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Experimental Evidence for the Existence of an Electron-Hole Liquid in II-VI Compounds

R. F. Leheny and Jagdeep Shah
Bell Telephone Laboratories, Holmdel, New Jersey 07733
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Measurements of optical absorption and gain in CdS and gain in CdSe show that for high excitation density optically excited carriers form an electron-hole liquid with binding energy of 13 meV for CdS and 2 meV for CdSe. The measurements are compared to a recent theory for electron-hole liquid formation in polar semiconductors.

We report measurements of optical absorption and gain for CdS in the presence of high-intensity optical pumping. The results of these measurements are in agreement with the expected behavior of a degenerate electron-hole liquid (EHL),[1] rather than with an interpretation based on exciton interactions.[2,3] We conclude that for conditions of high excitation density (HED), optically excited electrons and holes in CdS form a liquid with a binding energy of ~13 meV measured with respect to the free exciton.[4] In addition we present gain spectra, measured by the method of Shaklee and Leheny,[5] for a second II-VI compound, CdSe, where we find the data are also best described by an EHL bound by less than 2 meV. The magnitude of the binding energies for the liquid state as well as the spectral widths of the measured gain are in agreement with the theoretical predictions for EHL formation in polar compounds recently developed by Beni and Rice.[6]

Our measurement for CdS is made using two lasers, one as a pump and the other as a tunable probe. We find that there is a transition from gain to loss occurring at ~4883 Å for incident power density of $\sim 5\times10^5$ W/cm^2. Examination of the sample reflectivity indicates that the exciton contribution to the index of refraction is negligible under HED conditions. From these results we conclude that excitons do not contribute to the recombination kinetics. A similar conclusion has been drawn by Lysenko *et al.*,[4] using measurements of gain determined by the variation of luminescence intensity with excitation length similar to the measurement for CdSe reported here, but this measurement technique provides no information on changes in absorption resulting from HED. Goto and Langer[7] have investigated HED transmission for CdS and found an increase in absorption at longer wavelengths with increasing pump intensity. However, these investigators made use of an incoherent fluorescence source as a probe making measurements of amplification difficult, if not impossible, since the spectral brightness of the probe beam cannot be expected to exceed that of the sample luminescence. By using a tunable laser probe we have overcome this difficulty and we will show here that an accurate determination of *both* the gain and loss

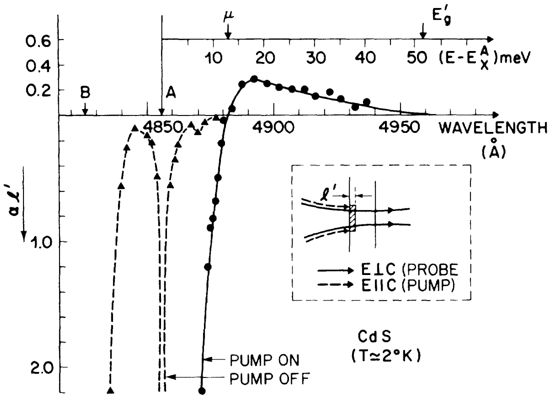

FIG. 1. Variation of probe beam transmission with pump laser turned on and off. Position of *A* and *B* excitons are illustrated with the energy scale measuring energy below the *A* exciton level. The position of the chemical potential μ and reduced band gap E_g' relative to the exciton deduced from the theory of Beni and Rice (Ref. 6) are indicated by arrows.

spectrum is possible.

The CdS transmission measurements were made using two dye lasers excited by a single nitrogen laser, with the dye laser outputs combined so that the pump laser ($\lambda \sim 4700$ Å) was polarized $E \| c$, while the probe laser ($4700 < \lambda < 5000$ Å) was polarized $E \perp c$ (see inset Fig. 1). After combining, the two beams were focused on a 50-μm pinhole which was refocused onto the sample with 1:1 optics. In this way, good overlap of the beams at the samples was assured. We have used a similar optical setup to investigate amplification in laser dyes and saturable absorption in GaP.[8] The transmitted beam was collected and passed through a spectrometer to eliminate unwanted fluorescence from either the dye lasers or the sample. The sample used was an as-grown platelet approximately 9 μm thick. The pump power incident on the sample was restricted to less than 10 W (~5 nsec pulsewidth) which, for an assumed lifetime of $\sim 10^{-9}$ sec and a diffusion length $l' \sim 1$ μm, implies carrier density $\sim 10^{18}$ cm^{-3}.[9]

Figure 1 shows typical pump-off and pump-on transmission spectra obtained for a pump intensity of $\simeq 5 \times 10^5$ W/cm^2. For the pump-off condition the absorption peak associated with direct excitation of the *A* excitons is clearly distinguishable with a region of relatively high transmission through the sample extending above the *A* exciton from 4835 to ~4850 Å. In the presence of the pump laser, we observe significant changes in absorption at wavelengths both below and above the *A* exciton, with the transmission being almost completely cut off for energies above the exciton. At lower energies, comparable changes in absorption occur with a rapid transition from loss to net amplification occurring at $h\nu \approx 2.537$ eV ($\lambda \simeq 4883$). At longer wavelengths, the probe beam is amplified with peak amplification factor $\exp(gl')$ of ~20% for 5×10^5 W/cm^2 incident. The spectral range of this amplification is found to extend to ≈4950 Å with no evident[10] structure. For over an order of magnitude variation in pump intensity, the transition from absorption to amplification occurs at the same energy (~2.537 eV) which lies ≃13 meV below the *A* exciton energy.

In a complementary measurement we have investigated the reflectivity of the sample under HED conditions. We find that for low pump intensity the reflectivity spectrum exhibits the sharp structure due to resonant excitation of *A* and *B* excitons, but under HED conditions this contribution of the exciton states to the reflectivity is significantly reduced[11] (ratio of $R_{\max}/R_{\min}$ at resonance down by a factor of 20). Furthermore the short wavelength edge of the interference fringes, due to multiple reflections between front and back of the sample in the region of the spectrum for which the sample is nonabsorbing, is shifted to ~4883 Å. This observation provides additional evidence that transmission through the excited volume of the crystal is cut off for wavelengths shorter than 4883 Å.

The data presented in Fig. 2 for CdSe were obtained with direct N_2 laser excitation in a manner that has been described in detail elsewhere.[12] The sample was an as-grown platelet. Note that the gain spectrum is essentially unchanged for a factor of 5 decrease in pump intensity. Unlike the 13-meV gap observed in CdS, the threshold for gain in CdSe occurs ≲2 meV below the *A* exciton state. The spectrum has a broad peak ≃16 meV wide, with a tail of decreasing gain extending to longer wavelengths. Reduction of the exciton contribution to the reflectivity of CdSe for HED has been reported by Akopyan and Roybirin.[13]

Since the earliest reports of HED luminescence and laser emission in II-VI compounds, there has been considerable effort to explain the observed radiative transitions in terms of exciton kinetics.[2,3] Before discussing our results in terms of an EHL, it is important to recognize that it would be difficult to reconcile our CdS transmission and reflection results with any simple exciton model. In explaining HED luminescence and gain spectra

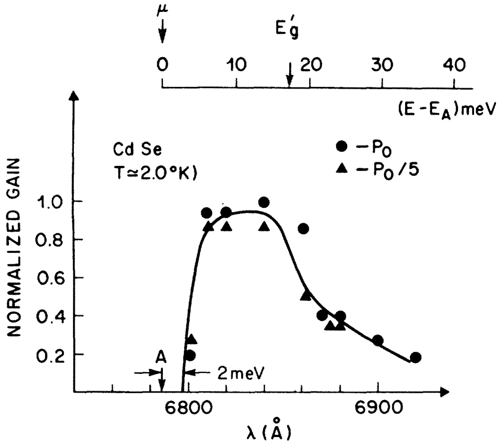

FIG. 2. Gain spectra measured for CdSe using N_2 laser pumping. These spectra were determined from measured variation of the luminescence emitted along the direction of a stripe excitation, with increasing excitation length, for $P_0 \simeq 10^6$ W/cm^2. The arrows indicate the calculated position of the chemical potential μ and reduced band gap E_g'.

in II-VI materials in terms of an exciton initial state, investigators have invoked scattering by either excitons or free carriers.[2,3] In these models the initial exciton emits a photon with either ionization of the second exciton or increased kinetic energy of the free carrier taking up the energy difference between the initial exciton and the photon. In either case, increasing excitation is expected to increase the probability for scattering, and therefore the gain, so that the photon energy at which gain equals loss is expected to be a sensitive function of the pump intensity as the gain increases while the exciton state broadens. In addition, the gain would[2] vary superlinearly with pump power. For the case of exciton scattering model, one would also expect a region of relatively low absorption between the free exciton and the short wavelength edge of the gain region.[3] These expectations are contrary to our observation of a smooth transition from amplification to attenuation at $\lambda \approx 4883$ Å, independent of pump intensity and previous observation of linear variation of gain.[12] The decrease in the exciton contribution to the reflectivity provides additional evidence that the excitons do not contribute significantly to the observed changes in transmission.

On the other hand, the assumption that the excitation is in the form of an EHL can provide a model to explain our observations. The region of a semiconductor containing an EHL can be viewed as having a reduced band gap along with a distribution of free carriers such that the lowest-lying states are filled according to Fermi statistics for the carriers present. For the case of direct gap materials, these filled states can be stimulated to recombine by probe photons, while the unfilled states (lying above the Fermi energy at $T = 0$°K) give rise to absorption. In this picture the width of the gain region corresponds to the sum of the carrier Fermi energies, while the short wavelength edge of the gain region corresponds to the chemical potential of the system. Under equilibrium conditions, the energy separation between the free exciton and threshold for absorption corresponds to the binding energy of the liquid. In the region containing EHL, no direct excitation of excitons is possible.

We can compare our measured values of EHL binding energy and chemical potential with the calculations of Beni and Rice.[6] Their calculation shows that the EHL in CdS has a minimum energy per pair at $n_{\min} = 2.6\times10^{18}$ cm^{-3}, from which we deduce the reduced band gap E_g' and the chemical potential μ, for $n_{\min}$ corresponding to the arrows shown in Fig. 1. The excellent agreement between the calculated and measured values leads us to conclude that, under HED conditions, an EHL with $n \approx 2.6\times10^{18}$, and binding energy of 13 meV is formed in CdS. For the case of CdSe, their calculations give a zero binding energy and $n_{\min} = 4\times10^{17}$ cm^{-3}, while our measurement yields an EHL with $n \approx 4\times10^{17}$ cm^{-3} and $E_B \leq 2$ meV. Although the calculation yields zero binding energy for CdSe, the small measured binding energy is not considered in serious conflict with the theory.

Since the liquid density in CdS is larger than the estimated average carrier density, it seems likely that phase separation into excitons and EHL occurs in the pumped region. For this case we expect that the transition wavelength for change from gain to loss will be independent of the pump intensity and that peak gain will increase linearly with the pump intensity as the volume of the sample containing EHL at constant density increases. Also the persistence of exciton features in the luminescence spectrum for HED conditions can be attributed to the presence of an unfilled region of crystal that can contain unperturbed free excitons.

We believe that a more detailed agreement between theory and measurement, with regard to gain line shape, can be achieved when the theory is further developed to include such effects as finite carrier temperature and carrier-phonon interaction. However the essential feature of the EHL model for CdS and CdSe, that excitation in the crystal can form a liquid state, has been established. CdS is the first direct-gap material to be shown to have a significant binding energy (~13 meV) for the liquid state; and this large binding energy suggests that additional experimental effort should be directed at defining this unique state.

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Electron-Hole Liquids in Polar Semiconductors

G. Beni and T. M. Rice
Bell Laboratories, Murray Hill, New Jersey 07974

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We calculate the ground-state energy of the electron-hole liquid including the coupling to LO phonons. We find that the electron-phonon interaction increases the stability of the liquid phase relative to excitons. We apply the theory to AgBr and to the direct band-gap semiconductors CdS, CdSe, and ZnS. We find that the electron-hole liquid is strongly bound in CdS and AgBr but only weakly so in CdSe and ZnS.

Recently the properties of electron-hole fluids have been studied [1-4] extensively in Ge and Si. The purpose of this Letter is to present a calculation[5] of the energetics of formation of the electron-hole (e-h) liquid in polar semiconductors. We find that the polar coupling increases the stability of the liquid phase. A similar conclusion has recently been reached independently by Keldysh and Silin.[6] Their approach, however, is limited to the very low or very high density regimes, whereas our method is applicable to arbitrary values of the e-h density. Of particular importance are the results for CdS and CdSe. The ground-state energy of the electron-hole liquid in CdS lies 13 meV deeper than the lowest exciton term while in CdSe it practically coincides with the lowest exciton term. These results are in good agreement with recent experiments.[7,8]

In polar semiconductors, the interaction between electrons (or holes) and lattice vibrations