Low-temperature photoluminescence spectra of doped Ge†

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We report on an investigation of the photoluminescence spectra of Li-, As-, Ga-, and Sb-doped Ge crystals with impurity concentrations between 10^{15} and 10^{17} cm^{-3}. Extensive data on the temperature, time, and pump power dependences of these spectra are presented for the spectral ranges where the no-phonon (NP line) and the longitudinal-acoustic-phonon assisted (LA line) edge emissions from the electron-hole droplet (EHD) are expected to occur. The spectral ranges covered are 730–740 meV and 705–720 meV. The LA line of Ge:As is observed to have the properties of the EHD for $T \lesssim 4.2$°K. On the other hand, time-resolved spectra show that different parts of the NP line of Ge:As decay at different rates. We conclude that the NP line has a contribution of impurity-induced emission from states other than the EHD. The LA lines of Ge:Li, Ge:Ga, and Ge:Sb are observed to possess pump power and time dependences similar to those observed for the NP line of Ge:As. The properties of these LA lines are interpreted in terms of impurity-induced emissions along with emission from the EHD. Comparison of the doped Ge spectra with those from doped Si suggest that the impurity-induced emission may be due largely to broadened "multiexciton complex" lines.

I. INTRODUCTION

The study of electron-hole droplets (EHD) in Ge and Si has received considerable attention in recent years.[1] In Ge with impurity concentration $N_i \lesssim 10^{14}$ cm^{-3}, the existence of EHD has been demonstrated by light-scattering[2] and junction-noise[3] experiments. In Ge with $N_i \sim 10^{15}$ cm^{-3}, no light-scattering results are available but junction-noise experiments strongly suggest that EHD do exist.[4] Below 10 °K, photoluminescence spectra of moderately heavy-doped Ge (we mean by moderately heavy doping, impurity concentration of 10^{16}–10^{17} cm^{-3} in this paper) are dominated by a broad line whose shape and position are nearly the same as those of the EHD line in pure Ge. This led the early investigators[5,6] to suggest that EHD do form in heavily doped Ge and that their critical temperature is higher than that in the less heavily doped Ge. The decay lifetimes of the EHD in heavily doped Ge:As and Ge:Sb were found to be shorter than the lifetime of EHD in pure Ge.[7] In As- and P-doped Ge, a so-called no-phonon line in addition to the familiar TA-, LA-, and TO-phonon assisted EHD lines was observed and was attributed to recombination of pairs in the EHD with the impurity atom taking up the "excess momentum."[6,7]

An unusual property of the EHD line in heavily doped Ge is its pump-power-dependent line shape, first reported by Novikov *et al.*[6] While the line was essentially identical to that of the EHD in pure Ge at high pump powers, it shifted towards higher energy and became narrower at lower pump powers. They attributed this to the formation at low pump powers of small droplets for which the surface energy contribution is observable. Extensive investigations of the line shape versus pump power were carried out by Martin and Sauer.[8] They reported that with increasing excitation power, the EHD line broadened on both the low- and high-energy side. The full width at half-maximum (FWHM) of the line varied smoothly with pump power, exceeding that of the EHD line in pure Ge at sufficiently high pump powers. Martin and Sauer offered Novikov's explanation for the behavior at low pump powers. They suggested that the results at high pump powers are due to a complete filling of part of the doped Ge sample with the electron-hole liquid.[9] One difficulty with this interpretation, noted by Martin and Sauer, is that one would expect to see a range of pump powers for which normal-size droplets are created but without sample filling. The FWHM of the line for this pump power range should be independent of excitation. This prediction is not observed experimentally. Timusk and Silin[10] have suggested, based on the results of far-infrared absorption measurements, that only small droplets pinned on impurity centers are formed in doped Ge.

Karuzskii *et al.*[11] have studied the liminescence decay and magneto-oscillation behavior of the LA-phonon assisted and the no-phonon EHD-like lines (henceforth referred to as the LA and NP lines, respectively) in Ge:As. They found very different results for the two lines. They suggested that the LA line is due to the EHD while the NP line is possibly due to emission from "multiexciton complexes."[12] In brief communications, Zhurkin *et al.*[13] have recently reported on studies of decay kinetics in As-doped Ge. Their results show that the decay kinetics are pump-power and doping-concentration dependent. They reported that the NP line shifted towards higher energy and nar-

rowed with increasing delay time.

Theoretical calculations of the properties of the EHD in doped Ge have been reported by a number of authors. Bergersen *et al.*[14] have treated the high-doping limit ($N_i \gtrsim 10^{17}$ cm^{-3}) which is outside of the doping range studied here. Birman and Mahler[15] and Smith[16] have predicted reduced EHD densities, compared to pure Ge, in Ge doped with 10^{15}–10^{17} cm^{-3} of shallow impurities. However, due to the unexplained pump-power dependence of the EHD-like line in heavily doped Ge, no unambiguous comparison of theory with experiment exists. On the whole, the understanding of the spectra in heavily doped Ge is rather poor.

In this paper, we present comprehensive experimental data which suggest that the broad EHD-like LA line in Ge moderately heavily doped with Li, Ga, and Sb and the NP line in Ge:As are in fact the result of two or more spectroscopically unresolved emission processes: one of them is the EHD while the rest are impurity-induced emissions. Since the temperature, pump power, and time dependences of these processes differ, their sum leads to the complicated results that will be reported. In contrast to these lines, the LA line in Ge:As shows much smaller effect of any impurity-induced emission at 2 and 4.2 °K. At these temperatures, this line is due mainly to EHD emission, and its properties as a function of doping agree very well with theoretical predictions. We shall discuss possible origins of the impurity-induced emissions.

This paper is organized as follows. In Sec. II, we describe sample preparation and experimental procedure. Section III is divided into four subsections containing, respectively, the results for Li-, As-, Ga-, and Sb-doped Ge. Summary and discussion of the results are presented in Sec. IV. Conclusions follow in Sec. V.

II. EXPERIMENT

A. Samples

The As-, Sb-, and Ga-doped Ge samples used were between 2 and 4 mm thick and had areas between 75 and 200 mm^2. Their flat faces were prepared by successive lapping with 40-, 15-, and 5-μm grits followed by a mechanochemical polish. To further minimize surface damage, they were then lightly etched in a 5:1 HNO_3:HF solution. Prior to each experiment they were rinsed with methanol and dried.

The Li-doped Ge samples were made by diffusing Li into high-purity Ge crystals ($N_A - N_D < 10^{11}$ cm^{-3}, ~5 mm thick). The diffusions were carried out at 350 °C for about 30 min. Differential resistivity measurements on samples so prepared showed that there is a dead layer at the surface about 100 μm thick. Below the dead layer is a 400-μm layer in which the Li concentration decreases from 6×10^{16} to 2.5×10^{16} cm^{-3}. Beneath this layer the doping profile is exponential with the doping level dropping about one decade per 200 μm. Following the diffusion, the samples were lapped with 5-μm grit to remove the heavily pitted dead layer created by the Li-diffusion process. They were then etched in a 3:1 HNO_3:HF solution and photoluminescence measurements were performed on the doped side. The lapping, etching, and measurement steps were repeated several times to cover the range of concentrations at the surface of 5.5×10^{16} to 5×10^{14} cm^{-3}.

B. Experimental apparatus

Excitation was provided by a RCA SG2007 GaAs laser diode. The sample under study was mechanically attached to a copper sample-holder block, and the laser was mounted a few mm perpendicularly above the sample's flat face. The sample holder was then placed inside a Janis Dewar. Temperatures above 4.2 °K were achieved with temperature regulated He vapor while below 4.2 °K, vacuum-regulated liquid-He bath was used for cooling. Temperature drift during the recording of a single spectrum was typically less than 5%. A calibrated Ge-sensor in contact with or in close proximity to the sample was used to monitor the temperature.

The recombination radiation from the illuminated face of the sample was collected and focused by two lenses onto the enetrance slit of a Spex 1400-II grating spectrometer. The lens combination has a magnification factor of 3. The maximum slit opening on our Spex is 3 mm, which allowed, at most, radiation within a 30 Å (1.2 meV) bandwidth and emerging from a 1-mm strip from the sample surface to be collected. The output from the spectrometer was focused onto the detector with an elliptical mirror. An InAs photovoltaic detector operated at either dry-ice or liquid-N_2 temperature was used. The InAs detector output was fed through a current amplifier to either a lock-in amplifier or a boxcar integrator. The processed signal was recorded on a strip-chart recorder. The rise time of the detection system was determined by measuring the sharp ($\ll$ 100-nsec rise time) GaAs laser pulse. The (0–90)% response time was less than 5 μsec and was independent of the light level incident upon the detector for the range of light levels involved here.

The outputs of the lasers used were calibrated at 5 °K using a calibrated Si photodiode. The laser spot on the sample was about 1 mm in diameter

as determined with an ir image converter. This spot size varied somewhat depending on the sample thickness. Laser powers quoted in this paper have not been corrected for reflection losses at the surfaces of the Ge samples.

Time-resolved spectra were measured using a boxcar integrator with a gate width of 2 μsec. Throughout this paper we will define the delay time t to be the time between the *beginning* of the current pulse through the GaAs laser and the *leading edge* of the boxcar gate pulse.

III. EXPERIMENTAL RESULTS

A. Ge:Li

In Fig. 1 the photoluminescence spectra at various temperatures of Li-doped samples are shown along with spectra from a pure sample. The spec-

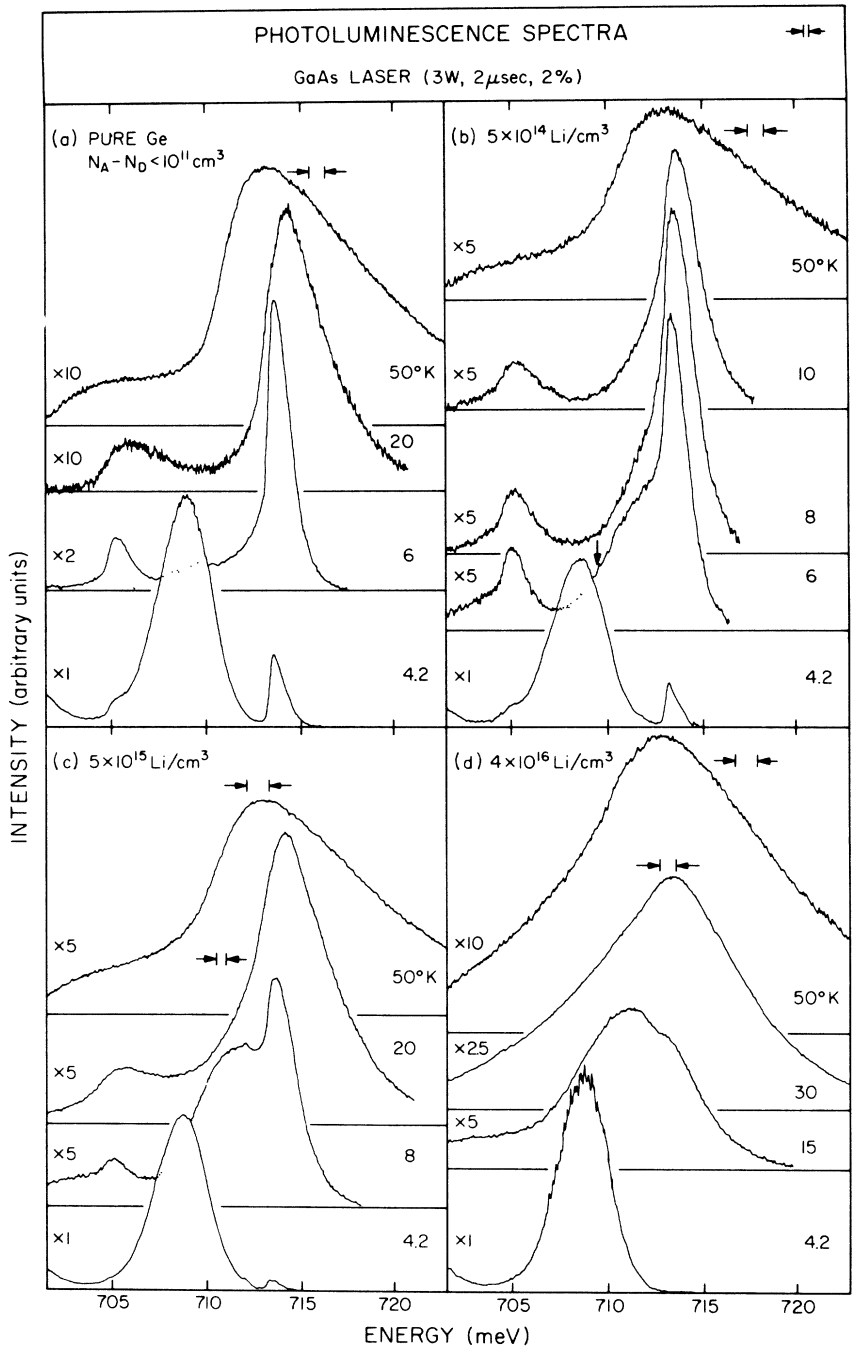

FIG. 1. Photoluminescence spectra of pure and Li-doped Ge at various temperatures. The GaAs laser power, pulse width, and duty cycle are indicated in that order below the title. Next to the title is the spectral resolution. Where resolution differed from that indicated near the title, it is indicated near the peak of the appropriate spectrum. The arrow in the 6 °K spectra in (b) indicates the peak of the EHD line as reported in Ref. 17.

tra presented in this section are not time resolved but should reflect the spectra near the time of maximum intensity.

In Fig. 1(a), the spectrum of pure Ge at 4.2 °K shows the well known[12] LA-phonon-assisted EHD and free-exciton (FE) peaks at 708.6 and 713.2 meV, respectively. The TO-phonon assisted replica of the FE and the EHD (not shown) lines appear at about 8.1 meV below their respective LA lines. As the temperature is raised above 4.2 °K, the EHD intensity drops quickly so that at 6.0 °K, which is close to the critical temperature of EHD formation,[17] the FE signal dominates the spectrum. The TO-phonon-assisted FE emission at 50 °K is joined with the LA-phonon-assisted line but nonetheless it is easily discernible. The shift of the line to lower energy at 50 °K is due to a reduction of the energy gap at this higher temperature.[18]

The spectra from the sample with a concentration of Li of 5×10^{14} cm^{-3} at the surface, Fig. 1(b), show essentially the same features as those from the high-purity Ge. In particular, the EHD line shape and position at 4.2 °K are identical to those in the high-purity Ge. At 6 °K, impurity-induced emission can be seen clearly as a shoulder on the low-energy edge of the FE line. It is unlikely that this emission is actually due to EHD for two reasons. First, the EHD line peak at 6 °K is at approximately 709.4 meV,[17] as indicated by the arrow on the 6 °K spectrum in Fig. 1(b). Even if some correction is allowed for the peak shift due to the interference of the strong FE line, the impurity-induced emission is peaked at a higher energy than the EHD line. Second, the FE line has a low-energy tail even at 8 °K, which is a temperature well above the critical temperature for droplet formation (we assume that the critical temperature is not changed by a doping level of 5×10^{14} cm^{-3}).

When the Li concentration at the surface is 5×10^{15} cm^{-3}, see Fig. 1(c), three significant changes occur in the photoluminescence spectra. First, the FE intensity at 4.2 °K is greatly reduced compared to that in lighter-doped Ge. Second, a bound-exciton (BE) line can be detected between the EHD and FE lines. It is located at about 712 meV, approximately 1 meV below the FE line in accordance with the Haynes rule.[19] Third, the EHD line appears to shift continuously with increasing temperature towards the FE line. It perturbs the low-energy edge of the FE line even at 20 °K. This description is the simplest and most straightforward one. However, there is striking similarity between the spectrum at 8 °K in Fig. 1(c) and the spectrum at 6 °K in Fig. 1(b). This and the discussion in connection with Fig. 1(b) in the preceding paragraph lead us to suspect that the EHD line at 8 °K in Fig. 1(c) might be due in part to impurity induced emission. As the temperature is raised above 6 °K, the tail on the FE line due to the impurity induced emission becomes more noticeable.

For the surface with 4×10^{16} Li/cm^3, we obtained the spectra in Fig. 1(d). There are three major observations we wish to make. First, at $T = 4.2$ °K, only the broad line resembling the EHD line is seen. It is not accompanied by either FE or BE emission. Second, this line shifts continuously with increasing temperature towards the FE line which first becomes unambiguously resolved at 15 °K. Remnants of this line are seen even at 50 °K where it fills the valley, present in the 50 °K pure-Ge spectrum, between the LA- and TO-phonon-assisted FE emission lines. Lastly, our 15 °K data is similar to that reported by Martin for Ge:In.[9] He interpreted the single broad line at high temperatures as being due to EHD. The data presented here where we see clear evidence of a shoulder due to the FE suggest that this author did not resolve the FE from the broad line. Hence, the agreement that he obtained in fitting the broad line to the theoretical electron-hole liquid-emission line shape was fortuitous.

There is some difficulty in interpreting even the low-temperature (say $T < 5$ °K) emission lines as due to EHD alone because of the pump-power dependence of the linewidth. In Fig. 2, we show the linewidth at 5 °K as a function of pump power for two different surface Li concentrations. The closed circles represent data from surface with 5×10^{15}-cm^{-3} Li concentration. There is no observable pump-power dependence and no difference

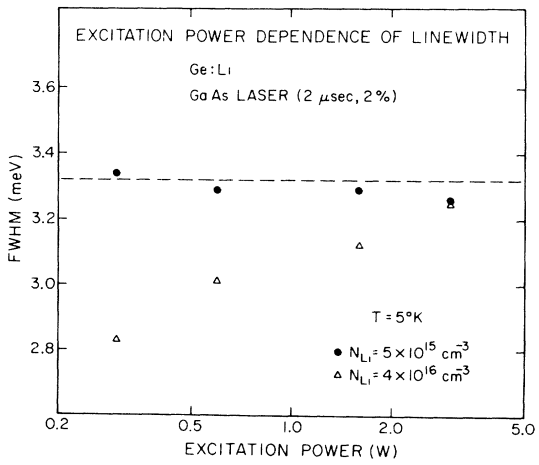

FIG. 2. Excitation-power dependence of the linewidth of the La-phonon-assisted line of lightly and heavily doped Ge:Li at 5 °K. The dashed line shows the pump-power independent EHD linewidth in high-purity Ge.

from the pure-Ge data which is represented by the dashed line. The data from a sample surface with 4×10^{16} cm^{-3} of Li at the surface are represented by open triangles and show clear pump-power dependence. The linewidth increases by about 0.4 meV for a pump-power increase of a factor of 10. This is qualitatively similar to the results reported by Martin and Sauer[8] for Ge:In, Ge:Ga, and Ge:Sb with comparable impurity concentration. We did not have sufficient excitation power to increase the FWHM of the line from Ge:Li above that of the EHD line in pure Ge.

B. Ge:As

The LA-phonon assisted spectra from Ge doped with 4×10^{15} As/cm^3 at various temperatures are similar to those for the 5×10^{15}-Li/cm^3 sample presented in Fig. 1(c). In addition, we have observed no pump-power or time dependence of the LA line within experimental uncertainty. These are expected properties of the EHD line. Similar behaviors were observed for Ge doped with about 10^{15} cm^{-3} of Sb or Ga so we shall concentrate only on heavily doped Ge in this section and in Secs. III C and III D.

The LA and NP lines are the most prominent features of the Ge:As photoluminescence spectra at low temperatures. The change of the LA line as a function of temperature is qualitatively similar to that presented in Fig. 1(d) for Ge:Li. The LA line appears to shift continuously to and merge with the FE line with increasing temperature. At 15 °K, the LA line is quite weak and is seen only as a shoulder on the FE line. The line that has been attributed to EHD emission without phonon assistance, the NP line, is at about 736 meV. It appears quite similar to the LA-phonon assisted line and also to the EHD line in pure Ge. The FWHM of the NP line at 4.2 °K is about 3.1 meV, slightly smaller than the 3.3 meV width of the LA-phonon-assisted EHD line in pure Ge. At 15 °K, the NP line is still the most intense line in the spectrum, but it has distinct shoulders on both the low- and high-energy side. A shoulder at about 738 meV is due to BE emission without phonon assistance,[20,21] while a shoulder at 730 meV, whose intensity is temperature dependent, is the TA-phonon-assisted companion of the LA line.[7]

We have found that time-resolved spectra can yield a wealth of information about these lines. All spectra reported in the rest of this paper are time resolved. They were obtained in the manner described at the end of Sec. II. In Fig. 3 we have the time-resolved spectra at 2, 4.2, 6, and 8 °K of a 2×10^{16}-As/cm^3 sample showing both the LA and NP lines. We will discuss these two lines separately.

At 2 and 4.2 °K, the LA-phonon-assisted line has relatively simple behavior. The FWHM and peak position of the line are nearly independent of the delay time. The BE line can be discerned at 4.2 °K for long delay times. Some shift of the peak of the line is detectable at 6 and 8 °K, suggesting that as the temperature is raised, some impurity-induced emission appear.

In contrast to the LA line, the NP line has very complicated behavior as a function of time. First, the peak of the NP line shifts noticeably with time at 2 and 4.2 °K. At 2 °K the total shift of the spectrum at $t=35$ μsec from that at $t=3$ μsec is 0.7 meV. At 4.2 °K, the shift is 1.3 meV between the spectra at $t=30$ μsec and $t=3$ μsec. Part of the NP line peak shift at 4.2 °K is due to the BE line which becomes clearly noticeable for long-time delays. Second, at 8 °K, the NP line which resembles the EHD line at short-delay times, decays continuously into a very narrow line at 736.1 meV. At $t=27$ μsec, its FWHM is about 2.2 meV and its shape is different from the theoretical EHD line shape.[12] The line at 739 meV is due to the BE. In the corresponding spectrum ($t=27$ μsec) at 6 °K, the region between the NP and BE lines is filled by some impurity-induced emission. The 6 and 8 °K spectra show that different parts of the broad EHD-like NP line decay at different rates so that the NP line is caused by at least two (besides the BE line) emission processes. It is natural to expect that the NP line at 2 and 4.2 °K is also due to two or more emission processes and that the shift of the NP line peak noted above is due to the changing relative intensity of the various emissions.

The decay transients of the sample were measured using 100-μsec excitation pulse. This pulse length allows the intensity of the EHD lines to approach steady state before the laser is shut off. The decay transients were obtained through the spectrometer. For the LA line the spectrometer was set at 708.6 meV while for the NP line, it was set at 736 meV. (The bandpass in both cases is about 1.2 meV.) The results are shown in Fig. 4. The LA line decays roughly exponentially with a lifetime of 23 μsec. The NP line decay is slower and is nonexponential. The negative curvature of the NP line is an experimental artifact caused by the limited bandpass of our spectrometer and the considerable shift of the NP line position as shown in Fig. 3. If the spectrometer is set to the high-energy side of the NP peak at $t=100$ μsec, then the decay is much slower. These results are consistent with the observation of Karuzskii *et al.*[11] who found that the NP line decays with two time constants. The decay transient at 4.2 °K is quite

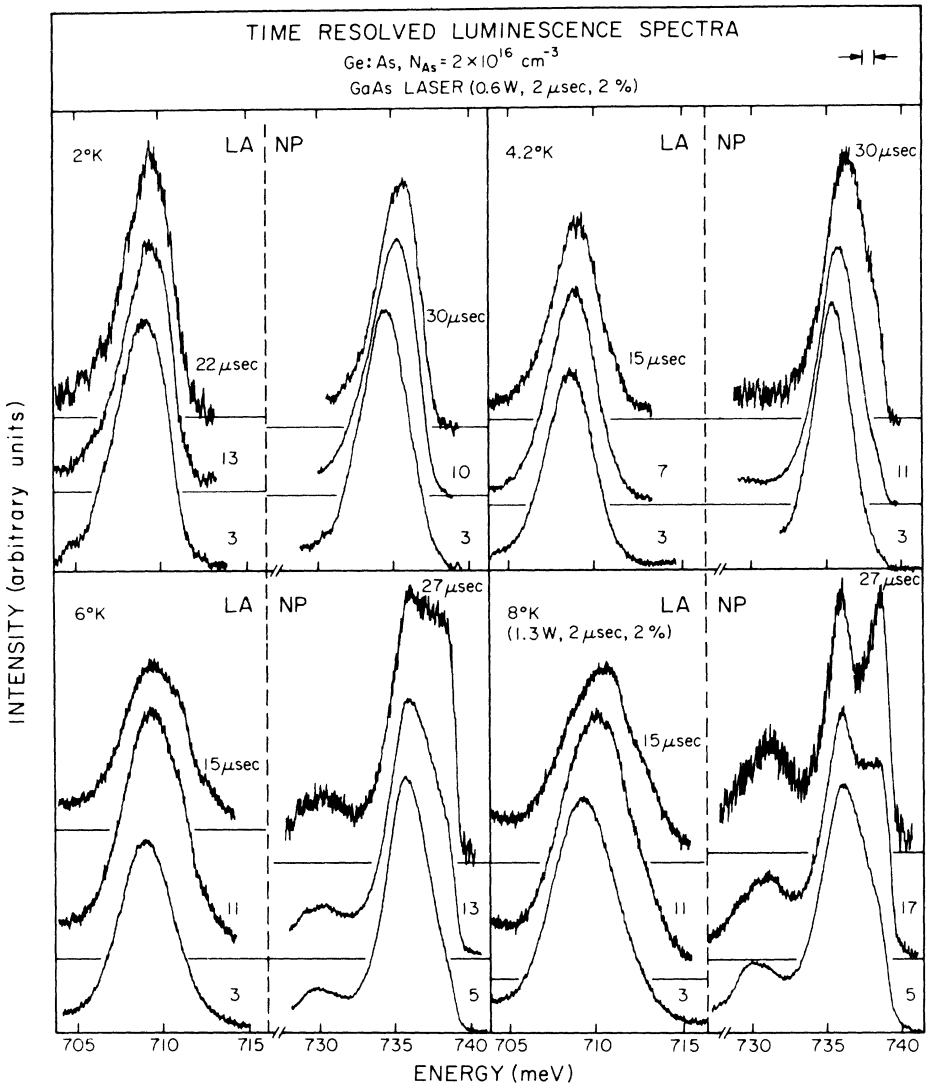

FIG. 3. Time-resolved photoluminescence spectra of Ge:As showing the LA-phonon-assisted and the no-phonon lines at four different temperatures. Excitation power used was 0.6 W, *except* for the LA-phonon-assisted line at 8 °K for which 1.3 W was used. The number associated with each spectrum is the time delay t as defined in Sec. IIB. Relative intensities of the spectra are arbitrary so that the heights of different spectra should not be compared.

similar to the decay at 2 °K. This similarity has also been observed in Ge doped with only 10^{15} cm^{-3} of impurities[22] and is markedly different from the results in pure Ge.[23]

Information on the origin of the LA line can be obtained by looking at the luminescence decay of the line as a function of temperature. Such data using *pulsed* excitation are presented in Fig. 5. At 2 and 4.2 °K, when the time-resolved spectra data above suggest that the peaks are due to EHD, the decays are as expected for the EHD; viz., the decay transients show both bulk recombination and "surface evaporation" effects.[23] If the broad lines at $T > 6$ °K are due to the EHD, we would expect the decay transients to show more and more downward curvature as temperature is raised and evaporation becomes more important. Instead, the decay transients for $T > 6$ °K are more nearly exponential. The slight decrease of the decay rate for $T \gtrsim 6$ °K at long delay times is real and, if the line did not shift with delay time out of the bandpass of our spectrometer, would be more prominent. Attributing the negative curvature observed in the $T < 4.2$ °K decay transients to "surface evaporation" is somewhat speculative. Since the FE emission is absent in the low temperature spectra of moderately heavily doped Ge, exactly *what* is evaporated is not at all understood.

We note that under different excitation conditions the decay transients are different. A dashed line corresponding to the data points for the LA line given in Fig. 4 is drawn in Fig. 5. Comparison of the dashed line with the 2 °K data points in Fig. 5 shows that the luminescence decay of the LA

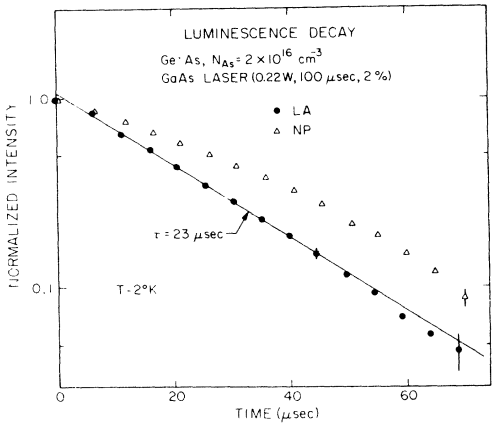

FIG. 4. Photoluminescence-intensity decay of the no-phonon and LA-phonon-assisted lines in Ge:As at 2 °K. The time zero is the time the GaAs laser is turned off.

line is slower when 100-μsec excitation pulses are used. This difference in the decay transients is also observed for pure Ge and is consistent with changes in the spatial distribution of the EHD which would result from changes in excitation conditions.[22]

In Fig. 6, the pump-power dependence of the LA and NP lines at 2 °K is shown. The LA line has essentially pump-power independent line position and FWHM, while the NP line broadens and shifts toward lower energy with increasing pump power.

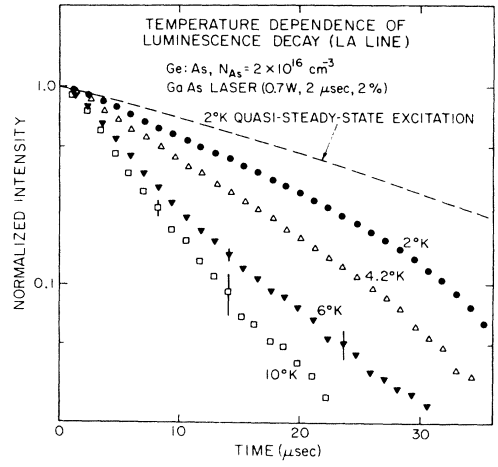

FIG. 5. Decay of the luminescence intensity of the LA-phonon-assisted line of Ge:As at various temperatures. Pulsed GaAs laser excitation was used. The LA line results in Fig. 4, for which 100-μsec excitation pulses were used to allow the LA line intensity to reach a steady state, are reproduced here as the dashed line for comparison purposes. The zero of time is approximately the time that the LA line intensity reached its maximum.

C. Ge:Ga

The temperature dependence of the spectra from Ge:Ga is qualitatively similar to that shown in Fig. 1(d). Figure 7 shows time-resolved spectra of a Ge sample with 2.5×10^{16} cm^{-3} of Ga impurity at 2, 4.2, and 8 °K. We make the following observations: First, considerable shift of the peak position with increasing delay time t is observed. The rate of peak shift as a function of delay time increases monotonically with temperature. At 2 °K the total amount of shift between $t = 3$ and 22 μsec is about 0.5 meV. While at 8 °K, the shift amounted to about 1 meV between $t = 2$ and 9 μsec. Part of the shift at 8 °K is caused by the emergence of the FE line with increasing delay time which is most visible in the $t = 9$ μsec spectrum. Second, there is a large change with delay time of the FWHM of the line at 2 °K. At $t = 3$ μsec, the line shape resembles the well known EHD line shape

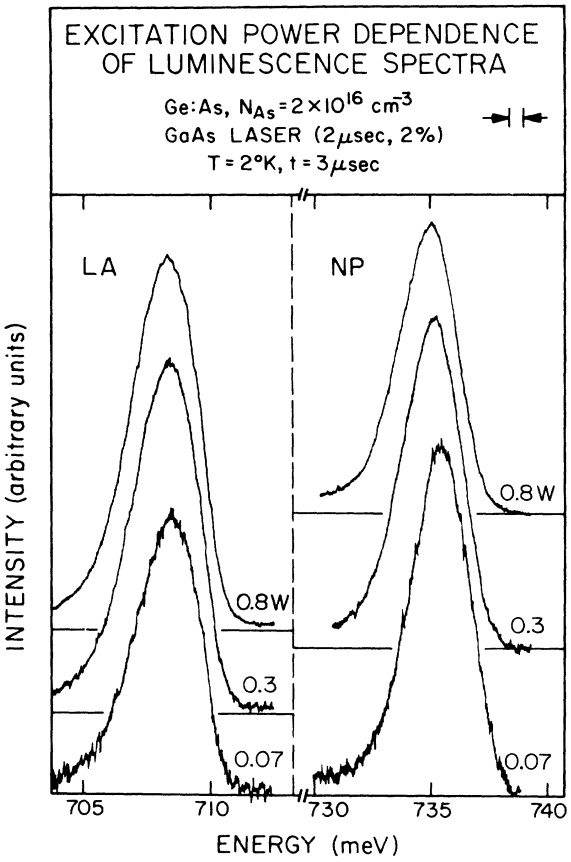

FIG. 6. Excitation-power dependence of the photoluminescence spectrum of Ge:As taken at a delay time of 3 μsec. Both the LA-phonon assisted and the no-phonon lines are shown. The excitation power is indicated at the right baseline of each spectrum. Relative intensities of the spectra are arbitrary.

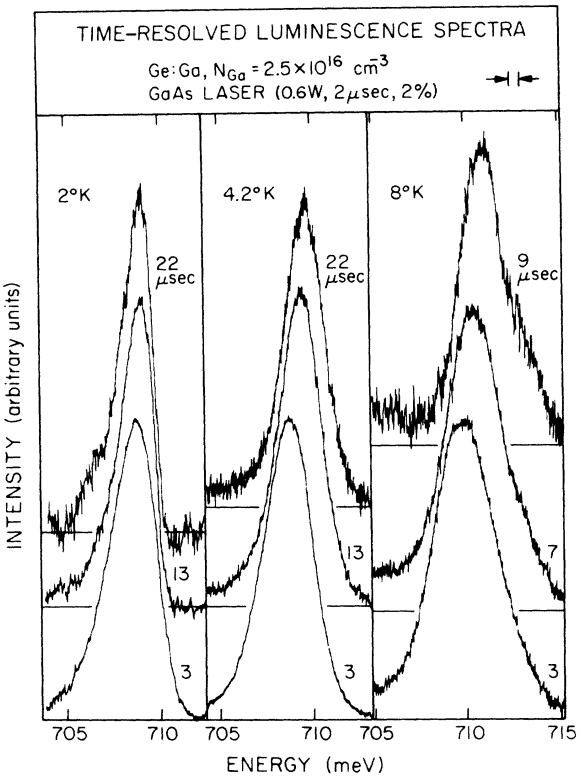

FIG. 7. Time-resolved spectra of LA-phonon-assisted line of Ge:Ga at three temperatures. The delay time t is shown to the right of each spectrum. Relative intensities of the spectra are arbitrary.

with a FWHM of 3.0 meV, corresponding to a density of 1.9×10^{17} cm^{-3}. However, at $t=22$ μsec, the line becomes much narrower and the high-energy edge becomes quite sharp. We have found it difficult to fit this spectrum using the theoretical EHD line shape. The sharp high-energy edge suggests that the states involved in the emission are localized; and, hence, do not exhibit thermal broadening due to motion.

The luminescence decay transients of a 4×10^{16}-Ga/cm^3 sample at 2 and 4.2 °K are shown in Fig. 8. At both temperatures two distinct decay rates are observed. The results can be fit quite well by sums of two exponentials, i.e., $I(t)\sim\exp(-t/\tau_1)+A\exp(-t/\tau_2)$. The values of the parameters obtained are, at 2 °K,

$$\tau_1=20\ \mu\text{sec},\quad \tau_2=76\ \mu\text{sec},\quad A=1.4;$$

and at 4.2 °K,

$$\tau_1=20\ \mu\text{sec},\quad \tau_2=59\ \mu\text{sec},\quad A=1.1.$$

The decay transients for a pump power of 0.09 W was unchanged within the noise level. The decay-transient data using pulsed excitation for temperatures up to 10 °K are presented in Fig. 9. Com-

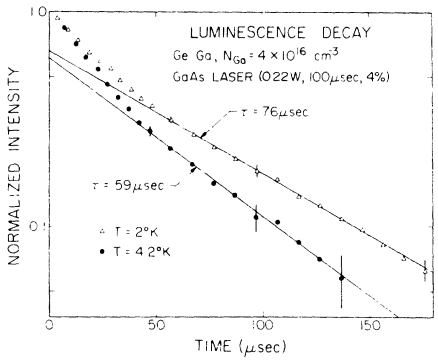

FIG. 8. Photoluminescence-intensity decay of the LA-phonon-assisted line in Ge:Ga at 2 and 4.2 °K. The zero of time marks the shutting-off of the laser. The straight lines are lines drawn through the data points for long delay times.

paring the data in Fig. 5 with that in Fig. 9, we note that the decay at 4.2 °K is qualitatively different in the Ge:As sample and the Ge:Ga sample. While the decay plotted on a semilog plot shows a negative curvature in the Ge:As case, the decay transients show a positive curvature in the Ge:Ga sample. On the other hand, the decays for the Ge:Ga-doped sample are similar to those of the Ge:As sample for $T\gtrsim6$ °K. This similarity suggests impurity-induced emission always plays a role in Ge:Ga sample and plays a role in LA line of the Ge:As sample for $T\gtrsim6$ °K.

It should be noted that, although two exponentials are sufficient to fit the decay transients, the possibility of the presence of more than two decay times can not be excluded. Experimentally it is difficult to resolve the decay of more than two

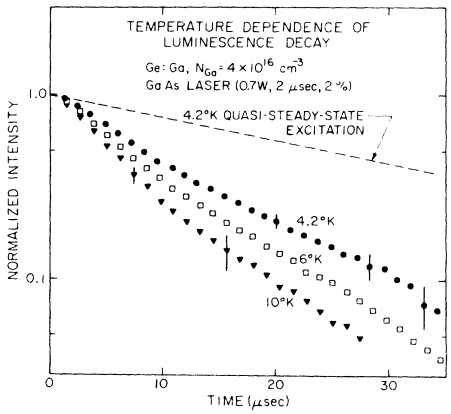

FIG. 9. Decay of the luminescence intensity of the LA-phonon-assisted line of Ge:Ga at various temperatures. Pulsed GaAs laser excitation was used. The quasi-steady-state excitation results at 4.2 °K in Fig. 8 are reproduced here as the dashed line for reference. The time zero is approximately the time the LA line intensity reached its maximum.

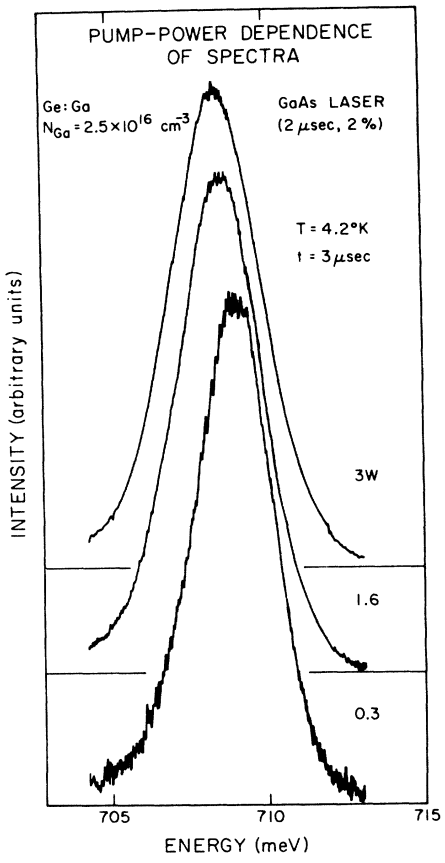

FIG. 10. Excitation-power dependence of the LA-phonon-assisted line in Ge:Ga at a delay time of 3 μsec. The pump power is shown at the right baseline of each spectrum. Relative intensities of the spectra are arbitrary.

components, especially if some decay times are not too different from each other.

In Fig. 10, the $t = 3$ μsec spectra of the 2.5×10^{16}-Ga/cm^3 sample for various pump powers at 4.2 °K are shown. The peaks shift towards lower energy and the linewidths increase with increasing excitation level. At 4.2 °K, a factor of 10 change in excitation power produced a 0.5-meV shift of the peak and a 0.5-meV change in the FWHM. At 6 °K, a factor of 4 change in pump power caused the peak to shift by 0.5 meV and the FWHM to change by 0.2 meV.

D. Ge:Sb

Figure 11 shows the 2 °K LA-phonon-assisted EHD line from high-purity Ge and the LA lines from Ge:As, Ge:Ga, and Ge:Sb samples. These results show that the peak in the emission line for Ge:Ga and Ge:As are rather close to the peak of the EHD line in pure Ge. In contrast, the data show that the peak of the emission line in Ge:Sb is shifted to lower energy by about 0.5 meV. This shift to lower energy is not understood at present, although calculations for the properties of the EHD in doped Ge suggest that such a shift of the EHD line might occur when impurity concentration approaches the Mott density.[15,16] The temperature dependence of the spectrum of the Ge:Sb sample is qualitatively similar to that of the 4×10^{16}-Li/cm^3 sample shown in Fig. 1(d).

Time-resolved spectra at 4.2 °K from the Ge:Sb sample showed a peak position independent of time delay. However, the linewidth decreased from 3.1 meV at $t = 2$ μsec to 2.5 meV at $t = 15$ μsec.

In Fig. 12, decay transients from the Ge:Sb sample are shown. The 2 °K data is nearly exponential with a time constant of 34 μsec. The 4.2 °K data show two time constants. Following the laser turn-off, the decay is fast for about 20 μsec before it becomes exponential with time constant of 28 μsec. When pumping power was decreased to 0.07 W, the transients remained essentially unchanged.

At 4.2 °K the FWHM of the EHD-like line de-

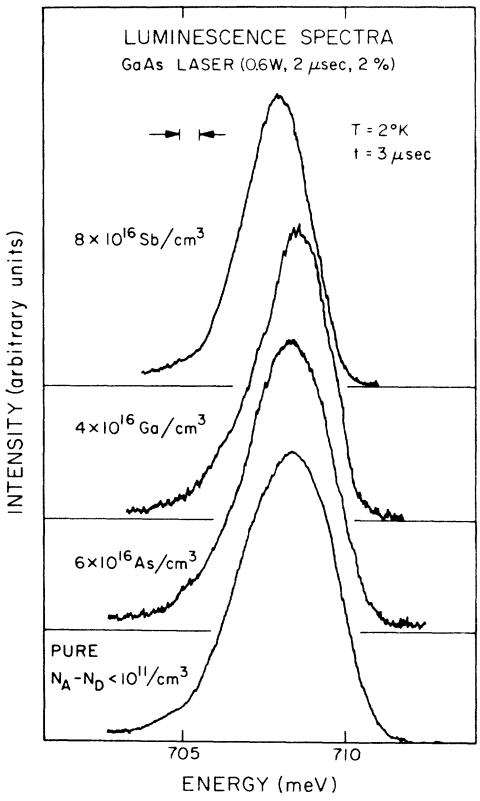

FIG. 11. Photoluminescence spectra of LA-phonon-assisted line at temperature of 2 °K from samples moderately heavily doped with Sb, Ga, and As as well as a high-purity Ge sample. Relative intensities of the spectra are arbitrary.

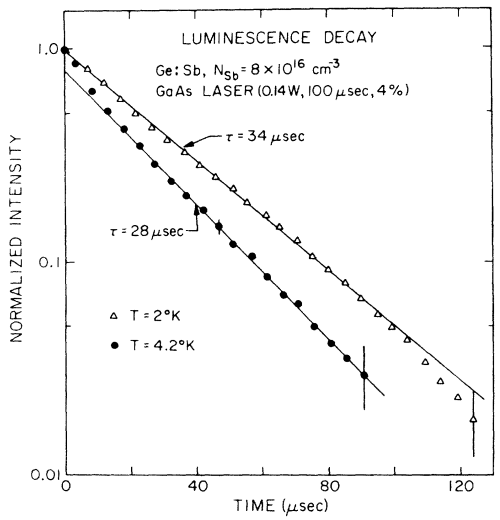

FIG. 12. Photoluminescence-intensity decay of the LA-phonon-assisted line in Ge:Sb at 2 and 4.2 °K.

creases from 2.7 meV to 1.9 meV with a reduction of pump power by a factor of 6. This is in good agreement with the observation of Martin and Sauer.[8] The position of the peak of the line is observed to be independent of the pump power.

IV. SUMMARY AND DISCUSSION

For Ge with impurity concentration up to a few times 10^{15} cm^{-3}, we have observed no changes of the properties of the EHD line from those of high-purity Ge. At temperatures close to the critical temperature of EHD formation, some impurity-induced emission can be seen which should not be confused with the EHD line. The decay transients of the EHD line in these lightly doped Ge crystals are quite different from those in the high-purity Ge and are dealt with in a separate paper.[22]

The properties of the EHD-like line in moderately heavily doped Ge are rather complex. The results are most easily interpreted by assuming the existence of impurity-induced emission.

A. LA line in Ge:As

The LA line in Ge:As is least affected by the impurity induced emission. In Ge:As, at low temperatures, say $T \lesssim 4.2$ °K, the LA line of Ge:As is dominated by the EHD emission so that we observe in the LA line properties of the EHD. We found the shape and position of the line to be essentially excitation power and time independent. Fitting the spectra to the well-known EHD line shape,[12] we obtained roughly linear decreases of both the density and chemical potential as a function of increased doping. For the 5×10^{16}-As/cm^3 sample, the density at 2 °K was $n = 1.9 \times 10^{17}$ cm^{-3} and the chemical potential is about 0.5 meV lower than that in pure Ge ($\Delta\mu = 0.5$ meV). These results are in excellent agreement with theoretical prediction[16] of n (0 °K) $= 2.0 \times 10^{17}$ cm^{-3} and $\Delta\mu = 0.55$ meV. The luminescence decay time of the EHD in Ge:As is about 23 μsec which is considerably shorter than the widely quoted 37 μsec for EHD in pure Ge.[23]

At higher temperatures, the FE and impurity induced emissions dominate the LA-phonon assisted spectrum. The impurity induced emission has a broad structureless line shape similar to the EHD line shape.

B. NP line in Ge:As and LA lines in Ge:Ga, Ge:Li, and Ge:Sb

Impurity-induced emission plays a large role in the NP line of Ge:As and in the LA lines of Ge:Li, Ge:Ga, and Ge:Sb. Its presence, spectroscopically unresolvable from the EHD emission, causes the above lines to show pump power and time dependences as well as two decay times.

It should be noted that the emission spectrum may not be coming uniformly from the sample. The spectrum could be made up of different components which are emitted with differing intensities from spatially distinct parts of the sample. Since the refractive index of Ge is rather large and the characteristic dimension of the region over which luminescence occurs is a few tenths of a mm,[24,25] it is difficult to measure spatially resolved spectra and our attempts have not led to conclusive results.

There are many possible mechanisms for the impurity-induced changes in the emission. We shall discuss some in detail and only mention others.

1. "Multiexciton complexes"

In Si samples with impurity concentration $\lesssim 10^{16}$ cm^{-3}, a series of narrow lines between the BE line and the peak of the EHD line have been observed.[26,27] These lines have been attributed to, but as yet unproven, emissions arising from transitions from neutral centers with n bound excitons to centers with $n-1$ bound excitons. They are usually referred to as "multiexciton complex" (MEC) lines. Martin[21] has reported observation of a similar series of lines in Ge with about 10^{15} cm^{-3} As and P impurities. He found that they are emitted without phonon assistance and have extremely low intensities. In Ge doped with $\gtrsim 10^{16}$ cm^{-3} of impurities MEC, if they exist, would most likely emit a broad line rather than a series of sharp lines for two reasons: First, the MEC lines

in Si have been observed to broaden and merge[28] at doping level of 10^{16}–10^{17} cm^{-3}. Since typical objects in Si are about half of the size of their counter part in Ge,[29] we expect broadening and merging of MEC lines to occur at doping level of 10^{15}–10^{16} cm^{-3} in Ge. Second, the total energy spread of the MEC lines is only about 3 meV in Ge compared to > 10 meV in Si. So the spacing between successive MEC lines in Ge would be rather small. One can find numerous similarities of spectra from doped Ge and doped Si, provided the doping levels are appropriately scaled to reflect the difference in characteristic lengths. These observations suggest the existence of a broad merged line due to MEC in Ge.

Comparison of Figs. 1(c) and 1(d) with Fig. 16 of Ref. 30 shows that the composite EHD and MEC lines in doped Si shift with temperature in a similar manner to the spectra in heavily doped Ge, viz. with increasing temperature, the composite spectrum shifts continuously towards and eventually merges with the FE line.

A broad line in which the emission from MEC can be resolved is observed in doped Si (see Ref. 8, Fig. 4). This broad line in Si has qualitatively the same pump-power dependence as seen in the single broad line observed in doped Ge. Hence, in Ge a line made up of emission from broadened and unresolved emission from MEC and perhaps EHD would possess a pump-power dependence like those observed for the NP line in Ge:As and the LA line in Ge:Li, Ge:Sb, and Ge:Ga.

The time dependence of the spectra in doped Ge can also be explained in a natural way once we assume that the EHD line is a composite of EHD and MEC lines. Measurements of the MEC decay times in Si show that different MEC lines have different decay times; the decay times monotonically decrease for lines approaching the EHD peak.[26] The intensity decays of these lines almost always show two decay constants.[26] The time resolved spectra in Fig. 11 of Ref. 27 show a shift towards higher energies and a narrowing of the combined width of the lines with increasing delay time. The observed complex EHD decay transients for the decay of the LA lines in Ge:Sb and Ge:Ga and the NP line in Ge:As is a consequence of the different decay times of the various components in the line. The LA line in Ge:As is relatively free of the effects of MEC emission so that its intensity decay is as expected of a EHD line.

For Ge as a function of doping at constant excitation, the BE intensity is maximum for doping in the range of ~ 10^{15} cm^{-3}, whereas the FE intensity is a monotonically decreasing function of (increased) doping. Both BE and FE are absent from the spectra when doping level exceeds ~ 10^{16} cm^{-3}. Similar observations on doped Si have been reported by Martin and Sauer.[8]

On the basis of the comparisons in this subsection, one might expect that, in heavily doped ($N_t \gtrsim 10^{17}$ cm^{-3}) Si:As or Si:P, where only broad NP and TO lines from the EHD are observed, the lines may actually be composed of differing amounts of EHD and broadened MEC radiation. There should be qualitative differences in all the properties of NP and TO lines. Verification of this point would strengthen the case for the MEC explanation for Ge.

2. *Bound-exciton banding*

In addition to a MEC band, a possible contribution to the impurity-induced emission comes from a broadened BE line. In analogy with the phenomenon of impurity banding in semiconductors,[31] we might expect that the interaction between an exciton and more than one impurity would lead to a broadening of the BE line. This interaction with a number of impurities will produce a broadened BE line in two ways. First, consider a single exciton interacting via an attractive interaction with a number of nearest-neighbor impurities. The energy of the ground state of the system made up of the exciton and a cluster of neutral impurities will depend on the number and spatial distribution of the neutral impurities. Since the impurities are distributed randomly, there are fluctuations in the spatial distribution of the nearest-neighbor impurities about any given impurity center. This leads to a distribution of values for the ground state energy of a *single* exciton interacting with an impurity and its nearest neighbor impurities. This interaction will lead to a broadening and shifting of the BE line with increased impurity concentrations. Estimates of the magnitude of this effect for impurity density of ~ 10^{16} cm^{-3} give broadening of the BE line on the order of 1 meV.[32] Second, as the pump power is increased, we are likely to increase the average number of excitons bound to impurity centers. Hence, we will be looking at the emission from varying number of excitons interacting with the impurity centers. This system will emit a line which broadens and shifts with increasing pump power. We have in this second case a possible mechanism to explain the observed broadening and merging of both the BE and MEC lines in moderately heavily doped Si.[28]

Excited states of the BE would broaden into bands at even smaller doping levels. We might expect the excited states of the BE to smear the low-energy threshold of the FE line while the band from the ground state of the BE becomes

TABLE I. Densities and temperatures obtained from theoretical linefits[a] to spectra at $t = 3$ μsec and various excitation powers for two doped Ge samples. The bath temperature was 2 °K. Excitation was provided by GaAs laser with 2-μsec-pulse duration and 2% duty cycle. The density of states effective masses for electrons and holes were taken to be 0.56 and 0.37, respectively.[b]

Excitation power (W)	Ge:Sb 8×10^{16} cm^{-3} T(°K)	$n(10^{17}$ cm$^{-3})$	Ge:Ga 4×10^{16} cm^{-3} T(°K)	$n(10^{17}$ cm$^{-3})$
1.3	3.0	1.4	3.5	2.1
1.1	2.9	1.4	3.0	1.9
0.9	3.0	1.3	3.0	1.8
0.7	2.8	1.2	2.5	1.6
0.5	2.3	1.1	2.5	1.3
0.2	2.0	0.9		

[a]R. B. Hammond, T. C. McGill, and J. W. Mayer, Phys. Rev. B 13, 3566 (1976).

[b]W. F. Brinkman and T. M. Rice, Phys. Rev. B 7, 1508 (1972).

either a distinct shoulder on or a low-energy peak separate from the FE line, depending on doping level. It is quite possible that the shoulder on the FE line between 6–10 °K in Figs. 1(b) and 1(c) are due in part to BE banding.

3. *Heating*

The introduction of impurities at concentrations of ~ 10^{16} cm^{-3} results in a decrease in the thermal conductivity by about a factor of 5 to 10.[33] This change in thermal conductivity raises the question of heating in the doped samples where it might be unimportant in pure samples.

To investigate the importance of heating, we assumed that the LA lines in Ge:Sb and Ge:Ga are due to EHD and carried out careful line fits to the spectra as a function of excitation. The results of the line fits are summarized in Table I; and in Fig. 13 we show a comparison of the experimental spectra with the best fitting theoretical spectra for two different excitation powers from the Ge sample with 8×10^{16} Sb/cm^3. The theoretical curves fit the experimental spectra quite well; although we have noted small but systematic deviations of experiment from theory on the high-energy tail of the spectra for all pump powers and for both samples. (This is not to be confused with the well-known deviations for the low-energy tail.[34]) The temperature needed to fit the data increased with increasing excitation power. However, due to the large increase in FWHM with pump power, higher densities were also required for higher pump powers. In addition, we note that the peaks shifted towards lower energies with larger excitation power and shorter delay time; whereas heating is expected to cause shifts in the opposite direction. Thus, we can rule out sample heating as the sole cause of the observed pump-power dependence of linewidth.

The maximum densities we obtained from the fits were 1.4×10^{17} cm^{-3} for the Ge:Sb sample and 2.1×10^{17} cm^{-3} for the Ge:Ga sample. Both are smaller than the 2.4×10^{17} cm^{-3} observed for pure Ge.[34] However, since smooth increase of the density with excitation power was observed, we believe that with sufficient pump power, density greater than 2.4×10^{17} cm^{-3} would be needed to account for the high-excitation results of Martin and Sauer[8] even if temperature rise is properly accounted for. It is possible that, for pump powers sufficiently low so as not to cause overheating of the sample, the lines in Ge:Ga, Ge:Li, and Ge:Sb are never entirely free of the interference from the impurity-induced line. Linefit results would therefore be meaningless.

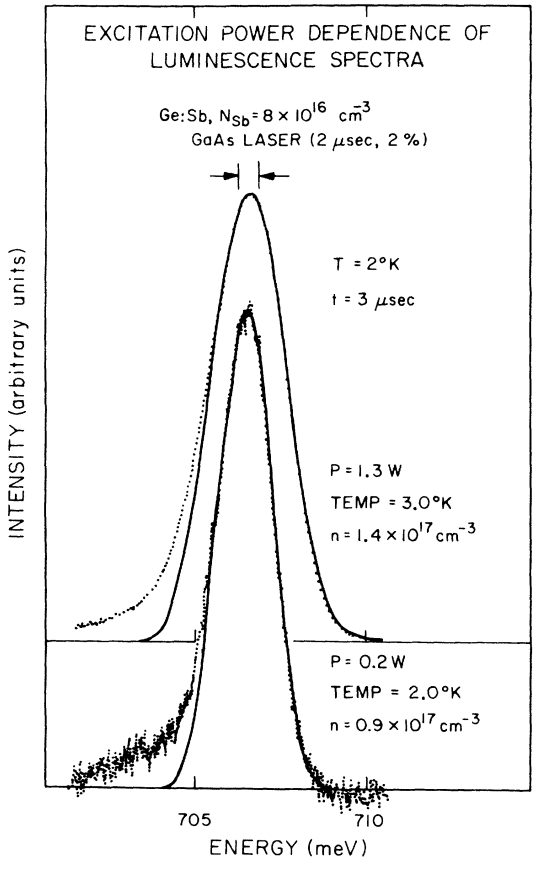

FIG. 13. Photoluminescence spectra at two excitation levels for Ge:Sb (dotted curves) at a delay time of 3 μsec. The relative intensity of the spectra is arbitrary. The solid curves are the best fitting theoretical EHD line shapes. The temperatures (TEMP) and densities (n) used for these fits are shown on the left of each spectrum below the pump power P. Bath temperature (T) for both cases was 2 °K.

4. Others

Other possible but unlikely causes of the complications of the doped Ge spectra are impurity-band to valence- or conduction-band transitions, existence of finite pressure on EHD, and partial sample filling by the electron-hole liquid. The last of these possibilities require further comment since it has been invoked to explain the pump-power dependence of the EHD linewidth in doped Ge.[8,9] Consider the results of the linefit for the Ge:Sb sample for 1.3-W excitation given in Table I. Taking into account the reflection loss at the Ge surface, the number of electron-hole pairs generated is 7×10^{12}/pulse. If we take the volume filled by the electron-hole liquid to be 1 mm^2 (laser spot size on the sample) by 300 μm deep,[24,25] the density of pairs generated by each laser pulse is 2×10^{16} cm^{-3}. This density is small compared to the fitted density of 1.4×10^{17} cm^{-3}.

The LA line in Ge:As is much less affected by the impurity-induced emission than the other LA lines in Ge:Li, Ge:Ga, and Ge:Sb. To understand the implications of this observation, we assume that the emission is made up of only two components, EHD and impurity-induced emission. (For convenience sake, we will refer to the latter as MEC.) The luminescence in the LA line then consists of two components

$$I_{\mathrm{MEC}}^{\mathrm{LA}}=N_{\mathrm{MEC}}R_{\mathrm{MEC}}^{\mathrm{LA}} \tag{1}$$

and

$$I_{\mathrm{EHD}}^{\mathrm{LA}}=N_{\mathrm{EHD}}R_{\mathrm{EHD}}^{\mathrm{LA}}, \tag{2}$$

where N_{MEC} and N_{EHD} are the effective number of pairs in MEC and EHD, respectively, and $R_{\mathrm{MEC}}^{\mathrm{LA}}$ and $R_{\mathrm{EHD}}^{\mathrm{LA}}$ are the rates for luminescence via LA-phonon emission by the two different components. Hence, we expect that

$$\frac{I_{\mathrm{MEC}}^{\mathrm{LA}}}{I_{\mathrm{EHD}}^{\mathrm{LA}}}=\left(\frac{N_{\mathrm{MEC}}}{N_{\mathrm{EHD}}}\right)\left(\frac{R_{\mathrm{MEC}}^{\mathrm{LA}}}{R_{\mathrm{EHD}}^{\mathrm{LA}}}\right). \tag{3}$$

The differences between the Ge:As, and Ge:Li, Ge:Sb, and Ge:Ga lines are due to a reduction in either $N_{\mathrm{MEC}}/N_{\mathrm{EHD}}$ or $R_{\mathrm{MEC}}^{\mathrm{LA}}/R_{\mathrm{EHD}}^{\mathrm{LA}}$ in the latter cases. It seems unlikely that the ratio of rates is significantly different for the donors. It seems more likely to us that $N_{\mathrm{MEC}}/N_{\mathrm{EHD}}$ is changed. Since the no-phonon decay channel is very weak[35] for the EHD and MEC in Ge:Li, Ge:Ga, and Ge:Sb, a large $N_{\mathrm{MEC}}/N_{\mathrm{EHD}}$ in them would only be reflected in the phonon-assisted lines.

The decay times for MEC in Ge:As and Ge:Ga are quite long (70 μsec in Ge:As at 1.5 °K,[11] and 76 μsec for Ge:Ga at 2 °K). Further, experiments on Ge doped with impurity concentrations of $\sim10^{15}$ cm^{-3} of shallow dopants exhibit decay times for free excitons which are essentially the same as those observed in pure Ge.[25] These results suggest a relatively slow rate of Auger recombination of the excitons bound to impurity centers in Ge. It is possible that the decay of free excitons occurs in both the doped and pure sample principally via some center (e.g., dislocations) other than the shallow dopants. If this is the case, then immobile excitons on a shallow dopant will decay at a rate slower than that for the free excitons.

V. CONCLUSION

We have reported the results of a study of the temperature, pump power, and time dependences of the photoluminescence spectra of Ge with doping level of up to 8×10^{16} cm^{-3}. For impurity concentration less than about 10^{15} cm^{-3}, the EHD line has properties similar to the EHD line in pure Ge. The LA line in Ge:As, with N_{As} up to 5×10^{16} cm^{-3} has properties which can be explained by the existing theories of EHD properties in doped Ge. The NP line in Ge:As and the LA lines in moderately heavily doped Ge:Li, Ge:Ga, and Ge:Sb have behaviors as functions of temperature, excitation power, and time unexpected of a EHD. It is rather difficult to explain these results without postulating the existence of additional lines caused by the impurities.

Comparing our data with those of doped Si, we found many correlations. These correlations suggest an interpretation of our data in terms of emission from electron-hole-droplet, broadened "multiexciton complex" lines, and BE bands. A more rigorous test of the theories of the properties of EHD in doped Ge must await further understanding of these impurity-induced emissions so that they may be sorted out from the EHD emission.

ACKNOWLEDGMENTS

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[1]C. D. Jeffries, Science 189, 955 (1975), and references contained therein.
[2]J. C. V. Mattos, K. L. Shaklee, M. Voos, T. C. Damen, and J. M. Worlock, Phys. Rev. B 13, 5603 (1976), and references contained therein.
[3]O. Christensen and J. M. Hvam, in *Proceedings of the Twelfth International Conference on the Physics of Semiconductors. Stuttgart, 1974*, edited by M. H. Pilkuhn (Teubner, Stuttgart, 1974), p. 56.
[4]J. M. Hvam and O. Christensen, Solid State Commun. 15, 929 (1974).
[5]A. S. Alekseev, V. S. Bagaev, T. I. Galkina, O. V. Gogolin, and N. A. Penin, Fiz. Tverd. Tela. 12, 3516 (1971) [Sov. Phys.-Solid State 12, 2855 (1971)].
[6]B. V. Novikov, R. L. Korchazhkina, and N. S. Sokolov, Fiz. Tverd. Tela. 15, 459 (1972) [Sov. Phys.-Solid State 15, 326 (1973)].
[7]C. Benoit à la Guillaume and M. Voos, Solid State Commun. 11, 1585 (1972).
[8]R. W. Martin and R. Sauer, Phys. Status Solidi B 62, 443 (1974).
[9]R. W. Martin, Phys. Status Solidi B 66, 627 (1974).
[10]T. Timusk and A. Silin, Phys. Status Solidi B 69, 87 (1975).
[11]A. L. Karuzskii, K. Betzler, B. G. Zhurkin, and V. P. Aksenov, *Molecular Spectroscopy of Dense Phases, Proceedings of the 12th European Congress on Molecular Spectroscopy* (Elsevier, Amsterdam, 1975), p. 139.
[12]Ya E. Pokrovskii, Phys. Status Solidi A 11, 385 (1972).
[13]B. G. Zhurkin, A. L. Karuzskii, V. P. Strahov, and V. A. Fradkov, Solid State Commun. 20, 207 (1976); and B. G. Zhurkin, A. L. Karuzskii, R. L. Korchazhkina, and V. A. Fradkov, *ibid.* 20, 341 (1976).
[14]B. Bergersen, P. Jena, and A. J. Berlinsky, J. Phys. C 8, 1377 (1975).
[15]G. Mahler and J. L Birman, Phys. Rev. B 12, 3221 (1975); and Solid State Commun. 17, 1381 (1975).
[16]D. L. Smith, Solid State Commun. 18, 637 (1976).
[17]G. A. Thomas, T. M. Rice, and J. C. Hensel, Phys. Rev. Lett. 33, 219 (1974).
[18]See, for example, V. P. Varshni, Physica (Utr.) 34, 149 (1967).
[19]J. R. Haynes, Phys. Rev. Lett. 4, 361 (1960).
[20]E. F. Gross, B. V. Novikov, and N. S. Sokolov, Fiz. Tverd. Tela. 14, 443 (1972) [Sov. Phys.-Solid State 14, 368 (1972)].
[21]R. W. Martin, Solid State Commun. 14, 369 (1974).
[22]M. Chen, S. A. Lyon, K. R. Elliott, D. L. Smith, and T. C. McGill, a preliminary account of this work appears in Nuovo Cimento (to be published).
[23]J. C. Hensel, T. G. Phillips, and T. M. Rice, Phys. Rev. Lett. 30, 227 (1973); C. Benoit à la Guillaume, M. Capizzi, B. Etienne, and M. Voos, Solid State Commun. 15, 1031 (1974); and R. M. Westervelt, T. K. Lo, J. L. Staehli, and C. D. Jeffries, Phys. Rev. Lett. 32, 1051 (1974).
[24]R. W. Martin, Phys. Status Solidi B 61, 223 (1974).
[25]M. Chen (unpublished).
[26]R. Sauer, Ref. 3, p. 42.
[27]K. Kosai and M. Gershenzon, Phys. Rev. B 9, 723 (1974).
[28]R. Sauer, Solid State Commun. 14, 481 (1974).
[29]T. P. McLean and R. Loudon, J. Phys. Chem. Solids 13, 1 (1960).
[30]R. Sauer, thesis (Stuttgart, 1973) (unpublished).
[31]V. I. Fistul', *Heavily Doped Semiconductors* (Plenum, New York, 1969), pp. 24–34.
[32]D. S. Pan, D. L. Smith, and T. C. McGill (unpublished).
[33]J. M. Ziman, *Electrons and Phonons* (Clarendon, Oxford, 1960), pp. 327–328, and references contained therein.
[34]G. A. Thomas, T. G. Phillips, T. M. Rice, and J. C. Hensel, Phys. Rev. Lett. 31, 386 (1973).
[35]The wave function of an electron localized near a donor is an admixture of Bloch functions at different points in the conduction band. Because of the small energy difference between the minima at the Γ and L points of the conduction band of Ge, the strong potential associated with the deeper donors, As and P, mix in states at the Γ point. This mixing makes the no-phonon recombination possible. The energy difference between the Γ and L point in the valence band of Ge is large so that one would not expect shallow acceptors to possess strong no-phonon transitions.