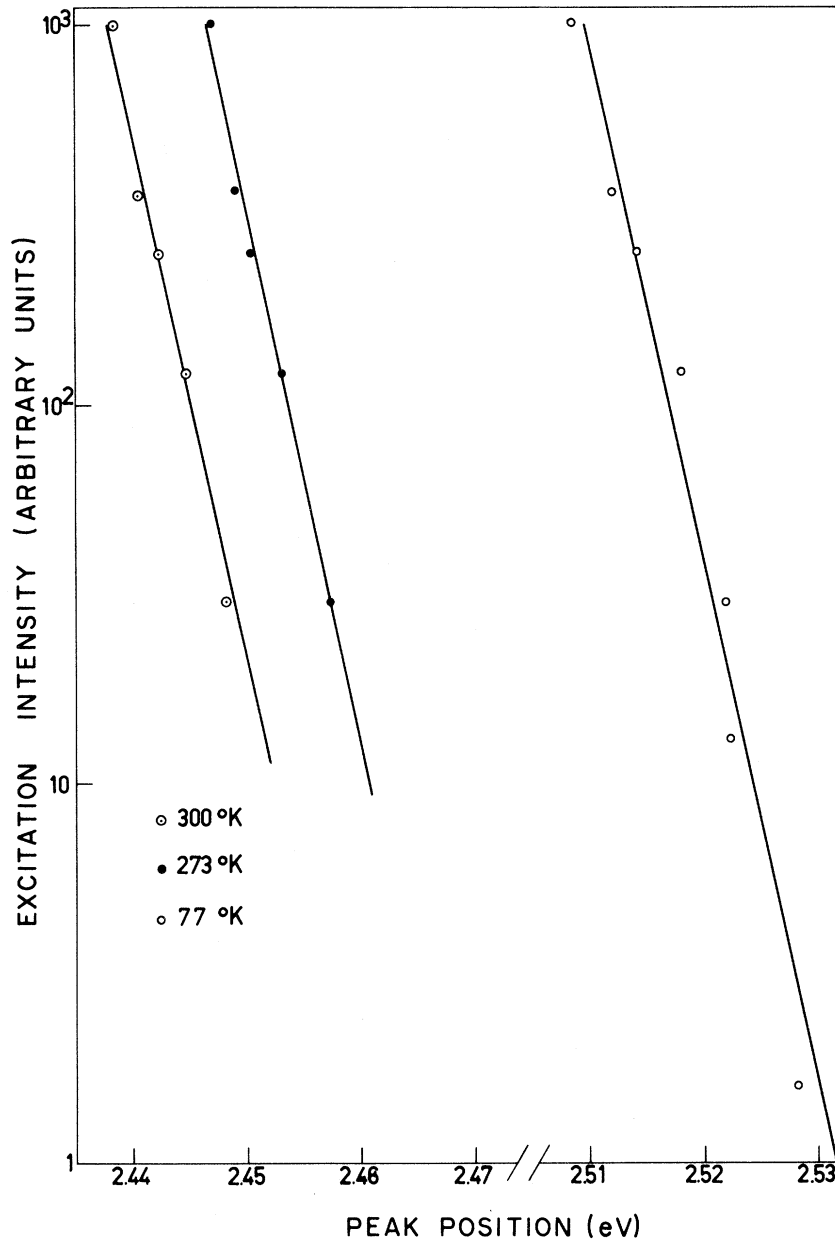


FIG. 3. Energy corresponding to the peak value of the emission band as a function of excitation intensity.

temperature  $T^*$  for the LO phonons. Recent experiments show that the effective temperature that characterizes the nonequilibrium population is dependent on the phonon wavelength: the smaller the wave number the larger the population excess.<sup>7</sup> The temperature  $T^*$  can be considered as an average temperature over the phonon (nearly zero) wave numbers that will be involved and consistent with an approximation to be introduced later [cf. Eq. (4)].

The Hamiltonian we use is

$$H = H_E + H_L + H_R + H_{eR} + H_{eL}, \quad (1)$$

where  $H_L$  and  $H_R$  are the energy operator of the LO phonon and the radiation, respectively,  $H_{eR}$  and  $H_{eL}$  are the interaction energies between electrons and radiation and electrons and LO phonons, and

$$H_E = \sum_{\vec{k}\alpha} [\epsilon_\alpha(\vec{k}) - \mu_\alpha] C_{\vec{k}\alpha}^\dagger C_{\vec{k}\alpha} + H_{Coul}, \quad (2)$$

with  $\alpha = c, v$  (conduction, valence bands) and  $H_{Coul}$  is the energy of the Coulomb interaction between electrons. An additional assumption will be made. Since we are considering the conduction and valence electrons as two independent systems of par-

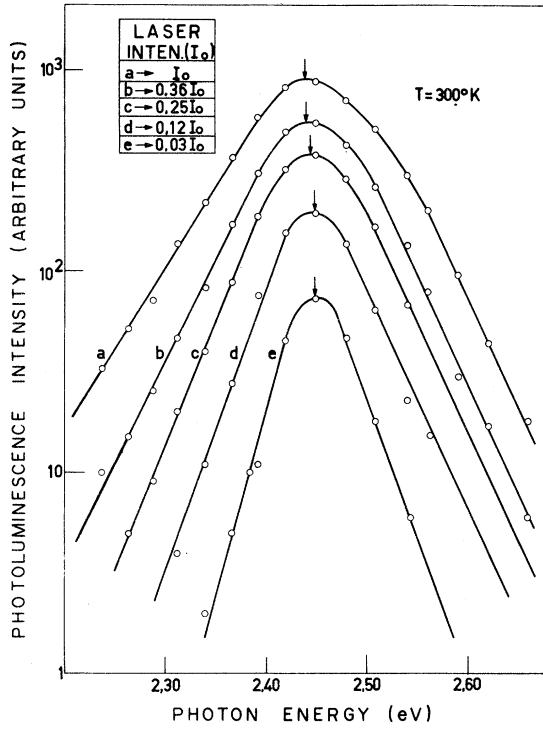


FIG. 4. Emission spectra of CdS at different excitation intensities. Thermal bath at room temperature.

ticles, interband Coulomb correlation and plasma effects will be neglected, keeping only intraband interactions. This is a crude approximation, which, however, introduces many-body effects that will result in a band-gap shrinkage,<sup>11</sup> but fails to give a structure that appears below the absorption edge due to electron-hole-plasma excitation.<sup>12,13</sup> This structure has been observed under appropriate conditions in GaAs,<sup>14</sup> but is smeared out in CdS by the superposition of the more intense phonon replicas discussed in this paper.

The intraband Coulomb interaction will be incor-

porated in the one-electron energies  $\epsilon_\alpha(\vec{k})$  in the form of the self-energy correction  $M_\alpha(k)$  as given by Hedin.<sup>15</sup> Neglecting electron lifetimes we will replace Hamiltonian (2) by

$$H'_E = \sum_{\vec{k}\alpha} [\epsilon_\alpha(\vec{k}) + M_\alpha(\vec{k}) - \mu_\alpha] C_{\vec{k}\alpha}^\dagger C_{\vec{k}\alpha} . \quad (3)$$

Observe that  $\mu_\alpha$  in Eq. (3) is now the renormalized chemical potential  $\mu_\alpha + M_\alpha(K_F)$ .

As a consequence of these assumptions the usual theory of optical transitions remains formally valid as for the case of free-band electrons in equilibrium, except that we replace the electron dispersion for the renormalized ones<sup>11</sup> and we introduce the quasiequilibrium distribution of excitations. Furthermore, we will approximate the Frölich interaction between electrons and LO phonons by the model Hamiltonian<sup>16</sup>

$$H_{eL} = -i\lambda^{1/2} \omega_0 (a^\dagger - a) \sum_{\vec{k}\alpha} C_{\vec{k}\alpha}^\dagger C_{\vec{k}\alpha} , \quad (4)$$

where  $\lambda$  is a coupling constant and  $\omega_0$  is the LO-phonon frequency. The electron-radiation interaction is

$$H_{eR} = \sum_{\vec{k}\alpha\beta} g_{\alpha\beta}(\vec{k},\vec{k}') C_{\vec{k}\alpha}^\dagger C_{\vec{k}'\beta} + H.C. , \quad (5)$$

where

$$g_{\alpha\beta}(\vec{k},\vec{k}') = \langle \vec{k}\alpha | (e/mc)\vec{A} \cdot \vec{p} | \vec{k}'\beta \rangle ,$$

with  $\vec{A}(\vec{r})$  being the semiclassical vector potential of the radiation field.

Concerning the statistical-mechanics aspects of the problem our standpoint, as previously discussed, consists of considering the system to be composed of four subsystems, conduction and valence-band electrons, LO phonons, and the thermal bath (acoustic phonons), which could be assigned different temperatures. These subsystems are supposed to come into internal equilibrium at temperatures  $T_\alpha$  in times  $\tau_\alpha$  much shorter than the recombination time  $\tau_r$ , and the relaxation times for contact with the thermal bath. Hence, the

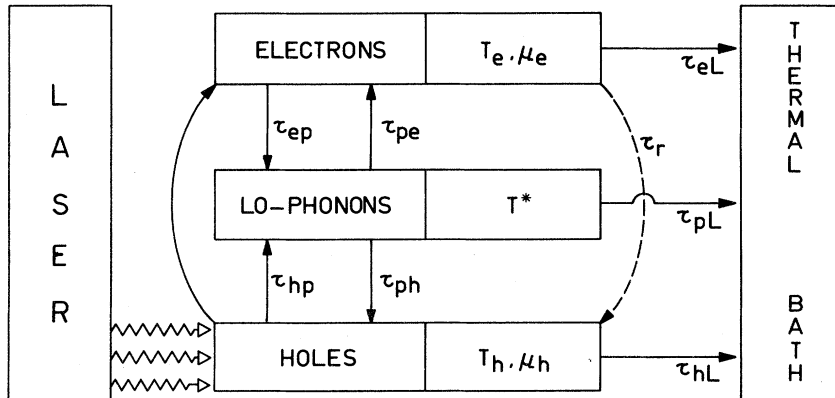


FIG. 5. Schematic description of the physical system considered in the text.

system may be described by a density matrix of the form

$$\rho(T_\alpha, \mu_\alpha) = \rho_c \rho_v \rho_{ph} \rho_{int}, \quad (6)$$

where

$$\rho_\alpha = \frac{1}{Z_\alpha} \exp\left(-\beta_\alpha \sum_{\vec{k}} [\epsilon_\alpha(\vec{k}) + M(\vec{k}) - \mu_\alpha]\right), \quad (6a)$$

$$\rho_{ph} = \frac{1}{Z^*} \exp\left(-\beta^* \sum_{\vec{q}} h\omega_0 (a_q^\dagger a_q + \frac{1}{2})\right), \quad (6b)$$

and  $\rho_{int}$  involves a small noncommuting part of the total Hamiltonian which is responsible for the ultimate establishment of thermal equilibrium.  $Z_\alpha$  and  $Z^*$  are the respective grand-partition functions of electrons and phonons.

The luminescence spectrum is given by

$$I(\omega) = \omega r_{\text{spont}}(\omega), \quad (7)$$

where  $r_{\text{spont}}(\omega)$  is the rate spontaneous emission of photons per unit volume into the solid angle  $d\Omega$  and the frequency interval  $d\omega$ . Using the Born expansion and the Van Hove method,<sup>17</sup> one finds

$$r_{\text{spont}}(\omega) = \int_{-\infty}^{\infty} dt e^{i\omega t} \langle v^\dagger(0) v(t) \rangle, \quad (8)$$

where  $\langle \dots \rangle$  stands for statistical average using the unperturbed part of the matrix density of Eq. (6). Here

$$v(t) = \sum_{\vec{k}\vec{q}} g_{vc}(\vec{k} - \vec{q}, \vec{k}) C_{\vec{k}-\vec{q}v}^\dagger(t) C_{\vec{k}c}(t),$$

with  $g$  given after Eq. (5).

A transformation to new variables  $C_{\vec{k}\alpha}$  by means of application of the unitary transformation

$$U(t) = \exp\left(-it \sum_{\vec{k}\alpha} \mu_\alpha C_{\vec{k}\alpha}^\dagger C_{\vec{k}\alpha}\right) \quad (9)$$

is introduced in order to properly refer to a unique zero of energy, which we choose at the bottom of the conduction band.

The rate of spontaneous emission of photons becomes

$$r_{\text{spont}}(\omega) = \sum_{\vec{k}\vec{k}'\vec{q}} g^*(\vec{k}', \vec{k}' - \vec{q}) g(\vec{k} - \vec{q}, \vec{k}) \times \int dt e^{i\omega t} F(\vec{k}, \vec{k}', \vec{q}; t), \quad (10)$$

where

$$F(\vec{k}, \vec{k}', \vec{q}; t) = \langle C_{\vec{k}'c}^\dagger C_{\vec{k}'-\vec{q}v} C_{\vec{k}-\vec{q}v}^\dagger(t) C_{\vec{k}c}(t) \rangle$$

and

$$\Omega = \omega - \mu_c + \mu_v.$$

Neglecting electron-hole correlation, dropping the phonon momentum  $q$ , and taking the matrix elements  $g(\vec{k}, \vec{k}') = g$  as  $\vec{k}$  independent, one can take advantage of Bosacchi and Robinson's results,<sup>18</sup> after a proper adaptation to the quasiequilibrium conditions of our model, to obtain

$$I(\omega) = \omega^2 |g|^2 \sum_{n=-\infty}^{\infty} \Phi_n(x) \sum_{\vec{k}} \{\exp[-\beta(\tilde{\epsilon}_{kv} - \mu_v)] + 1\}^{-1} \times \{\exp[\beta(\Omega + \tilde{\epsilon}_{kv} - \mu_v)] + 1\}^{-1} \times \delta(\Omega - \tilde{\epsilon}_{kc} + \tilde{\epsilon}_{kv} + \mu_c - \mu_v + n\omega_0), \quad (11)$$

where

$$\Phi_n(x) = \exp[-x + (\frac{1}{2}n\beta^*\omega_0)] I_n(x),$$

with  $x = \lambda \coth(\frac{1}{2}\beta^*\omega_0)$ ,  $\beta^* = 1/K_B T^*$ ,  $I_n(x)$  is the modified Bessel function of index  $n$ , and  $\tilde{\epsilon}_{\vec{k}\alpha} = \epsilon_{\vec{k}\alpha} + M_\alpha(\vec{k})$ .

Next we specify Eq. (11) using numerical values appropriate to CdS. Conduction- and valence-bands energies and chemical potentials are chosen as  $\epsilon_c(\vec{k}) = k^2/2m_c$ ,  $\epsilon_v(\vec{k}) = -E_g - k^2/2m_h$ ,  $\mu_c = k_F^2/2m_e + M_c(k_F) - (\frac{1}{16}\pi^2)(T/T_{FC})^2$ ,  $\mu_v = -E_g - k_F^2/2m_h + M_v(k_F) + (\frac{1}{16}\pi^2)(T/T_{FV})^2$ , where  $3\pi^2 k_F^3 = n$ , with  $n$  the concentration of photoelectrons. We neglected correlation effects between valence band electrons (for which  $r_S \geq 10$ ), and the results of Hedin for  $M_c(k)$  are used.<sup>15</sup> This quantity is almost  $\vec{k}$  independent and one finds for CdS,  $M(k)/E_g \simeq -0.007\kappa$ , where  $\kappa = k_F r_B^*$ . (Let us observe that we have used 33 Å and 20 meV for the exciton Bohr radius and exciton rydberg, respectively. The presence of  $M_c(\vec{k})$  in the combination  $\epsilon(\vec{k}) + M(\vec{k})$  produces an effective shrinkage of the band gap, and therefore contributes to the shift of  $I(\omega)$  towards lower energies. Note that for  $\kappa$  of the order of unity one finds  $M(0) \sim 15$  meV, which is smaller than the Hartree-Fock result.<sup>11</sup> It is also used  $\epsilon_0 = 10.5$ ,  $m_e = 0.17$ ,  $m_h = 0.71$ ,  $\omega_0 = 36$  meV,  $E_g = 2.56$  eV, and  $\lambda = 0, 8$ .)

Four phenomenological parameters are left open in Eq. (11), namely, the photoelectron density  $n$ , and the effective temperatures  $T_c$ ,  $T_v$ , and  $T^*$  whose direct evaluation is not possible. These parameters will be chosen as to give a reasonable fitting of the experimental data. We do not attempt here a careful fitting, since we believe that would not be consistent with the different approximations already done in order to obtain  $I(\omega)$ . Our principal aim is just to show that *the shift of the peak position towards low energies and the modification of the slope of the edges of the logarithmic spectra with increasing laser intensity is a result of Coulomb correlation and nonequilibrium distribution of electrons and phonons.*

The calculated and experimental luminescence spectra are shown in Fig. 6. As already noted,<sup>18</sup> the multiphonon thresholds are evident and the square-root singularity at them are due to the simplify model used here [Eq. (4)]. It is expected that inclusion of lifetime effects, a more appropriate momentum dependence of the interaction potential and the inclusion of the deformation potential interaction should smooth the edges of the

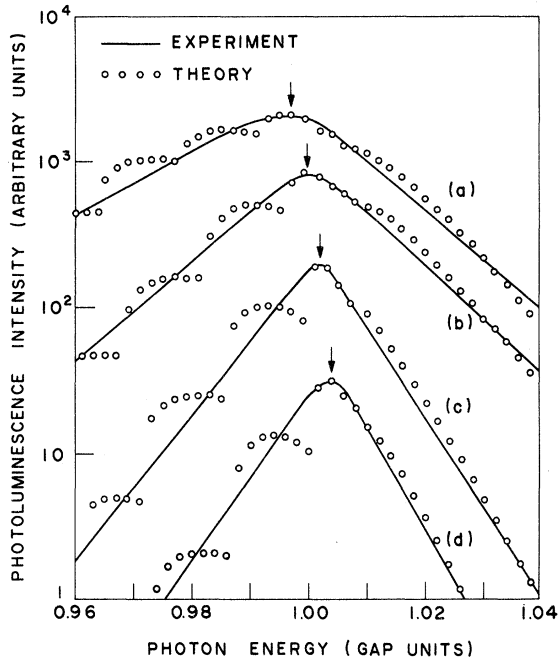


FIG. 6. The calculated and experimental luminescence spectra of CdS: (a)  $\kappa=0.96$ ,  $T^*=1790^\circ\text{K}$ ,  $T_e=210^\circ\text{K}$ ; (b)  $\kappa=0.64$ ,  $T^*=680^\circ\text{K}$ ,  $T_e=200^\circ\text{K}$ ; (c)  $\kappa=0.38$ ,  $T^*=295^\circ\text{K}$ ,  $T_e=130^\circ\text{K}$ .

calculated  $I(\omega)$ . Such smoother shouldered slope of  $\ln I(\omega)$  has actually been observed in CdS, improving the quantitative agreement between experimental and calculated values.<sup>19</sup>

The fitting with the experimental results of Sec. III was attempted by appropriate choice of the effective LO-phonon temperature  $T^*$  and the electron

temperature  $T_e = T_c = T_v$ . The high-energy side of the spectrum broadening is a result of the enhancement of the phonon replicas with increasing  $T^*$ , i.e., as a result of the increasing excitation. Figure 7 shows the dependence of the energy parameter  $E_0$  with the phonon effective temperature. A tendency to saturation at high-excitation levels can be observed. It should be noted that a similar behavior of  $E_0$  versus lattice temperature is observed in GaAs.<sup>20</sup>

The broadening of the high-energy side of the spectrum is also observed and accounted for our theory. The slope of  $\ln I(\omega)$  in this region can be characterized by a temperature  $T_s$  such that

$$KT_s = \left( \frac{d \ln I(\omega)}{d\omega} \right)^{-1}. \quad (12)$$

This temperature agrees at low temperatures and in equilibrium conditions with the temperature of the electrons,<sup>10</sup> being then practically the lattice temperature. The value of  $T_s$  increases with increasing laser intensity, and has been interpreted as the temperature of the carriers thermalized in a quasiequilibrium condition.<sup>2,21</sup> However, for the strong-excitation levels used in the experiments of Sec. III, which produce phonon effective temperatures of nearly  $2000^\circ\text{K}$ , the (absorption) phonon replicas enlarge the high-energy tail of the luminescence spectrum. Hence,  $T_s$  is no longer the effective electron temperature, except at very low-excitation energies and low temperatures. Figure 8 shows  $T_e$ ,  $T^*$ , and  $T_s$  vs  $\kappa$  (let us recall that  $\kappa$  is proportional to the cubic root of the injected photoelectrons density).

Finally, Fig. 9 shows the shift of the peak energy of the emission band as a function of  $\kappa$ . The

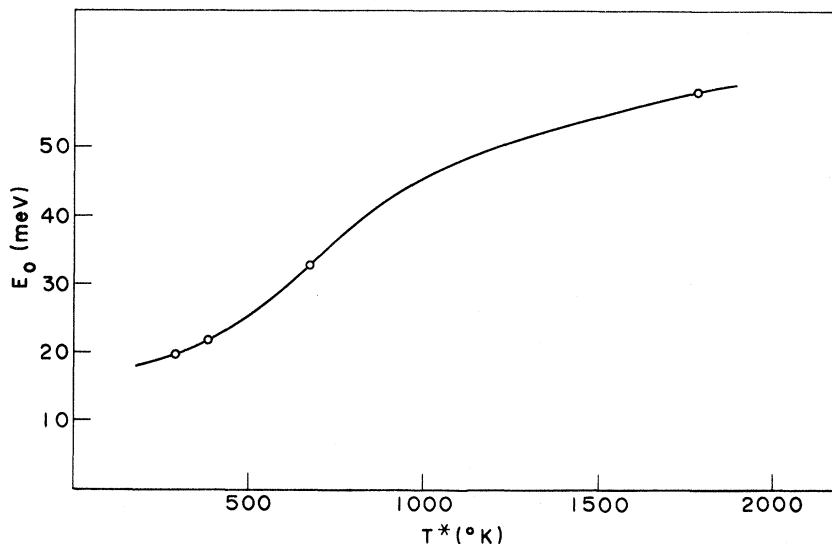


FIG. 7.  $E_0$ , the inverse of the low-energy slope of  $\ln I(\omega)$ , vs the LO-phonon effective temperature.

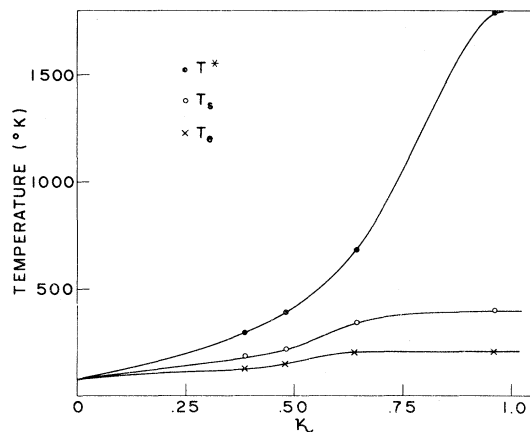


FIG. 8. Effective temperature of phonons  $T^*$ , the effective temperature of electrons  $T_e$ , and the temperature  $T_s$  defined in Eq. (12) as a function of the parameter  $\kappa$ .

slope  $|dE_{\text{peak}}/d\ln\kappa|_{\text{theor}}$  is found to be nearly 20.8 meV, whereas from the experimental data of Sec. III is found  $|dE_{\text{peak}}/d\ln\kappa|_{\text{expt}} \approx 22.2$  meV, once it is assumed that there exists a linear relationship between photoelectron concentration and laser intensity. The opposite "Burnstein-Moss shift"<sup>22</sup> is, for the excitation levels considered, not yet competitive with the combined "energy-band-gap shrinkage" added to the tail contribution of the phonon side bands.

## V. DISCUSSION AND CONCLUSIONS

We presented an experimental study of the photoluminescence spectrum of CdS in conditions of high-excitation levels. Our results, together with information collected from other kind of experiments, show that nonequilibrium distribution of optical phonon and charge carriers determine the behavior and shape dependence of the luminescence spectra.

In Sec. IV we devised a theory that describes the recombination spectrum in direct-gap semiconductors in conditions of strong illumination. Numerical calculations were performed for the case of CdS in the experimental conditions described in Sec. III.

According to our results the injected carrier density produces self-energy corrections that account for almost all of the shift of the peak position at not too high levels of injection. At high levels

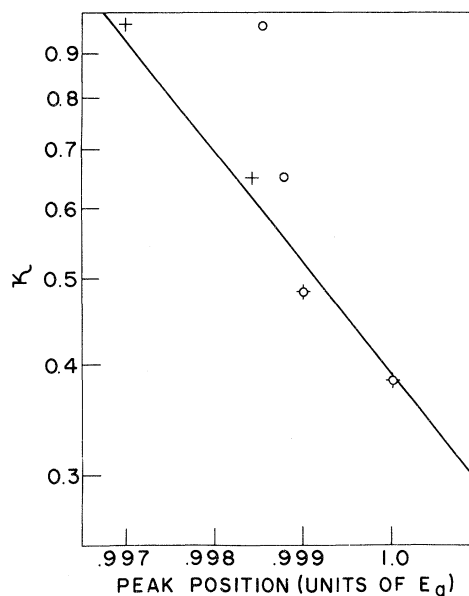


FIG. 9. Calculated peak position of the luminescence spectra of CdS vs  $\kappa$ : (O) including Coulomb correlation only, and (+) idem plus electron-phonon interaction as described in the text.

the Burnstein-Moss shift becomes competitive with the "band-gap shrinkage." However, at high intensities a shift towards lower energies continues to occur as a result of the superposition of the phononless line with the tails of the phonon replicas.

The low-energy edge of the spectrum, i.e., the region described through the so-called Urbach rule,<sup>23</sup> is essentially governed by the phonon replicas and therefore strongly depends on the population of hot phonons, that we described by the effective temperature  $T^*$ . This side of the spectrum shows a very weak dependence on the electron temperature and density. (This is not general, depending on the material and experimental circumstances the low energy electron-hole plasma excitation can introduce additional observable structure.<sup>13,14</sup>) On the other hand the high-energy side depends on both electron and phonon nonequilibrium distributions.

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