Observation of Electron-Hole Liquid in GaP

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Luminescence spectra of high-purity GaP at high pump intensity demonstrate the existence of an electron-hole-liquid phase. Line-shape analysis yields $n_0 = 6\times10^{18}$ cm^{-3} for the liquid density and $\varphi_0 = 14$ meV for the liquid binding energy in agreement with theoretical values. The liquid critical temperature is estimated to be $T_c \simeq 40$°K.

We present new results on the high-intensity luminescence spectra of high-purity GaP which demonstrate the formation of an electron-hole liquid (EHL) in this indirect-gap, III-V compound semiconductor. The observed luminescence line shape agrees well with our calculation of the expected line shape for EHL recombination in this material and yields a liquid density of $n_0 = 6\times10^{18}$ cm^{-3}, and a liquid binding energy relative to the free exciton of $\varphi_0 = 14$ meV. These results provide the first experimental evidence for EHL formation in GaP and further demonstrate the universality of this phenomenon in semiconducting materials of high purity. The properties of EHL in Ge and Si[1] have been extensively studied and shown to be in good agreement with theoretical calculations for the liquid phase.[2] There have also been reports of EHL formation in direct-gap materials CdS[3] and GaAs.[4] Our results for GaP are particularly important in light of this continuing interest in the properties of semiconducting materials at high excitation intensities since we show that the values of liquid density and binding energy determined experimentally are in good agreement with calculated values, thus demonstrating the accuracy of these theoretical calculations. In addition, these results in high-purity GaP are significant since the possibility of doping GaP with isoelectronic impurities[5] (N and Bi) and the polar nature of GaP suggests new directions of EHL research with this material.

The measurements reported here were made on an epitaxial layer (~20 μm thick) of high-purity GaP (nitrogen ~ 10^{14} cm^{-3} with some sulfur and silicon impurities also present) grown on a GaP substrate. At low excitation intensity free-exciton emission was observed for $T \geq 20$°K, with bound-exciton luminescence dominating below this temperature.[6] The luminescence was excited by a cavity dumped Ar^+ laser (15 nsec pulsewidth, 10^5 pulses per second) operated at $\lambda = 4579$ Å and focused to a spot ~100 μm on the sample. For this wavelength the pump beam is absorbed in a distance comparable to the epitaxial-layer thickness. The luminescence was dispersed by a double spectrometer and detected by a photon-counter system having a time resolution ≈ 10 nsec.

The low intensity (0.2-mW cw corresponding to 2 W/cm^2) luminescence spectrum at 2°K, shown in Fig. 1(a), is dominated by sharp bound-exciton lines A and B (due to N) and C (probably due to S or Si) and their phonon replicas.[5,6] In contrast the high-intensity spectrum,[7] (4×10^4 W/cm^2, pulsed) shown by the solid line in Fig. 1(b), is completely dominated by a broad band of emission extending from ~5375 to 5550 Å. We show below, on the basis of temperature and excitation dependence, as well as decay kinetics, that radiative recombination of electron-hole pairs within in EHL of density 6×10^{18} cm^{-3} is responsible for this broad band in GaP.

An important characteristic of the EHL is that in a given material the liquid density is a function only of T and, in particular, is independent of the average pair density created by optical excitation.[1] As a result the spectral line shape of EHL luminescence is independent of excitation intensity, I. Figure 1(b) demonstrates that the observed broad emission band has this character. Neglecting the sharp bound-exciton features on the high-energy side, we note that the dashed spectrum, corresponding to $I = 4\times10^3$ W/cm^2, when normalized at 5480 Å, superposes the spectrum obtained for a pump ten times more intense. Furthermore, the decay kinetics of this emission band is very different from that of the bound ex-

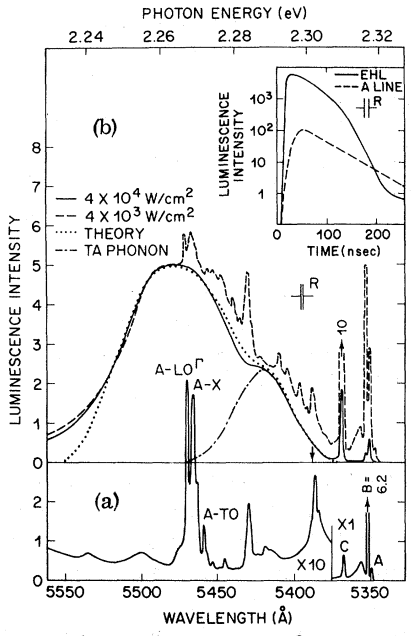

FIG. 1. Luminescence spectra of GaP at 2°K for (a) low excitation intensity and (b) high excitation intensities. The dotted curve is the calculated spectrum with three overlapping phonon bands. The calculated TA-phonon-assisted EHL spectrum is also shown. The arrow indicates the calculated position of $\mu_0 - \hbar\omega_{TA}$ at $T = 0$°K. The inset shows time evolutions of EHL (at 5500 Å) and the A exciton. The weak signal at 5500 Å beyond 200 nsec is probably unrelated to EHL.

citons, as shown in the inset of Fig. 1(b). The bound exciton decays exponentially with a time constant of ≈ 55 nsec,[8] while the broad emission begins to decay with a time constant of ≈ 35 nsec and cuts off at $t \approx 200$ nsec. This 35-nsec time constant agrees with the calculated Auger recombination time for a carrier density of 6×10^{18} cm^{-3} in GaP.[9] The sharp cutoff is typical of what is observed for EHL in Ge at intermediate temperatures.[10] At the lowest intensity for which the characteristic broad emission is well defined, we estimate that the average photoexcited carrier density is about two orders of magnitude less than $\sim 6\times10^{18}$ cm^{-3} consistent with the separation of carriers into a low-density gas and a high-density EHL[1] at this pump intensity.

These observations give strong qualitative support to the identification of this broad emission band as due to EHL recombination. We now show that the observed line shape agrees with the calculated line shape for an EHL of density 6×10^{18} cm^{-3} in GaP. The conduction-band minimum in GaP is at the X point of the Brillouin zone and electron-hole recombination requires phonon assistance. Three zone-edge phonons are allowed ($E_{TA} = 12.8$ meV, $E_{LA} = 31.3$ meV, and $E_{TO} = 46.5$ meV). The energy separation between these phonons is less than the expected width of the EHL band so that their overlap results in a single broad band, as observed. We have calculated the spectrum as a sum of three appropriately displaced bands of different intensities but with the same shape. The line shape for a single band is calculated as a convolution integral of the electron and hole density of states and the occupation probability functions for electrons and holes[1] using the following values of reduced carrier masses: $m_{lh} = 0.13$, $m_{hh} = 0.54$, $m_e = 0.40$, $m_{op} = 0.12$ (the optical mass). With these masses we find that the best fit to the data can be obtained with $n_0 = 6\times10^{18}$ cm^{-3} and carrier temperature $T = 20$°K.[11] The relative strength of the phonon bands is given by TA:LA:TO = 0.53:1:0.88.[12] This fit, shown in Fig. 1(b) by the dots, is quite good except at low energy where two-phonon processes [LO$^{\Gamma}$(51.5 meV) + TA, LA, or TO] also contribute to the experimental spectrum. The figure also illustrates the calculated liquid line shape and the position of the chemical potential μ_0 at $T = 0$°K for the TA phonon sideband.

From the position of μ_0 we can deduce the liquid binding energy relative to the free-exciton energy and find $\varphi_0 = 14 \pm 1$ meV. In comparing this experimental value to theoretical binding energy, one needs to know the exciton binding energy E_B. Experimental values range from 10 meV[12] to 13 meV[13] and the theoretical estimate is ≈ 17 meV.[14] Combescot has calculated[15] $n_0 = 4.7\times10^{18}$ cm^{-3} and $\varphi_0 + E_B = 20$ meV. Vashishta *et al.*[16] have calculated $n_0 = 6.5\times10^{18}$ cm^{-3} and $\varphi_0 + E_B = 27.6$ meV. Beni and Rice have extended their calculation of polaron effects[17] in EHL to GaP and find $n_0 = 7.1\times10^{18}$ cm^{-3} and $\varphi_0 + E_B = 29.9$ meV.[18] While there remains some uncertainty in the exact values, particularly in the absence of an accurate measurement of the exciton binding energy, we judge the agreement between experiment and theory to be good. This analysis of the low-temperature data establishes the existence of an EHL phase in GaP, and we now consider spectra obtained at higher temperatures in terms of this result.

For ultrapure Ge and Si, the EHL phase is observed only when the excitation intensity exceeds a certain threshold value. However, sharp thresholds are not observed in doped Ge and Si. Our sample of GaP is not as pure as the best Ge and Si, and impurity-related recombination domi-

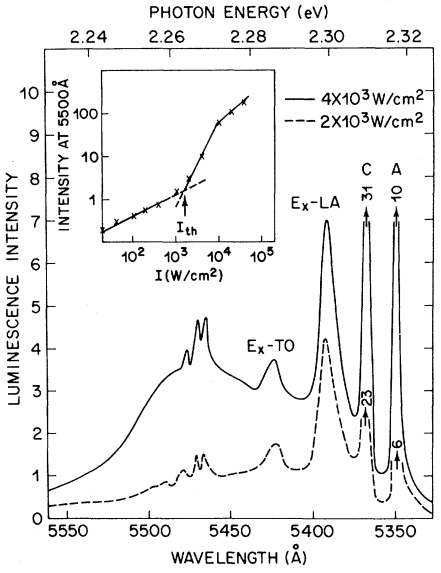

FIG. 2. Luminescence spectra of GaP at 30°K at two intensities near threshold. Luminescence intensity vs excitation intensity is shown in the inset.

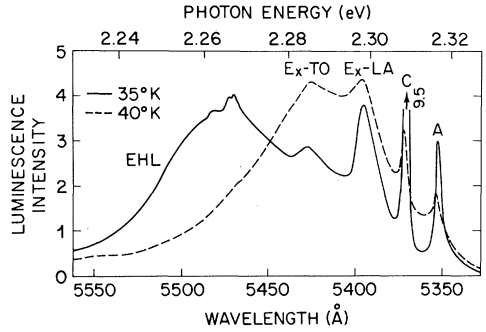

FIG. 3. Luminescence spectra of GaP at two temperatures for $I = 4\times10^4$ W/cm^2.

nates the low-intensity spectrum below ~20°K and no well-defined threshold is observed at these temperatures. However, threshold behavior is observed at 30°K where free-exciton emission is strong even at low intensity.[6] Spectra illustrating this threshold behavior are shown in Fig. 2. Doubling the excitation intensity from 2 to 4×10^3 W/cm can be seen to result in substantial increase in the broad emission band. The variation of luminescence at a fixed wavelength ($\lambda = 5500$ Å) with pump intensity shows a break corresponding to the threshold (see inset Fig. 2). Above this threshold the integrated intensity of the liquid recombination far exceeds that due to any other radiative recombination channel.

Finally, there is a critical temperature T_c, above which the broad band we have identified with EHL recombination does not exist. Spectra obtained with ~10^{18} pairs/cm^3 created per pulse at $T = 35$ and 40°K are compared in Fig. 3. We see that the broad emission band characteristic of EHL recombination is present at 35°K but not at 40°K, indicating that the critical temperature for EHL in GaP is ~40°K. The long low-energy tail on the TO-phonon-assisted exciton at 40°K is similar to the tail observed in Si at high excitation.[19] It may be related to the exciton-plasma Mott transition, but more experiments will be necessary to understand its origin in GaP. The spectrum at 35°K shown in Fig. 3, illustrates the difficulty that one encounters in GaP at high temperatures. Since the three phonon sidebands of excitons and EHL are of comparable strength, it is very difficult to determine the EHL density as a function of temperature. Further purification of GaP will probably be necessary before the gas-liquid coexistence curve in the phase diagram of EHL can be determined.

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[7]The time evolutions of the broad-band emission and exciton lines are different. For the spectra in Fig. 1(b), the gate on photon counter was delayed ~25 nsec from the beginning of the laser pulse (see inset, Fig. 1).

[8]The observed decay time of ~55 nsec for A exciton suggests heating of the sample to ~10°K. The carrier temperature may be slightly higher.

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a carrier temperature of 10°K and increasing density n_0 by a few percent. From our results we estimate that if EHL were created close to 0°K, its density would be $(6.5-7)\times 10^{18}$ cm^{-3}.

[12]For exciton absorption, the measured ratios for TA:LA:TO are 0.27:1:0.4 [P. J. Dean and D. G. Thomas, Phys. Rev. 150, 690 (1966)]. The different ratios observed for EHL may be attributed to relaxation of selection rules caused by large Fermi wave vector for electrons in EHL.

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Determination of Relaxation Time in Bulk Superconductors

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A method for studying nonequilibrium effects and their $\vec{k}$-space anisotropy in bulk superconductors near T_c is reported. The relaxation time in single-crystal In determined directly by this method, $\tau(t)=0.77\times 10^{-10}(1-t)^{-1/2}$, represents confirmation, both in form and magnitude, of the Schmid-Schön predictions for the relaxation of the magnitude of the order parameter near T_c. The associated electron-phonon inelastic scattering time is in excellent agreement with that determined for the comparable portion of $\vec{k}$ space by cyclotron resonance.

We report[1] a method for studying nonequillibrium superconductivity and its $\vec{k}$-space anisotropy in bulk superconductors near T_c, and the direct observation by this method of the relaxation time $\tau(t)$ for high-purity, single-crystal indium satisfying $\tau(t)=0.77\times 10^{-10}\,(1-t)^{-1/2}$ sec; here t is the reduced temperature, referred to the zero-field critical temperature $T_c(0)$. In thin-film experiments, Peters and Meissner[2] (Sn) and, later, Schuller and Gray[3] (Al) reported a divergence of $\tau(t)$ near T_c. The data were found to be incompatible with the form $(1-t)^{-1}$, obtained[4] for gapless superconductors. It was inferred that the divergence must be of the form $(1-t)^{1/2}$.[5] It was possible in the present work to test the magnitude and form of the divergence of $\tau(t)$ near T_c more definitively than heretofore, in part as a result of the following: (1) The $T_c(0)$ broadening $\delta T_c(0)$ <1 mK, as compared with 15–20 mK commonly encountered in thin films,[6] so that the form of the divergence could be meaningfully tested to t $=0.999$; (2) the method minimizes commonly encountered complications due to subsequent pair-breaking (cf. Ref. 6) by a phonon emitted upon pair formation, and to quasiparticle branch imbalance[7]; and (3) the interaction has a $\vec{k}$-space selectivity in the single crystal. The measured $\tau(t)$ represents confirmation of the Δ^{-1} temperature dependence, i.e., the form $(1-t)^{-1/2}$, predicted by Schmid and Schön[8] for the relaxation near T_c of the magnitude of the order parameter Δ: $\tau_\Delta=\pi^3T/7\zeta(3)\tau_{e\text{-}ph}\Delta^{-1}$, where ζ is the Riemann zeta function and $\tau_{e\text{-}ph}$ the inelastic electron scattering time by phonons. From our experimentally determined numerical coefficient 0.77×10^{-10} (sec) we obtain $\tau_{e\text{-}ph}=1.2\bar{6}\times 10^{-10}$ (sec). [A factor of 2 is required by the fact that two quasiparticles are involved in each pair-forming process (cf., Ref. 5, p. 4869)]. This is in excellent agreement with the $\tau_{e\text{-}ph}$ from (N state) cyclotron resonance,[9] $\tau_{e\text{-}ph}=1.2\bar{7}\times 10^{-10}$ sec, identifiable with the same $\vec{k}$-space locus as is selected by the present interaction, i.e., the "cap" portion of the central-plane effective zone[10] $\perp[001]$. Note that $\tau_{e\text{-}ph}$ is in general highly anisotropic, rendering questionable any detailed comparisons of $\tau_{e\text{-}ph}(\vec{k})$ measured in polycrystals. Since the present method makes possible measurements on bulk single crystals and incorporates a $\vec{k}$-space selectivity, it becomes possible to identify measured times τ_Δ and $\tau_{e\text{-}ph}$ with *particular regions* of Fermi surface, and directly to determine