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# Picosecond spectroscopy of CdSe at high excitation densities

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We report time-resolved spectra of CdSe luminescence at high excitation densities and superfluid-helium temperatures. Measurements are taken that separate various spurious effects, which tend to distort such data. Density inhomogeneity effects and excitation-induced absorption and gain are shown to be important in interpreting the data. Time-resolved measurements are extended to much later time delays than previously reported. At short time delays, i.e., immediately following the pulsed excitation, the luminescence is shown to derive from an electron-hole plasma. Fitting the time-resolved spectra to a plasma line-shape function shows that the plasma, when overpumped, expands into the crystal in times that are short compared to 20 ps. These fittings also give $E_B = E_x - E(n_0) = 3$ meV, where $E_x$ is the free-exciton energy and $E(n_0)$ is the minimum of the ground-state energy per pair curve of the electron-hole plasma. The 3-meV value agrees fairly well with theory. With increasing time delay, the plasma emission is shown to go over to $M$-band emission and finally to bound-exciton emission. Polarization measurements indicate that the $M$ band derives from $I_2$-band luminescence from the deep regions of the crystal, which has been distorted by absorption while passing through an electron-hole plasma lying close to the surface of the crystal. We also show that spontaneous $P$ bands do not exist and that stimulated $P$ bands derive from an electron-hole plasma. We propose an explanation for why the energy of the $P$ band scales with the free-exciton binding energy in different II-VI semiconducting compounds.

## I. INTRODUCTION

The physical processes that occur at high excitation densities (HED) and low temperatures in optically excited semiconductors have been studied extensively. The term HED refers to densities high enough so that interactions between the excitations are important. The most detailed work in this field involves the exciton-gas electron-hole—liquid phase transition that occurs in indirect-gap semiconductors. Similar work has been done in direct-gap semiconductors, but here the situation is much less clear.[1] The lack of clarity may be traced, in part, to the large optical-transition probabilities, the short excitation lifetimes, and the high impurity content typical in the direct-gap semiconductors that have been studied. The large optical-transition probabilities give rise to self-absorption and stimulated-emission effects which distort the spontaneous luminescence spectra. The short lifetime encourages inhomogeneities in the excitation density and complicates the theory of the exciton-gas electron-hole—liquid phase transition.[2] The short lifetime also necessitates intense laser pumping, which causes heating effects. The high impurity content gives rise to intense impurity luminescence, which contaminates the intrinsic spectra at HED. Some authors have avoided the problem of stimulated emission by measuring the gain-absorption spectra rather than the luminescence spectra.[3] However, even these spectra may sometimes be distorted by frequency-selective feedback and saturation.[4] Here we measure the luminescence of the direct-gap semiconductor CdSe at HED. Measurements which separate some of the effects discussed above are taken.

Two basic models have been used in the literature to explain the phenomena occurring at HED in direct-gap semiconductors: the exciton-exciton—collision model and the electron-hole—plasma (EHP) model.[1] The exciton-exciton—collision model assumes that as the excitation density is increased, exciton-exciton collisions become more frequent, and that these collisions give rise to the new luminescence bands that appear at HED. For example, two excitons collide to form an excitonic molecule which then decays into a photon and an exciton; or, two excitons collide, causing one to dissociate and the other to recombine, emitting a photon. In CdSe, the $M$ band has been attributed to the first of these processes and the $P$ band to the second.[1] The exciton-exciton—collision model predicts that a series of fairly sharp bands should appear at HED in the luminescence spectra at energies below the free-exciton band. The EHP model assumes that with increasing excitation density the excitons dissociate to form an EHP and that many-body effects cause the band gap "seen" by the plasma to be renormalized to smaller values. The EHP model predicts that a single very broad luminescence band should appear at HED.

We argue that our data derive from an EHP and from stimulated-emission, self-absorption, and density inhomogeneity effects. We also argue that exciton-exciton—collision processes do not contribute to the luminescence in experiments similar to ours. We propose a new model for the $M$ band and present new data that support a previously proposed model for the $P$ band.[5] We also take measurements of the parameters of the EHP in CdSe. In our discussion we will, on occasion, assume that experimental results from the literature on CdS can be applied to CdSe, since the two substances are very similar.

## II. EXPERIMENTAL DETAILS

We studied CdSe at HED and superfluid-helium temperatures using picosecond spectroscopy. Figure 1 shows a schematic of the picosecond spectrometer. The laser is a cw mode-locked rhodamine-6G dye laser synchronously pumped by an acousto-optically mode-locked argon-ion laser. The laser is described in Refs. 6 and 7. The laser emits a series of 20-ps pulses separated by 10 ns, and may be tuned over several hundred angstroms. One-half of the laser beam is used to excite the CdSe (immersed in superfluid helium); the other half is sent to a variable optical delay line (a prism on a slide). The luminescence of the CdSe and the laser beam returning from the delay line are overlapped in a $LiIO_3$ crystal which is phase-matched by angle tuning for sum-frequency mixing. A monochromator selects a narrow band of the sum-frequency signal, which is then measured with a photomultiplier and a lock-in amplifier. The only part of the luminescence that contributes to the sum-frequency signal is the part that actually passes through the $LiIO_3$ simultaneously with the laser pulse, and that is at a frequency equal to the difference of the sum frequency (as defined by the monochromator) and the laser frequency.

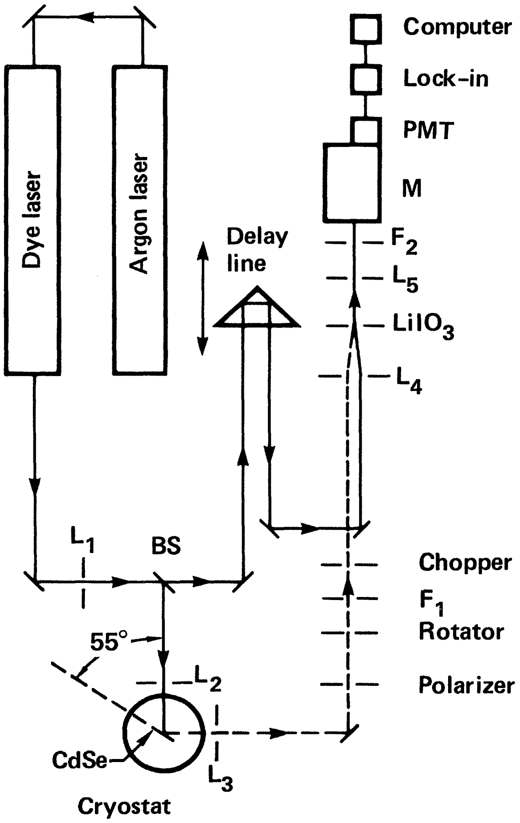

FIG. 1. Schematic view of the experimental arrangement. $L_1$ is a collimating lens; $L_2$, $L_3$, $L_4$, and $L_5$ are lenses; $F_1$ is a filter that passes the CdSe luminescence and blocks the laser light; $F_2$ is a filter that passes ultraviolet and blocks visible light; *BS* is a beam splitter; *M* is a monochromator; and PMT is a photomultiplier tube. The plane of the paper is the horizontal plane.

By tuning the laser while leaving the delay line, the $LiIO_3$, and the monochromator alone, we can record a time-resolved spectrum of the CdSe luminescence. By lengthening the time-delay line, we can record the time decay at a particular frequency. Thus the $LiIO_3$ serves as an up-conversion light gate. The time and frequency resolutions attained were 20 ps and 3 Å. This method of taking time-resolved spectra is susceptible to various distortions when the spectra become too broad in frequency. We can show that, in this particular experiment, these distortions are negligible. We can also obtain time-integrated spectra by removing the $LiIO_3$ from the setup.

Because of the high repetition rate of the laser, low noise of the up-conversion process, and signal-averaging capabilities of the setup, our picosecond spectrometer is much more sensitive than the Nd-laser Kerr-cell type of picosecond spectrometer used in other studies of II-VI semiconductors.[8,9] This higher sensitivity enables us to use much smaller excitation spots (thereby lowering the gain length and the effect of stimulated emission), and to take time-resolved spectra out to much larger time delays (out to 5 ns after excitation). The higher sensitivity also permits us to lessen the temperature effects by using lower pumping powers. In addition, the clean transverse-mode structure and the repeatability from shot to shot of the dye laser are helpful in obtaining clean data.

The CdSe was excited by a 20-ps-long laser pulse at about 580 nm, focused to a 10-$\mu$m-diam spot, to give a peak power of 40 $\mathrm{MW\,cm^{-2}}$. If one ignores diffusion and recombination during the laser pulse and uses the photon flux, the reflectivity (0.3), and the absorption constant ($3\times10^4\ \mathrm{cm}^{-1}$) to estimate the initial excitation density, then one obtains $5\times10^{19}$ electron-hole pairs per $\mathrm{cm}^3$. This is well above the density at which excitons should become close packed ($1.5\times10^{18}\ \mathrm{cm}^{-3}$ from Ref. 10), the Mott density at 0 K ($2\times10^{14}\ \mathrm{cm}^{-3}$ from Refs. 11 and 12), and the minimum of the theoretical ground-state energy per pair curve of the EHP ($5.4\times10^{17}\ \mathrm{cm}^{-3}$ from Ref. 12).

The surface of the CdSe excited by the laser beam lies in the vertical plane (see Fig. 1). The *c* axis of the CdSe lies in the horizontal plane and in the plane of the crystal surface. CdSe is an optically uniaxial crystal of wurtzite crystal structure. The crystal was inclined, as shown in Fig. 1, and the luminescence was observed in a direction 90° from the direction of the exciting laser beam. Both the vertical (*V*) and the horizontal (*H*) polarizations of the luminescence were measured. Note that *V* involves only $\vec{E}\perp c$-allowed transitions, while *H* involves both $\vec{E}\perp c$- and $\vec{E}\parallel c$-allowed transitions. Both platelet samples (some tens of micrometers thick and a few millimeters on a side) and bulk crystals were measured.

## III. RESULTS

In platelet samples, two or more glowing spots could be observed, one where the laser beam struck the face of the CdSe (*W* spot), and others at the edges of the platelet (*S* spots). The *S* spots did not appear in bulk crystals. The *S* and *W* spots were typically separated by a couple of millimeters. By focusing images of these spots on the

$LiIO_3$, or on the slits of a monochromator, we could obtain a complete set of data for the *S* and *W* spots separately. The line between the *W* spot and an *S* spot was always perpendicular to the edge of the platelet. Figure 2 shows time-integrated spectra of the *S* and *W* spots for a typical platelet sample. For comparison, the spectrum at low pumping power is also shown. It is well known that the $I_2$ ($I_1$) band of the low-pump-power spectrum arises from the decay of an exciton bound to a neutral donor (acceptor). The *S*-spot light probably travels nearly parallel to the surface of the platelet by total internal reflection (TIR) from the front and back surfaces, and escapes at the edges since the conditions for TIR are not satisfied there.[13] Because of the large index of refraction ($n = 3$), *W* light that is refracted at the idealized plane of the surface travels nearly perpendicular to the surface. Since the laser-spot size on the surface of the CdSe is much greater than the absorption depth, we expect that the *S*-spot light will "see" a much longer gain length than the *W*-spot light. Thus, it is reasonable to suppose that *W* is mostly spontaneous emission, and *S* is mostly stimulated emission.[7] The time-decay curves of *S* and *W* are consistent with this interpretation (see Figs. 3 and 4). By up-converting scattered laser light, we could show that the *W* spot rose simultaneously with the laser pulse, while the *S* spot was delayed (Fig. 3). The time decay of the *S* spot is much more rapid than that of the *W* spot and is strongly dependent on the pumping intensity (Figs. 3 and 4). All of these observations are consistent with *S* being mostly stimulated and *W* being mostly spontaneous.

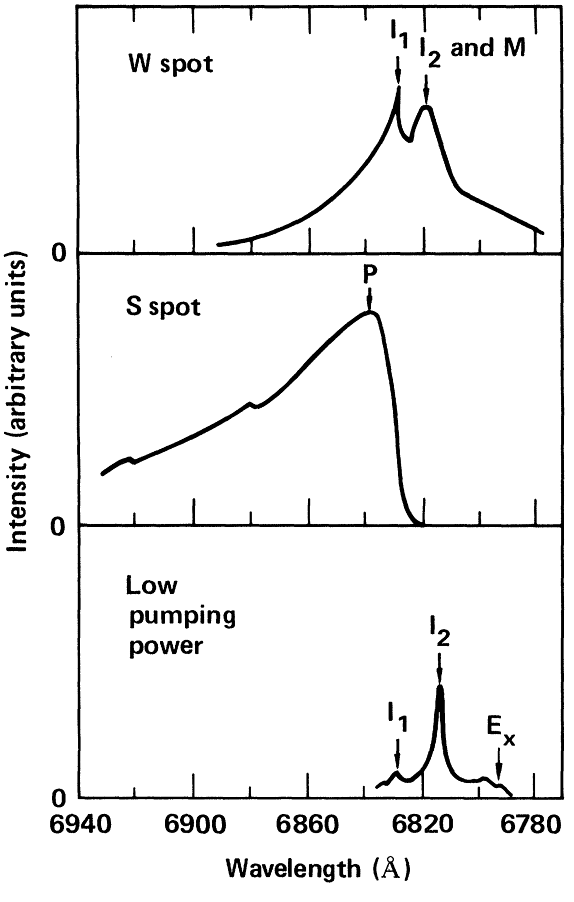

FIG. 2. Unpolarized time-integrated spectra of the high-pump-power *W* and *S* spots and of the low-pump-power *W* spot for a platelet sample. Throughout this paper, the term high pump power refers to 40 MW cm$^{-2}$ for 20 ps on a 10-$\mu$m-diam spot.

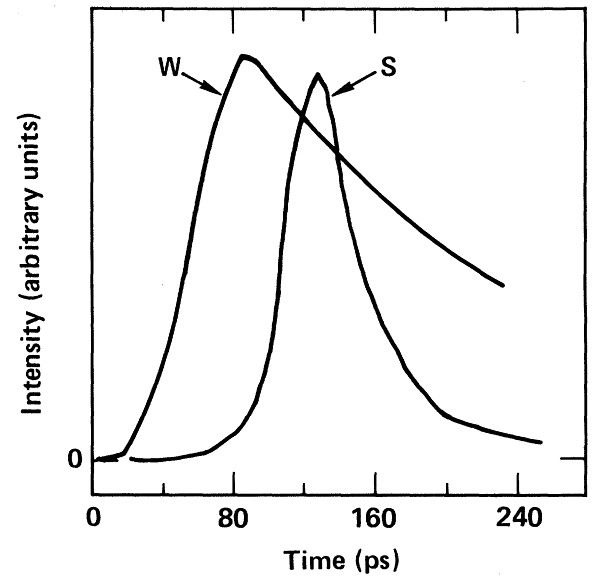

FIG. 3. Relative time dependence of the *S* and *W* spots in the vertical polarization. Both of these curves were taken at 684.5 nm. If we plot the time-resolved signal for the *S* spot as a function of time and wavelength, we find that the maximum of the function occurs at 684.5 nm. The total signal intensities, integrated over all wavelengths, are qualitatively similar to these curves. Time equal to 0 is arbitrary. *W* rises promptly with the laser pulse; *S* is delayed.

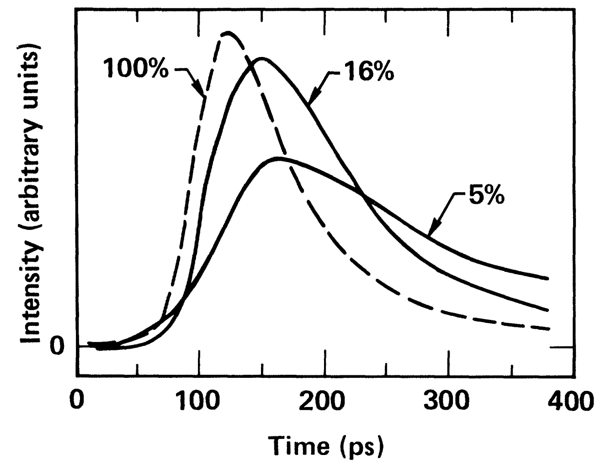

FIG. 4. Relative time dependence of the *S*-spot luminescence in the vertical polarization at 684.5 nm as a function of pumping power at 100%, 16%, and 5% of 40 MW cm$^{-2}$. Time equal to 0 is arbitrary.

Consider the $I_1$ band in the high-pump-power time-integrated spectrum of the $W$ spot in Fig. 2. This band appeared in all crystal samples, both platelets and bulk, that had a low-pump-power spectrum similar to that shown in Fig. 2. This high-pump-power $I_1$ band does not appear in the time-resolved spectra at any delay time. The geometry of the experiment is such that the time-integrated spectra see a much larger area on the surface of the CdSe than do the time-resolved spectra. The spatial selectivity of the time-resolved spectra results because only that part of the luminescence overlapping the focused laser beam inside the $LiIO_3$ contributes to the signal. Thus, this discrepancy between the time-integrated and the time-resolved spectra would be resolved if the $I_1$ band came from the outer edges of the $W$ spot (but not from the edges of the crystal). To check this possibility, we focused a magnified image of the $W$ spot on the slits of a monochromator and obtained a time-integrated spectrum of the outer edge of the high-pump-power $W$ spot. It consisted only of the $I_2$ and $I_1$ bands, with little broad background. The $I_1$ band was the more intense of the two bands. In the low-pump-power spectra of this crystal, the $I_2$ band was much more intense than the $I_1$ band. Thus, this spectrum cannot be explained solely as luminescence excited by stray dye-laser light.

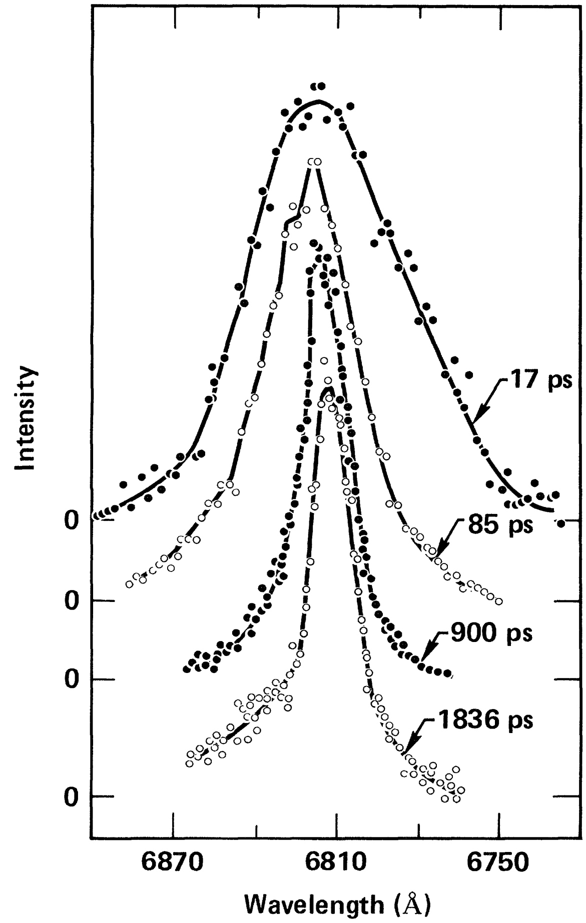

FIG. 5. Time-resolved spectra of the high-pump-power $W$ spot at different delay times for a bulk crystal sample. The $W$-spot intensity departs from zero at 0 ps and peaks at 85 ps. Curves show vertical polarization. The solid lines are hand drawn to fit the data points.

All of the above observations are consistent with the following model for the $I_1$ band of the high-pump-power $W$ spot. The spectrum of the stimulated emission of the $S$ spot in Fig. 2 indicates that broadband gain exists at the wavelength of $I_1$. Therefore it is reasonable that $I_1$ luminescence from the low-excitation-density outer edges of the $W$ spot could be amplified by one pass through the high-excitation-density (broadband) central region of the $W$ spot.[14] $I_1$ luminescence traveling parallel to the surface of the crystal should see the longest gain length and be amplified the most. Such amplified $I_1$ light may be scattered out of the crystal by surface roughness to give a signal that increases with the amount of surface area seen by the detector. Therefore it may be prominent in the time-integrated spectra (which see a large surface area) and missing from the time-resolved spectra (which see a small surface area).

According to this model, both the $S$ spot and $I_1$ band of the high-pump-power $W$ spot are stimulated emission off of the same broadband gain. The differences in their spectra could be due to the fact that they are emitted at different times or in different directions. Since $I_1$ is

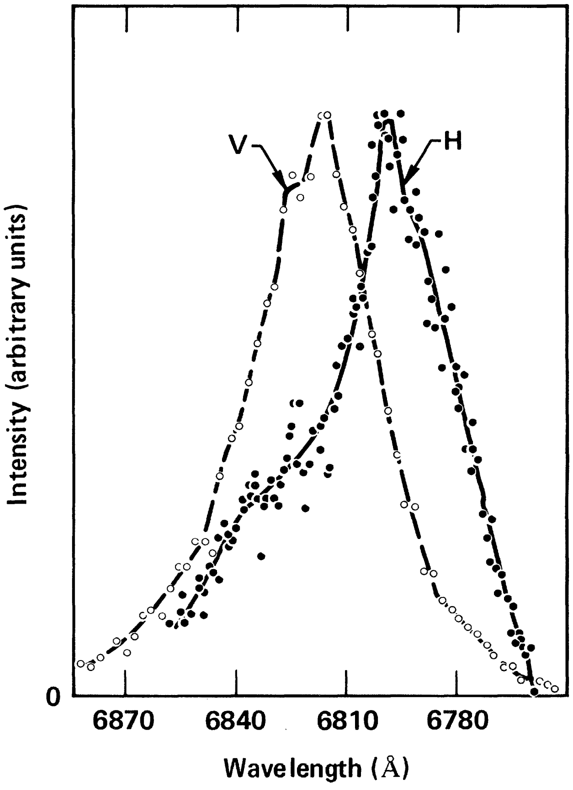

FIG. 6. Time-resolved spectra for the $V$ and $H$ polarizations of the high-pump-power $W$ spot of the same crystal sample as in Fig. 5. These curves were taken at a time delay corresponding to the peak of the time-decay curve. The two curves were scaled to equal height and are hand drawn to fit the data points.

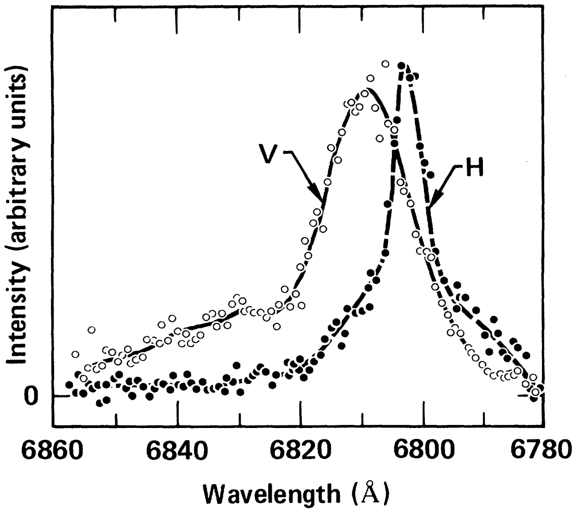

FIG. 7. Spectra that differ from those in Fig. 6 only by time delay. Spectra were taken 2.2 ns after excitation. The two curves were scaled to have the same peak height. The peak height of $V$ at this time delay is about 1/40th of its maximum value.

brighter than $I_2$ in the outer edges of the high-pump-power $W$ spot, while dimmer than $I_2$ in the low-pump-power spectra, $I_1$ must see a higher gain than $I_2$ in the high-excitation-density center region of the $W$ spot. This observation is consistent with measurements discussed below. The above discussion points out the importance of avoiding light from the edges of the excitation spot when seeking to measure spontaneous emission in these types of experiments.[15] We will assume that the light seen in the time-resolved spectra of the $W$ spot travels nearly perpendicular to the surface.

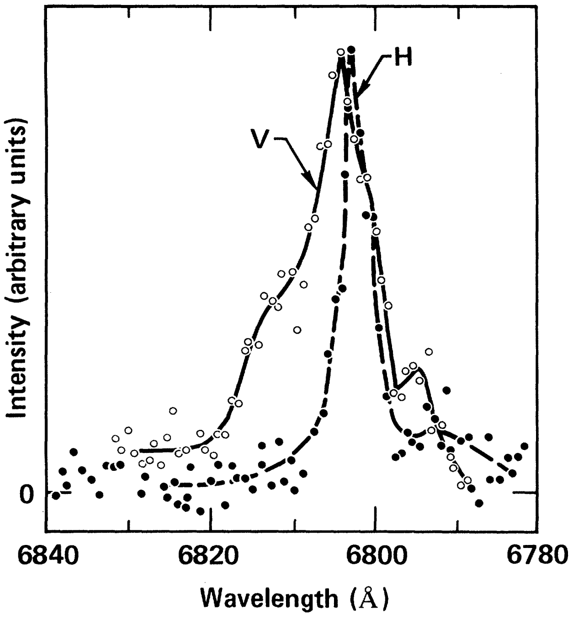

FIG. 8. Spectra that differ from Figs. 6 and 7 only by time delay. Spectra were taken 5.1 ns after excitation. The two curves were scaled to have the same peak height. The peak height of $V$ at this time delay is about 1/700th of its maximum value.

The time-resolved spectra of the $V$ polarization of the high-pump-power $W$ spot at different delay times are shown in Fig. 5. The spectra of the $V$ and $H$ polarizations of the high-pump-power $W$ spot are compared at different delay times in Figs. 6–8. Note that $H$ lies on the high-energy side of $V$ at all times.

### A. Early times and the EHP

We first analyze the spectra at early times. Since at early times the spectra are too broad and at energies too high to be explained by the exciton-exciton—collision model, we assume that we are dealing with an EHP. Within the context of the EHP model, we will explain the frequency shift at early times between $V$ and $H$ seen in Fig. 6.

One possible difference between $V$ and $H$ is that $V$ may contain only luminescence from $\vec{E}\perp c$-allowed transitions, while $H$ may contain luminescence from both $\vec{E}\perp c$- and $\vec{E}\|c$-allowed transitions. In the EHP model, transitions between the conduction band and the highest (or $A$) valence band are allowed for $\vec{E}\perp c$, while transitions between the conduction and the next-highest (or $B$) valence band are allowed for both $\vec{E}\perp c$ and $\vec{E}\|c$. The $A$ and $B$ valence bands are separated by 26.4 meV at low pumping powers.[12] This energy separation is expected to change little when the band gap is renormalized at HED.[16] Thus, luminescence involving the $A$ and $B$ valence bands should be shifted by about 26 meV or 100 Å. In Fig. 6, $V$ and $H$ are shifted by only about 20 Å. Therefore this shift cannot be due to the $B$ valence band's appearing more strongly in $H$ than in $V$. At late times (Figs. 7 and 8) it is also true that the $V$,$H$ shift is not due to an $\vec{E}\|c$ process, since the sharp peak that dominates $H$ at late times is observed to disappear when we look in a direction perpendicular to the $c$ axis. We conclude that the $V$,$H$ shift is not due to an $\vec{E}\|c$ process at any time delay.

While the $B$ band is not primarily responsible for the $V$,$H$ shift, it may still contribute to the spectra. Luminescence from the $B$ band following picosecond excitation was observed by Yoshida *et al.*[17] These authors observed that the initial decay of the $B$-band luminescence was more rapid than that of the $A$-band luminescence. From this observation, they deduced that holes optically excited into the $B$ band decay to the $A$ band with a relaxation time of 35 ps. They observed that the $B$-band light appeared when they pumped at 532 nm and did not appear when they pumped at 665 nm. 665 nm lies between the $A$- and $B$-band gaps at low excitation densities and above the $A$- and $B$-band gaps at HED. When going from 532 to 665 nm, they also lowered the pumping power by a factor of 10. They explained the absence of the $B$-band luminescence under 665-nm pumping by stating that a 665-nm photon lacks the energy to excite a hole into the $B$ band, since it lies inside the $B$-band gap at low excitation densities. Actually, since 665 nm lies above the $B$-band gap at HED, it should excite holes into the $B$ band. Note that excitations created by $A$-band transitions will renormalize the band gaps in times short compared to the 20-ps pulse length of the laser used in their experiment.[18]

It seems more likely that the $B$-band luminescence disappeared because the lower pumping power created a cooler plasma in which fewer holes were thermally excited into the $B$ band. If lowering the pumping power was sufficient to depopulate the $B$ band, then the $B$ to $A$ relaxation time must have been faster than the time resolution of their experiment (20 ps). Their observation that the $B$-band luminescence decayed more rapidly than the $A$-band luminescence probably derived not from a resolvable relaxation time for $B$-to-$A$ transitions, but rather from a rapid cooling of the plasma leading to a rapid decrease in the thermally excited population of $B$. The appearance of the $B$-band luminescence in Ref. 17 probably derived from very high pumping powers, creating a very hot plasma, which thermally populated the $B$ band. Our data appear to correspond to much lower pumping powers. Therefore the results of Ref. 17 do not imply that the $B$ band is appreciably populated in our experiment, even though we do pump above the $B$-band gap. We will assume that the $B$ band is not appreciably populated in our experiment. Under this assumption, the analysis of our data indicates that the ratio of the value of the hole Fermi function at the top of the $B$ band to its value at the top of the $A$ band never exceeds $10^{-3}$, and is $10^{-6}$ at the delay time corresponding to Fig. 6. Therefore our assumption is self-consistent.

We now discuss other possible causes for the $V,H$ shift within the model of band-to-band transitions from the conduction band to the $A$ valence band. In the independent-particle theory of the band-to-band transition spontaneous-emission line shape, the $\vec{k}$ of the photon drops out in the sum over states, since it is much smaller than the $\vec{k}$ of most of the electrons. Therefore the direction of the photon does not influence the line shape. Thus, in the absence of absorption or gain, $V$ and $H$ should have the same line shape, since by symmetry they must have the same line shape for photons traveling parallel to the $c$ axis. However, in the presence of absorption or gain, $V$ and $H$ need not have the same line shape.

In the excited region of the crystal, the relevant absorption and gain coefficient is that of the plasma. Since $\vec{E}\|c$-allowed transitions are assumed to be unimportant, we have $\alpha_H/\alpha_V \cong \cos^2(\theta)=0.08$. Here, $\alpha_V$ and $\alpha_H$ are the absorption constants seen by the $V$ and $H$ polarizations, respectively, and $\theta$ is the angle between the $c$ axis and the $\vec{k}$ of the photon. The value of 0.08 follows from Snell's law with an index of refraction of 3. We assume that the $V,H$ shift derives from the different gain-absorption constants that are seen by the two polarizations.

If we assume that all of the luminescence results from a plasma of homogeneous density, then we must conclude that $V$ is a distorted version of $H$, distorted by gain or absorption. That $V$ is at lower energies than $H$ is qualitatively consistent with the fact that a plasma has absorption on the high-energy side of its luminescence and gain on the low-energy side of its luminescence. Thus, the theoretical spontaneous-emission line-shape function for the plasma should be fit to $H$ rather than to $V$.

We have fit the experimental spectra at early times (using a nonlinear least-squares-fit computer program) with the independent-particle spontaneous-emission line-shape function in which crystal momentum is not conserved, namely

$$I_{\text{sp}}=s\int_0^1 dy\, E^2[y(1-y)]^{1/2}\{1+\exp[(Ey-\mu_e)/k_BT]\}^{-1} \times(1+\exp\{[E(1-y)-\mu_h]/k_BT\})^{-1}\,, \qquad (1)$$

where $E=h\nu-E_g$, $h\nu$ is the photon energy, $E_g$ is the renormalized band gap, $\mu_e$ and $\mu_h$ are the electron and hole quasichemical potential, respectively, $T$ is the plasma temperature, $k_B$ is Boltzmann's constant, and $s$ is a constant. The potentials $\mu_e$ and $\mu_h$ were calculated as functions of $T$ and the pair density $n$ by means of the approximate functions given in Ref. 16. The parameters in the fitting program were $n$, $E_g$, $T$, and $s$. Once the fit has been done and the values for the parameters have been obtained, the associated gain curve may be calculated using[5]

$$\alpha\sim\{\exp[(h\nu-\mu_e-\mu_h-E_g)/k_BT]-1\}I_{\text{sp}}\,. \qquad (2)$$

It is reasonable to use this fitting function since, in fitting it to experimental gain curves, it has been shown to give similar values for the fitted parameters as were obtained using a more sophisticated many-body fitting function.[2]

The fitting function in Eq. (1) fits the $H$ spectra in Fig. 6 poorly. If we use this fit to calculate the corresponding gain curve from Eq. (2), we find that the peak of the gain curve coincides with the peak of the $H$ luminescence curve. If the $V$ spectra were a distorted version of the $H$ spectra, that is, distorted by gain or absorption by the plasma, then the peak of the $V$ spectra should coincide with the peak of the $H$ spectra and the gain curve. But the peak of the $V$ spectra in Fig. 6 lies at lower energies than the peak of the $H$ spectra. Thus, the model of a homogeneous plasma is not consistent with the data.

There is a reasonable alternative model that allows us to make sense of the computer fits and other observations. This model has the excitation density $n$ decreasing with distance from the crystal surface and has appreciable amounts of luminescence coming from the deep, low-$n$ region as well as from the high-$n$ surface region. The luminescence spectrum is known to shift to longer wavelengths with increasing $n$. Thus, we expect the deep region to luminesce at shorter wavelengths than the surface region. As before, we assume that the high-density region is an EHP. As can be seen from Eq. (2), the plasma tends to have gain on the long-wavelength side of its spontaneous emission and absorption on the short-wavelength side of its spontaneous emission. Since the deep luminescence should lie on the short-wavelength side of the plasma luminescence, it should primarily see the absorption (rather than the gain) of the plasma. For this reason, absorption, rather than gain, will be stressed in this discussion. Since the deep luminescence lies at shorter wavelengths than the plasma luminescence, it should be absorbed by the surface plasma more strongly than the plasma absorbs its own luminescence. In this model the frequency shift between $H$ and $V$ arises because absorption by the surface region causes the deep region to contribute more strongly to the $H$ polarization, where the absorption is smaller, than to the $V$ polarization. Since the deep region must make a noticeable contribution to $H$, this model assumes that without self-absorption the deep region and the surface region are of comparable brightness. The relative brightness of the two regions is not obvious since the relative thickness of the two regions and the kinetics of the luminescence decay in the deep region are not known.

According to this model, the plasma line-shape function should be fit to the $V$ spectra, since the plasma is a high-density model and the $H$ spectra are more strongly contaminated by low-$n$ luminescence. There are two forms of distortion that may cause the $V$ spectra to fit the plasma spontaneous-emission line-shape function poorly. In the low-plasma-absorption limit, $V$ may be a mixture of both the high- and low-$n$ regions. In the high-plasma-absorption limit, the deep, low-$n$ luminescence will be completely absorbed by the surface region, but the surface luminescence may be distorted by self-absorption within the surface region. It is possible that neither of these distortions to the $V$ spectra is important since the surface region absorbs the deep luminescence more strongly than its own luminescence. This is because the surface region absorbs its own luminescence as $[1-\exp(-\alpha l)]/\alpha l$, and it absorbs the deep luminescence as $\exp(-\alpha l)$, where $l$ is the depth of the surface region. Also, the deep luminescence lies at higher frequencies than the surface plasma luminescence and therefore is absorbed more strongly. Since $l$ is not known, the only reasonable course of action is to try to fit the $V$ spectra at early times to an EHP line shape without taking into account either form of distortion. A good fit would be an indication that these distortions were not important.

The fittings of the early-time high-pump-power $V$ spectra of the $W$ spot to Eq. (1) are shown in Figs. 9 and 10. Figure 9 corresponds to a time early on the rising edge of the time-decay curve; Fig. 10 corresponds to a time at the peak of the time-decay curve. Note that the pair densities given by both fits, $n=4.9\times10^{17}$ and $3.7\times10^{17}$ cm$^{-3}$, are fairly close to the calculated value (Ref. 12) of $5.4\times10^{17}$ cm$^{-3}$ for the density $n_0$ at which the ground-state energy per pair $E(n)$ of the EHP is a minimum. Note also that these values of $n$ are much smaller than the initial value of $n$ estimated earlier from the laser power and the absorption depth ($5\times10^{19}$ cm$^{-3}$). Fittings to steady-state gain spectra in the literature have also shown that it is difficult to pump very far above $n_0$ (Ref. 2). These observations are consistent with the theory of an EHP since a plasma created by surface excitation at 0 K will push into the crystal under pressure if the plasma is pumped to $n$ greater than $n_0$ (Refs. 5 and 19). These measurements indicate that the plasma expands into the crystal on a time scale short compared to the 20-ps time resolution of this experiment.

The parameters obtained from the fittings may also be compared to the calculated values for $E(n_0)$ at 0 K. The fittings determine $n$, $T$, and $E_g$. The renormalized band gap $E_g(n,T)$ should vary little with temperature in the relevant temperature and density region.[20] Thus, the value of $E_g$ obtained from the fit may be used for the 0-K value of $E_g$. The chemical potential at 0 K is then

$$\mu(n,0)=\mu_e(n,0)+\mu_h(n,0)+E_g\ ,$$

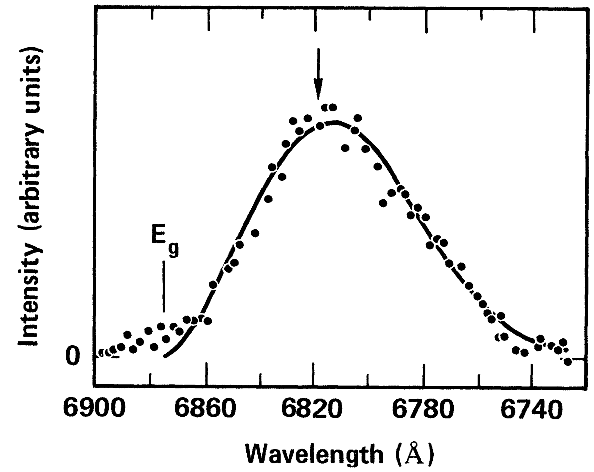

FIG. 9. Time-resolved $V$ spectrum of the high-pump-power $W$ spot of the same crystal sample as in Fig. 5. The spectrum was taken at a time delay corresponding to a point one-tenth of the way up the rising edge of the intensity-vs-time curve. The solid line is a fit of Eq. (1) to the data (solid circles). The fitted values are $n=4.9\times10^{17}$ cm$^{-3}$, $T=43$ K, and $E_g=1.8034$ eV. The arrow marks the location of $\mu_e+\mu_h+E_g$.

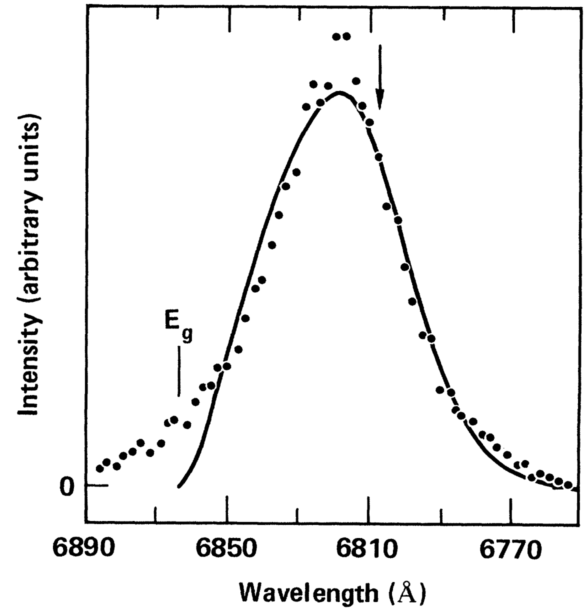

FIG. 10. Spectrum that differs from Fig. 9 only in terms of the time delay. The spectrum was taken at a time delay corresponding to a point at the peak of the intensity-vs-time curve. The fitted values are $n=3.7\times10^{17}$ cm$^{-3}$, $T=20$ K, and $E_g=1.8063$ eV. The arrow marks the location of $\mu_e+\mu_h+E_g$.

where $\mu_e$ and $\mu_h$ are the quasichemical potentials.[21] Given $n$ and $E_g$ from the fittings, we may calculate $\mu_e(n,0)$ and $\mu_h(n,0)$ using the effective masses listed in Ref. 12 and obtain $\mu(n,0)$. The results are $\mu(n,0)=679.8$ and 680.1 nm for Figs. 9 and 10, respectively. The values of $\mu(n,0)$ thus obtained from the fittings may be related to the theoretical curve of $E(n)$ in Ref. 12 through the equation $\mu(n,0)=E(n)+ndE(n)/dn$ (Ref. 21). If we assume that the curve in Ref. 12 has the correct shape, then we may estimate $E(n_0)$ using the equation

$$\mu(n',0)=E(n_0)+[E(n')-E(n_0)]+n'[dE(n)/dn]\,|_{n'}\,,$$

where $\mu(n',0)$ and $n'$ are the values obtained from the fit, and $E(n')-E(n_0)$ and $n'[dE(n)/dn]\,|_{n'}$ are obtained from the curve in Ref. 12. The latter two quantities will be small since $n'$ is close to $n_0$ in both fittings. The results are $E(n_0)=679.8$ and 679.5 nm for Figs. 9 and 10, respectively. That both curves give nearly the same answer indicates this is not a matter of picking the proper time delay to obtain the correct answer. Use of the average of the two fitted values for $E(n_0)$ gives the binding energy $E_B=E_{\text{ex}}-E(n_0)$ to be 3 meV, where $E_{\text{ex}}$ is the free-exciton energy. The theoretical value for $E_B$ is $-4$ meV (Ref. 12). A different theoretical treatment gives $n_0=8.3\times10^{17}$ cm$^{-3}$ and $E_B=5$ meV (Ref. 20). Given the spread in the theoretical predictions (which derives, in part, from $E_B$ being the small difference of two large numbers[12]), the values obtained from the curve fitting seem to be in reasonable agreement with theory. Our value for $E_B$ is close to the 2-meV value obtained from gain spectra in Ref. 3, even though temperature corrections were not made in Ref. 3.

In summary, the high-pump-power early-time $V$ spectra of the $W$ spot fit the plasma line shape fairly well, and give values for the parameters of the fit that agree fairly well with theory. This is some indication that the possible distortions to the $V$ spectra discussed above are not important. This is also some indication that the two-depth model is correct, since it justified fitting the $V$ spectra rather than the $H$ spectra. From Eq. (2) it can be seen that the transition from gain to loss for the plasma occurs at $h\nu=\mu_e+\mu_h+E_g$. This number can be calculated from the fittings and is marked by an arrow in Figs. 9 and 10. The $V$ curve of Fig. 6 is the curve fitted in Fig. 10. By transferring the arrow in Fig. 10 to Fig. 6, we can see that the absorption by the surface plasma is in the right spectral position to be consistent with the idea that the high-frequency deep luminescence in $H$ does not appear in $V$ since it is absorbed by the surface plasma.

Our early-time $V$ spectra[7] are very similar to time-resolved spectra (obtained with a different type of picosecond spectrometer) published in Ref. 8. We apparently used lower initial pumping powers than were used in Ref. 8, and thus had a lower initial plasma density and temperature. We fit the data to the same fitting function as was used in Ref. 8. The parameters of the fittings ($E_g$, $n$, and $T$) obtained in Figs. 9 and 10 are nearly identical to the parameters obtained in Ref. 8 for two curves at later delay times. The observed increase of $n$ with $T$ in both experiments is consistent with the dependence of $n$ on $T$ observed in 10-ns-pump gain measurements.[2]

We followed the luminescence spectra to much longer time delays than in Ref. 8. Yoshida and co-workers found that at late times the plasma spectral shape became independent of time and persisted to the longest time delays measured (900 ps). As we will discuss later, we found that the line shape did not go to a steady state because it became contaminated by $I_2$-band bound-exciton luminescence in times less than 900 ps. The difference in the two experiments may be that their higher pumping powers heated the lattice above 25 K, where the bound exciton ionizes.[5] The difference in the two experiments might also derive from their plasma dissipating more slowly due to higher initial pumping power or larger pumping spot size, or it might derive from their using purer samples (if this was the case).

### B. Late times and the $M$ band

The analysis of the early-time spectra indicated that a plasma is in the crystal and that density inhomogeneity and self-absorption effects are important. We will use these observations to construct a model for later times from a reasonable extrapolation of the early-time model.

Let us consider a number of points. At sufficiently late times, the deep region should emit the low-pumping-power spectra, which for the crystals discussed here is dominated by the $I_2$ impurity band. It is possible that the surface region is still a plasma when this happens, since the surface region started out at a higher excitation density than did the deep region. The absorption by the surface plasma that kept the deep luminescence out of the $V$ spectra at early times is excitation-induced absorption and, as such, should decrease with time. Thus, at late times, some of the deep luminescence may show up in $V$. The gain-absorption curves for the plasma calculated from the early-time fittings, as well as measured gain-absorption curves (using 10-ns pulse excitation) from the literature,[22] indicate that $I_2$ should lie on the absorption part of the curve and $I_1$ should lie on the gain part of the curve. This is consistent with the observation (made earlier in the discussion of the high-pump-power $I_1$ band in Fig. 2) that the gain at $I_1$ is greater than the gain at $I_2$, assuming that the EHP is the gain medium responsible for the amplification of the $I_1$ band. Note that the characteristic shape of a plasma-gain curve at the relevant densities and temperatures is such that the absorption part varies very rapidly with wavelength, while the gain part varies slowly. Thus, an $I_2$ band passing through the plasma will tend to be shifted to longer wavelengths by the strongly wavelength-dependent plasma absorption.

A reasonable extrapolation of the early-time model to late times has an EHP close to the surface, $I_2$ deeper, and the absorption by the plasma small enough to permit some of the $I_2$ luminescence to be seen in the $V$ spectra. According to this model, the $H$ and $V$ spectra at late times should differ in two ways. First, the $I_2$ band in $V$ should be shifted to longer wavelengths with respect to the $I_2$ band in $H$ since the plasma absorption is larger in $V$. Second, the fraction of the luminescence that comes from the plasma should be higher in $V$ than in $H$. This is because in $V$ the impurity luminescence is absorbed more strongly than the plasma luminescence, whereas in $H$ the absorption of both impurity and plasma luminescence should be small.

The model described above qualitatively agrees with the $V$ and $H$ spectra at 2.2 and 5.1 ns (Figs. 7 and 8). The main peak in the $H$ polarization in Figs. 7 and 8 is at the wavelength of the $I_2$ band of the low-pump-power spectra. When observed in a direction perpendicular to the $c$ axis, this late-time peak in $H$ disappears. Thus, it is from an $\vec{E}\perp c$-allowed transition, as is the low-pump-power $I_2$ band. We therefore assume that the main peak in $H$ at 2.2 and 5.1 ns is the $I_2$ band. The $V$ spectra at 2.2 ns are dominated by what is usually called the $M$ band in the literature.[1] We attribute the $M$ band to a superposition of broadband plasma luminescence and deep $I_2$ luminescence shifted in wavelength by surface-plasma absorption. Others have attributed the $M$ band to the decay of an excitonic molecule. We attribute the long-wavelength tail in $V$ at 2.2 ns to plasma luminescence. It is consistent with our model that this tail is more prominent in $V$ than in $H$. The same statements hold for the 5.1-ns spectra as for the 2.2-ns spectra, except at 5.1 ns the absorption by the plasma is smaller.

There are other observations that support the above model for the $M$ band. All the spectra shown here were taken from crystals in which the low-pump-power spectra are dominated by the $I_2$ band. We also took data in crystals in which the low-pump-power spectra are dominated by the $I_1$ band. We refer to these as $I_2$- and $I_1$-type crystals, respectively. For $I_2$-type crystals, the 2-ns $V$ spectra are dominated by the $M$ band, as shown in Fig. 7. For an $I_1$-type crystal, under identical pumping conditions, the 2-ns $V$ spectrum is separated from the 2-ns $V$ spectrum of an $I_2$-type crystal by an amount close to the $I_2$,$I_1$ frequency spacing at low pump power. This frequency shift is apparent by 800 ps and suggests that the $M$ band is due to impurity luminescence, rather than anything intrinsic (such as an excitonic molecule).

Note that the $H$ spectra at late times (Figs. 7 and 8) imply that, in the absence of absorption, $I_2$ is the brightest species in the crystal. This is consistent with $I_2$ showing up in $V$ in spite of its being absorbed enough to be shifted in wavelength.

The time-decay curves of $V$ and $H$ are consistent with the above model. The time-decay curves of $V$ and $H$, taken at the central frequencies of their respective bands, are very similar. The logarithm of the intensity-versus-time curves for both polarizations have a slope of about (350 ps)$^{-1}$ from the peak of the curve to $\sim$500 ps. At that point, the slope of the curve changes to (900 ps)$^{-1}$ and remains at this value to 2 ns. The value of 900 ps is reasonable for either a bound-exciton lifetime or a free-exciton trapping time.[23] The data discussed above suggest the following model. At early times the $V$ luminescence is dominated by an EHP, which (at least at early times) decays with a time constant of about 350 ps. At around 500 ps, the $V$ luminescence becomes dominated by $I_2$ luminescence. This does not imply that the plasma is gone, but merely that the bound excitons are brighter. That $V$ and $H$ have the same decay rate at late times, and that $H$ is primarily the $I_2$ band while $V$ is primarily the $M$ band, also suggests that the $M$ band is $I_2$ luminescence.

Contamination of the plasma luminescence at late times by impurity luminescence makes studying the late-time properties of the plasma impossible. For this reason, the data presented here are not useful for studying either the electron-hole—liquid phase transition or the Mott transition.

The main reasons for attributing the $M$ band to an excitonic molecule are that it is a narrow band (a characteristic of excitonic models) that appears at HED near the wavelength predicted theoretically for the excitonic molecule band. The plasma model, on the other hand, predicts a luminescence band much broader than the $M$ band. The model given above for the $M$ band allows a narrow excitonic-type band to exist at excitation densities at which a plasma would be expected to exist. When exciting CdSe or CdS (the two crystals are very similar) with long-pulse lasers (lasers that have pulses much longer than the luminescence lifetime), it has been found that the $M$ band first appears at a pumping power of about 10 kW cm$^{-2}$ (Refs. 1, 24, and 25). Plasma-type—gain curves for CdS have been measured at pumping intensities as low as 10 and 25 kW cm$^{-2}$ (Refs. 2 and 26). Thus, it is reasonable to suppose that the $M$ band starts to appear at pumping levels where an EHP starts to form. Furthermore, the $M$ band sometimes persists to much higher excitation densities, where it is increasingly clear that excitons should become unbound due to screening.[5]

Assume that our model for the $M$ band is correct and consider how the luminescence spectra should behave as the pumping power of a long-pulse laser is increased above the point at which the EHP starts to form. The plasma gain $gl$ measured in a direction perpendicular to the surface of the crystal is observed to increase with increasing pumping power.[2] Here $g$ is the gain coefficient and $l$ is the depth of the plasma region. This is consistent with the idea that the plasma may resist being compressed, thereby causing $l$ to increase with increasing pumping power. Therefore it is reasonable to suppose that absorption by the plasma will also increase with increasing pumping power. With increasing pumping power, the transition between gain and absorption has been measured to move to longer wavelengths.[2] Both the increase in $l$ and the movement of the gain-absorption crossover to longer wavelengths will cause the plasma absorption at the wavelength of $I_2$ to increase with increasing pumping power.[27]

Therefore, as one increases the pumping power, the slowly varying long-wavelength wing of the $I_2$ band, where the plasma absorption is smaller, should become enhanced, forming the $M$ band. The peak of $I_2$ should gradually slide to slightly longer wavelengths. Eventually, both $M$ and $I_2$ should become completely absorbed by the plasma and disappear from the spectrum. Qualitatively, this is what is observed.[25,28] Measurements of the plasma-gain curve show that the plasma has positive gain that varies slowly with frequency at the wavelength of the $I_1$ band.[22] Therefore, according to our model, the $I_2$ band should saturate at lower pumping powers than the $I_1$ band. This too is observed.[25,28]

Our model for the $M$ band does not explain all of its properties as reported in the literature. This may be because, under different experimental conditions, different mechanisms may yield a band at the wavelength of $M$ (Ref. 1). For example, when using large excitation spots, stimulated emission at the wavelength of $M$ is sometimes observed along the plane of the crystal surface.[28] Such a stimulated $M$ band cannot be explained using our model and may well be due to phonon-assisted $I_2$ recombination, as claimed in Ref. 28. There are reasons for thinking that the $M$ band in our experiment is not stimulated and therefore is not due to phonon-assisted $I_2$ recombination. First, as discussed earlier, the spatial resolution provided by the up-conversion light gate successfully discriminated against a similar band of stimulated emission at the wavelength of $I_1$. In addition, no $M$ band was observed in the time-integrated spectra of the outer edges of the $W$ spot. Second, the early-time spectra were successfully analyzed by assuming that they were spontaneous emission. Since the measured value of the plasma-gain coefficient is higher than the measured value of the phonon-assisted $I_2$ recombination-gain coefficient, it is unlikely that the CdSe crystal would not lase at early times and would lase at late times.[2,28] Third, the measured value of 900 ps for the time-decay constant at late times is reasonable for spontaneous emission involving bound excitons.[23]

Similarly, we do not argue that the excitonic molecule does not exist in CdSe. We argue that in experiments similar to ours, the $M$-band luminescence derives from our model, rather than from excitonic molecules.

### C. *P* band

The $P$ band appears at about 684 nm in the time-integrated $S$-spot spectra of Fig. 2. The $P$ band has been attributed to stimulated emission from an EHP,[5] and to a spontaneous or stimulated process in which two excitons collide, causing one to be excited or to dissociate and causing the other one to recombine, emitting a photon.[1] We present new data that support the former of these two interpretations.

The $P$ band appears in the time-integrated spectra of the $S$ spot and does not appear in the time-integrated spectra of the $W$ spot (Fig. 2). The time-decay curves in Figs. 3 and 4 show that $S$ is stimulated and $W$ is spontaneous. This shows that stimulated emission is capable of giving a $P$-type band when no such band appears in the spontaneous spectra.

The exciton-exciton—collision regime should occur at excitation densities lower than those of the EHP regime and higher than those of the bound-exciton regime. Therefore the $P$ band, if caused by spontaneous emission from exciton-exciton collisions, should appear in the time-resolved spectra of $W$ at time delays longer than the EHP and shorter than the bound excitons. We have argued that the earliest curves in Fig. 5 are due to an EHP and that the latest curves are mostly bound-exciton luminescence. We have the sensitivity to follow the decay all the way from the plasma to the bound excitons, and the $P$ band never appears (Fig. 5). This suggests that spontaneous emission from exciton-exciton collisions does not give a $P$ band, and that when $P$ is observed, it is due to stimulated emission.

Figure 3 shows that the $P$ band (or the $S$-spot emission) is a spike of stimulated emission that is emitted at early times. Fitting the theoretical line-shape function to the $W$ spectra shows that an EHP is in the crystal at such early times. Therefore $P$ appears to be stimulated emission from an EHP.

One of the arguments in favor of the exciton-exciton—collision model of the $P$ band is that the $P$ band lies at about two exciton binding energies below the band gap in several different II-VI semiconducting compounds.[29] That the $P$ band should scale with the free-exciton binding energy is obvious in the exciton-exciton—collision model, but it is not obvious in the plasma model.

To see why stimulated emission from an EHP should scale with the free-exciton binding energy, consider a number of points. The measured plasma-gain curves show positive gain at the location of the $P$ band, but the maximum plasma gain occurs at wavelengths shorter than the $P$ band.[3,29] In our experiment, and possibly in other experiments reported in the literature, $P$-band luminescence travels through the unexcited region of the crystal. Since $P$ is stimulated emission, it is reasonable that it may go into the unexcited part of the crystal in any experiment to increase its feedback. In these types of experiments, with their large gains and small crystals, it is difficult to definitely exclude this possibility. Over long distances in an unexcited crystal, the cutoff of transmission is defined in some crystal samples by absorption into $I_1$ and $I_2$. See, for example, Fig. 1 of Ref. 30. This figure shows that at low excitation densities the transmission is 1.0 at the wavelength of $P$, 0.5 at the wavelength of $I_1$, and 0 at the wavelength of $I_2$. This is the transmission through a crystal some tens of micrometers thick. In such a crystal, stimulated emission from an EHP that passes through the unexcited part of the crystal would peak at the wavelength of $P$, rather than at the peak of the plasma-gain curve. The location of the $I_1$ and $I_2$ impurity bands in different II-VI semiconducting compounds is known to scale with the free-exciton binding energy.[31]

We conclude that the $P$ band is stimulated emission from an EHP that has a high-energy cutoff defined by impurity-band absorption in the unexcited part of the crystal. The $P$ band scales with the exciton binding energy because it is a broad, poorly defined peak that has a high-energy cutoff that scales with the exciton binding energy.

## IV. SUMMARY

Time-resolved spectra of CdSe luminescence at HED have been reported. Excitation-induced absorption and gain and density inhomogeneity effects have been shown to be important in interpreting the data. The early-time luminescence was fit to an EHP line-shape function. The plasma was shown to expand into the crystal when pumped above $n_0$ in times short compared to 20 ps. The value of $E_B$ was estimated from the fitting to be 3 meV, which agrees fairly well with theory. The late-time emission contained the *M* band. A model for the *M* band that involves the interaction between the high- and low-density regions of the crystal has been proposed. We showed that *P*-band emission from the edges of platelet samples was stimulated emission from an EHP. We also proposed an explanation for why such emission scales with the free-exciton binding energy.

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