Picosecond optical measurement of free-carrier, intervalence-band, and indirect absorption in germanium at high optically created carrier densities

Arthur L. Smirl, J. Ryan Lindle, and Steven C. Moss
Department of Physics, North Texas State University, Denton, Texas 76203
(Received 6 March 1978; revised manuscript received 15 August 1978)

It has been suggested that enhanced intervalence-band and Coulomb-assisted indirect-absorption effects may be significant at the high optically created carrier densities encountered in the recent excite and probe experiments performed in germanium using intense picosecond optical pulses with a wavelength of 1.06 μm, and that these processes may result in an absorption versus carrier-density curve containing a minimum. Such a curve could then be combined with a recombination process to explain the results of the excite and probe experiments. Here, we report measurement of the combined free-carrier, intervalence-band, and indirect absorbance in thin germanium samples during these excite and probe experiments by exciting at 1.06 μm and by probing both at 1.06 μm and with a Raman-generated probe at 1.55 μm. The measurements suggest that these processes are significant at the high optically created carrier densities encountered in the present excite and probe experiments; however, they do not introduce a minimum in the absorption versus carrier-density curve as originally suggested.

I. INTRODUCTION

Recently, studies of the optical properties of high-density electron-hole plasmas generated in undoped germanium by intense ultrashort pulses have provided direct information concerning ultrafast electronic processes.[1-12] Among these studies are the measurement of the enhanced transmission of single ultrashort optical pulses through germanium[1,5] and the measurement of the temporal evolution of this enhanced transmission on a picosecond time scale using the excite and probe technique.[3,5] In the first of these experiments, the nonlinear transmission of a single picosecond 1.06-μm pulse was investigated as a function of incident optical pulse energy for sample temperatures of 100 and 297 K. The resulting data, reproduced from Smirl *et al.*,[5] are shown in Fig. 1 along with theoretical curves to be discussed later. In the second study, the sample was first irradiated by an excitation pulse of sufficient energy to cause the transmission of the germanium to be enhanced. This initial pulse was then followed at various time delays by a weak probe pulse, of the same wavelength, that measured the temporal evolution of the germanium transmission. Probable-pulse transmission data for various delay times and for sample temperatures of 100 and 297 K are presented in Fig. 2, again taken from Smirl *et al.*[5] The latter mea-

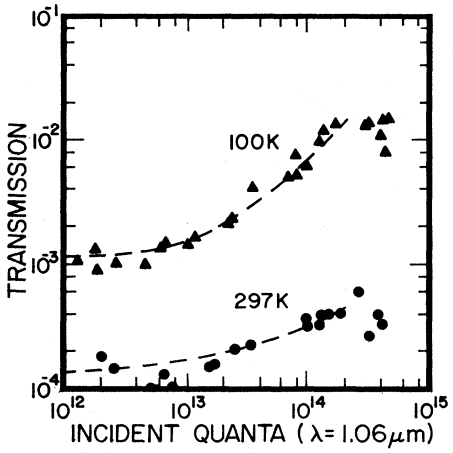

FIG. 1. Transmission of a 5.2-μm-thick germanium sample at 1.06 μm as a function of incident quanta at 1.06 μm for sample temperatures of 100 and 297 K. The dashed lines are theoretical curves from Elci *et al.* (Ref. 7). The data are from Smirl *et al.* (Ref. 5).

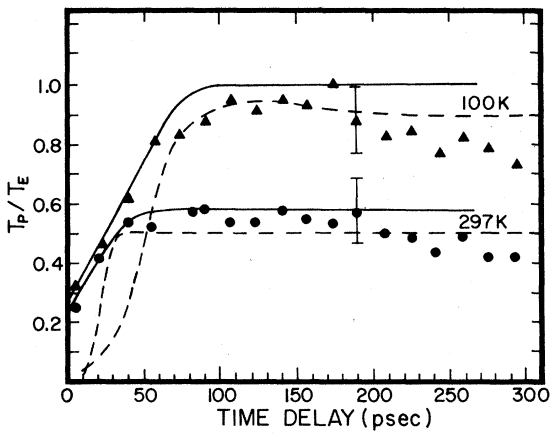

FIG. 2. Probe-pulse transmission vs delay between the excitation pulse at 1.06 μm and the probe pulse at 1.06 μm for sample temperatures of 100 and 297 K. The data are plotted as the normalized ratio of probe-pulse transmission to excitation-pulse transmission, T_P/T_E, arbitrary units. The dashed lines are theoretical curves from Elci *et al.* (Ref. 7). The solid lines are theoretical curves from van Driel (Ref. 15). The experimental data are from Smirl *et al.* (Ref. 5).

 © 1978 The American Physical Society

surements reveal that the probe transmission increases for approximately 100 psec following excitation for a sample temperature of 100 K; however, the rise in probe transmission is less than 40 psec at 297 K. Originally, Shank and Auston[3] attributed this rise in the probe transmission to a saturation of the absorption caused by a filling of the optically coupled conduction-band states and a depletion of the valence-band states by direct band-to-band transitions induced by the excitation pulse. Thus, the optically created carrier density, and consequently the increase in probe transmission, follows the integrated optical pulse energy. This interpretation was based on observations performed only at room temperature. As we shall later demonstrate, the rise in probe transmission at room temperature is indeed indistinguishable from other integration effects, in agreement with this interpretation. However, such a model cannot account for the slower rise observed at 100 K. Elci *et al.*,[7] in a recently proposed model, have attributed this rise in the probe transmission to a cooling of a hot electron-hole plasma created by the excitation pulse. In sharp contrast to this interpretation, Auston *et al.*[12] have stated that they expect the energy relaxation time to be too short to account for the rise in probe transmission. Indeed, Auston and McAfee[13] have suggested a plausible alternative explanation for the temporal evolution of the probe transmission in terms of enhanced Coulomb-assisted indirect absorption, intervalence-band absorption, and Auger recombination. This explanation does not require hot-electron effects.

Here, we report measurements of the *combined* free-carrier, intervalence-band, and indirect absorbance in thin germanium samples at a wavelength of 1.55 μm during excite and probe experiments at a wavelength of 1.06 μm. Our interests in these measurements are twofold. First, we want to ascertain whether or not free-carrier, intervalence-band, and indirect absorption effects are important in excite-probe experiments at 1.06 μm. Second, if these effects are important, can they, together with Auger effects, account for the rise in probe transmission.

In Sec. II, we briefly review the model presented by Elci *et al.*[7] and emphasize the processes, or omission of processes, that are relevant to the present measurements. In addition, in Sec. III, we briefly describe a model suggested by Auston and McAfee[13] that accounts for the rise in probe transmission without employing hot-electron effects. These reviews are then followed in Sec. IV by a description of the experimental apparatus and techniques for measuring the combined contributions of free-carrier, intervalence-band, and indirect absorption processes to the excite and probe response of germanium. Section V presents a discussion of our results, and the final section, Sec. VI, our conclusions.

II. COMMENTS ON THE HOT-ELECTRON MODEL

Briefly, according to the model proposed by Elci *et al.*[7], the transmission of a single optical pulse through a thin (5.2-μm-thick) germanium sample as a function of incident pulse energy (Fig. 1) and the transmission of a weak probe pulse as a function of time delay after an energetic pulse (Fig. 2) can be accounted for in terms of direct band-to-band absorption, free-carrier absorption, phonon-assisted intervalley scattering, phonon-assisted carrier relaxation, carrier-carrier collisions, and nonradiative recombination in the following manner. When an excitation pulse is incident on the germanium sample, the unreflected portion of the pulse enters the sample where most of it is absorbed by direct transitions, creating a large density of electrons (holes) in the central valley of the conduction (valence) band. The electrons are rapidly ($<10^{-14}$ sec) scattered to the conduction-band side valleys by long-wave-vector phonons. Carrier-carrier scattering events, which occur at a rate comparable to the direct absorption rate, ensure that the carrier distributions are Fermi-like and that both electron and hole distributions have the same temperature, which can be different from the lattice temperature. Since the photon energy $\hbar\omega_0$ is greater than either the direct energy gap E_0 or the indirect band gap E_G, such a direct absorption event followed by phonon-assisted scattering of an electron to the side valleys results in the photon giving an excess energy of $\hbar\omega_0 - E_G$ to thermal agitation. This excess energy results in an initial distribution temperature (approximately 1500 K for a lattice temperature of 300 K) due to direct absorption that is greater than the lattice temperature. Thus, the single-pulse transmission would begin at its Beer's-law value and increase as a function of incident optical pulse energy because of the partial filling (depletion) of the optically coupled states in the conduction (valence) band as a result of direct absorption. Other processes such as free-carrier absorption and nonradiative recombination events (i.e., Auger and plasmon-assisted recombination) can further raise the carrier temperature during the passage of the excitation pulse, while phonon-assisted intravalley relaxation processes can reduce the carrier temperature.

After the passage of the excitation pulse, the interaction region of the sample contains a large number of carriers (10^{19}–10^{20} cm^{-3}) with a high

distribution temperature. The final temperature is determined by the number of quanta in the excitation pulse and the relative strengths of the nonradiative recombination and the phonon-assisted relaxation rates as discussed by Latham *et al.*[10] As time progresses, the distribution will continue to cool by phonon-assisted intravalley relaxation. Experimentally, the probe pulse interrogates the evolution of the distribution after the passage of the excitation pulse and is a sensitive measure of whether the optically coupled states are available for absorption or are occupied. Immediately after the passage of the excitation pulse, the probe transmission is small since the electrons (holes) are located high (low) in the conduction (valence) bands because of the high distribution temperature, leaving the states that are optically coupled available for direct absorption. Later, as the distribution temperature cools and carriers fill the states needed for absorption, the transmission increases. The subsequent slow fall in probe transmission at longer delays, as seen in Fig. 2, is attributed to carrier recombination, which reduces the carrier density and once again frees the optically coupled states for absorption, and to diffusion.[3,11]

The theoretical fits from Elci *et al.*[7] to the single-pulse-transmission data and probe-pulse data are shown as dashed lines in Fig. 1 and Fig. 2. Given the complexity of the problem, the overall fit can be regarded as satisfactory. Nonlinear transmission measurements in which the energy band gap of the germanium sample was tuned by hydrostatic pressure[8] have been accounted for by this model as well.

Despite the apparent successes of this model, some basic questions remain concerning the roles of the various physical processes in determining the saturation and temporal evolution of the optical transmission of thin germanium samples under intense optical excitations. Elci *et al.*[7] noted that their calculations included only a limited number of the possible electronic interactions and contained serious assumptions that warranted further theoretical and experimental investigation. The major assumptions were the following: (i) The carrier-carrier collision rate was assumed to be high enough to justify taking the carrier distributions to be Fermi-Dirac. Ferry[14] has recently reexamined this approximation by calculating the time and energy dependence of the distribution function at the high carrier photogeneration rates encountered here. He concludes that on a time scale of tens of picoseconds the distribution function does indeed approximate a Fermi distribution; however, on shorter time scales it contains a δ-function-like spike located at the optically coupled states. Thus, for purposes of calculating the probe-pulse transmission, one may reasonably assume the distribution is Fermi-like. (ii) Carrier Fermi energies and temperatures were taken to depend only on time, rather than on both space and time, thus ignoring the pulse-propagation and carrier-diffusion problems within the optical interaction region of the sample. Therefore, parameters describing the electron-hole plasma, such as the electron number, must be viewed as spatial averages throughout the sample volume. Elci *et al.*[11] have recently extended their previous model, through a simple calculation, to indicate the possible effects of carrier diffusion on these optical measurements.

Elci *et al.*[7] noted at the outset that their work contained only a few of the many possible electronic interactions. Recent studies[4,12-14] indicate that processes other than those named above may be important. Most of these effects, such as band-gap narrowing,[14] intervalence-band absorption,[13] Auger recombination[4] and Coulomb-assisted indirect absorption,[12] are only observed at large carrier densities. The possible importance of including these processes in any interpretation of the rise in probe transmission is demonstrated in the following sections. One of the main objectives of the present study is to investigate the effects of the combined intervalence-band, Coulomb-assisted indirect, and free-carrier absorption and Auger recombination on the excite and probe measurements at 1.06 μm.

In the previous two paragraphs, we have outlined the assumptions and omissions of the initial hot-electron model; however, there is another problem associated with the original calculations that is of importance to the present work. The physical constants for germanium, specifically the electron-phonon coupling constants, are not well-known enough to allow a precise calculation of the energy relaxation rate. Latham *et al.*[10] have previously discussed this point in detail. For the theoretical fits shown in Fig. 2, the electron-phonon coupling constants are chosen as 6×10^{-4} erg cm^{-1} for a lattice temperature of 297 K and 2×10^{-4} erg cm^{-1} at 100 K. These values are within the range of the accepted theoretically and experimentally determined values listed by Latham *et al.*[10]; however, they are much lower than the mean value of 1×10^{-3} erg cm^{-1} as obtained from an average of the eight values listed. Since the carrier cooling rate is proportional to the square of the electron-phonon coupling constant, the fitted values result in carrier cooling rates that are 3 and 25 times slower than that obtained by using the average value. In fact, a repetition of the original calculations substituting the *average* electron-phonon coupling

constant shows (see Latham *et al.*,[10] (Fig. 8) that carrier cooling is too rapid to account for the rise in probe transmission, in complete agreement with the claims by Auston *et al.*[12] However, van Driel[15] has recently calculated the influence of hot phonons on the carrier-energy relaxation rate in these problems. These calculations suggest that the long equilibration time for the hot carriers is due to a relaxation bottleneck produced by a buildup of the optical-phonon population on a picosecond time scale. The results of these calculations, taking into account optical-phonon heating and employing only a single average temperature-independent electron-phonon coupling constant, are shown as solid curves in Fig. 2. Note that the inclusion of hot phonons accounts for one of the major discrepancies between the original theory and experiment. Namely, in contrast to the original theory that predicted a delayed, steep rise, the present theory shows a steep rise with gradual leveling off in agreement with the data. The solid curves in Fig. 2 were taken directly from van Driel.[15] The agreement between the modified theory and experiment is remarkable; however, this agreement should be regarded as somewhat fortuitous in view of the simplifications of the model, the limited number of processes included, and the uncertainty in many of the physical constants.

For emphasis, we now summarize the principal points of this section: (i) According to Elci *et al.*, the rise of the optical transmission of the germanium with time as monitored by a weak probe pulse is attributed to the cooling of a hot-electron–hole plasma, created by the absorption of the excitation pulse. (ii) In view of the above discussions and in the absence of any direct experimental evidence, the authors regard the question of the magnitude of the energy relaxation rate and the question of the origin of the rise of the probe transmission as open. It is in this spirit of suggesting plausible alternative models for evaluation that McAfee and Auston[13] first suggested the possibility of describing the rise in probe transmission in terms of free-carrier, intervalence-band, and Coulomb-assisted indirect absorption together with Auger recombination. This model is reviewed in Sec. III.

III. INDIRECT, INTERVALENCE-BAND, AND FREE-CARRIER ABSORPTION AND AUGER RECOMBINATION

In direct contrast to the above model, Auston and McAfee[13] have recently suggested an alternative explanation for the delayed probe-pulse transmission in germanium without requiring the introduction of hot-electron effects. In fact, their suggested explanation is based on three of the processes neglected by the original calculations of Elci *et al.*[7]: Auger recombination, Coulomb-assisted indirect absorption, and intervalence-band absorption. Specifically, this model is based on experiments by Auston *et al.*,[4] on 300-μm-thick samples, that are interpreted as demonstrating that Auger-recombination effects are important on picosecond time scales; on the observation of enhanced indirect Coulomb-assisted absorption in heavily doped n-type germanium by Haas[16]; and on the observation of strong intervalence-band absorption between the light- and heavy-hole and split-off valence bands in p-type germanium by Newman and Tyler.[17] Since the present work is an attempt to experimentally investigate the role of these processes in determining the evolution of the optical properties of germanium *at high carrier densities*, we shall briefly state the conclusions of these last two works. We then review the manner in which enhanced indirect absorption and intervalence-band absorption together with Auger recombination could account for the probe transmission versus time delay after an intense excitation pulse in thin germanium samples.

Haas[16] reports that the indirect absorption rises more rapidly with photon energy in n-type germanium than in pure germanium. The effects considered as sources for this extra absorption are (i) modification of the band structure by impurities, (ii) impurity-assisted indirect transitions, and (iii) Coulomb-assisted indirect transitions, where the virtual scattering of the electrons from the central to the side valley is by electron-electron scattering. Haas concludes that at high concentrations electron-electron scattering dominates the indirect transitions. If we extrapolate his results, they suggest that, at an optical wavelength of 1.06 μm and electron densities as large as 2×10^{20} cm^{-3}, the indirect-absorption coefficient might be as large as 10^4 cm^{-1}.

Newman and Tyler[17] report measurement of the free-hole absorption in p-type germanium as a function of impurity and carrier concentration. The effects to be considered in explaining the strong observed free-hole absorption at high carrier concentrations are (i) modification of the band structure by impurities, (ii) band-to-band transitions between light- and heavy-hole valence bands and the split-off valence band as the position of the Fermi level changes within the valence band with doping, and (iii) indirect transitions induced by charged-impurity centers. They conclude that their observations suggest that both intervalence band transitions and impurity-assisted indirect transitions contribute. In experiments employing undoped samples, where the carriers are generated by optical absorption, only the *intervalence-band* process will be significant. If their results

are extrapolated to a photon energy of 1.17 eV and a concentration of 2×10^{20} cm^{-3}, the free-hole absorption coefficient could again be as large as 10^4 cm^{-1}.

The suggestion of an alternative explanation for the delayed probe transmission of optically excited germanium without requiring phonon-assisted relaxation of hot electrons is based on the two mechanisms discussed above. In particular, it is based on the details of the way germanium absorption might vary with increasing optically created carrier density. Consider the behavior of the total absorption coefficient as the carrier density increases because of band-to-band transitions during the passage of an intense excitation pulse. (The carrier temperature is taken to be that of the lattice, since all carrier energy relaxation processes are assumed to be too rapid for observation, in contrast to Elci *et al.*[7]) The *direct* absorption coefficient will decrease with increasing density as optically created electrons (holes) clog the states needed for optical absorption in the conduction (valence) band. Meanwhile, as the density increases, the additional mechanisms discussed previously, Coulomb-assisted indirect absorption, intervalence-band absorption, and free-carrier absorption, increase. Thus, the absorption coefficient could initially decrease with increasing density, as the direct absorption coefficient saturates, then increase with increasing density, as the free-carrier, intervalence-band, and indirect absorption coefficients dominate. In short, the fact that the direct absorption coefficient decreases with increasing carrier number and that the enhanced intervalence-band, free-carrier, and Coulomb-assisted indirect absorption coefficients increase can result in introducing a minimum in the absorption versus density relationship as suggested by Auston *et al.*[12] We denote the density at which the minimum absorption might occur as n_{min}. The rise in the probe transmission with time can now be accounted for by combining the details of the way the absorption saturates with carrier density together with a monotonic decrease in carrier density with time due to Auger recombination in the following manner. The absorption of the excitation pulse creates an initial carrier density greater than n_{min}. As the carrier density is decreased by Auger recombination, the absorption coefficient of the sample will decrease in time until the carrier density reaches n_{min}, then increase. Thus, the probe transmission will increase then decrease if the initial, optically created carrier density is greater than n_{min}. We shall henceforth refer to the model described in this section as the recombination model because of the role of the Auger recombination.

For emphasis, we summarize the features of the two models that are essential for comparison with present measurements. We note, once again, that Elci *et al.*[7] attribute the rise in probe transmission with delay after an excitation pulse to phonon-assisted cooling of a hot carrier distribution and that free-carrier, intervalence-band, and Coulomb-assisted indirect transitions were either omitted from the model or judged to be insignificant. Auger-recombination processes were omitted from this model. The recombination model accounts for the rise in probe transmission by combining Auger recombination with an absorption versus density relationship containing a minimum. We stress that the success of the second model, as it now stands, depends on the absorption decreasing then increasing with carrier density: *there must be an absorption minimum.*

IV. EXPERIMENT

The particular experimental configuration used to measure the contributions of intervalence-band, free-carrier, and indirect absorption to the generation and evolution of dense, optically created electron-hole plasmas in thin germanium samples is depicted in Fig. 3. This arrangement is similar to the arrangement utilized by Auston *et al.*[4] In this application of the excite and probe technique, a high-density plasma is created by direct absorption of an intense excitation pulse, and the evolution of the plasma is monitored by a second probe pulse. The excitation pulses were selected by a laser-triggered spark gap and a Pockel's cell from trains of pulses produced by a mode-locked Nd-glass laser. The pulses were 5 to 10 psec in duration and had peak powers of approximately 10^8 W at a wavelength of 1.06 μm, and they produced a measured irradiance of approximately 1×10^{-2} J/cm^2 when focused on the crystal surface. The

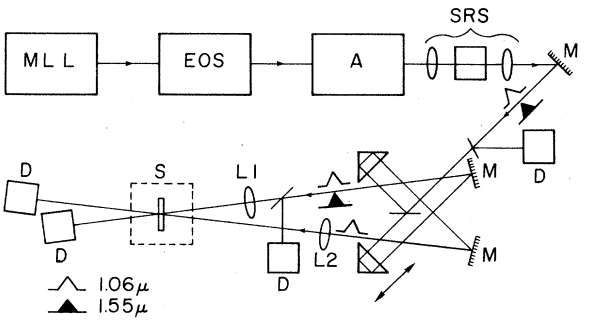

FIG. 3. Block diagram of the experimental configuration for excite and probe measurements at 1.06 and 1.55 μm, where MLL denotes the mode-locked laser, EOS the electro-optical switch, A the laser amplifier, SRS the stimulated-Raman-scattering cell, M a mirror, D a detector, $L1$ and $L2$ lens, and S the sample.

plasma produced by the absorption of the excitation pulse was probed using weak pulses of two types: one had an energy greater than the direct energy band gap for germanium, and the other had an energy less than the direct gap but greater than the indirect gap. The former was derived from the excitation pulse using a beam splitter as shown in Fig. 3. The latter, having a wavelength of 1.55 μm, was produced by stimulated Raman scattering in benzene. The desired probe wavelength was selected by employing either a thick wafer of silicon to reject the 1.06-μm radiation or narrow bandpass optical filters to reject the 1.55-μm radiation. Other wavelengths generated by the stimulated scattering in benzene, such as 1.18 μm, were rejected by carefully selected interference filters. We emphasize that the energy of a quanta at 1.06 μm (1.17 eV) is sufficient to excite direct band-to-band transitions in germanium as well as free-carrier, intervalence-band, and indirect transitions; whereas, the energy of a quanta at 1.55 μm (0.80 eV) falls below the direct band gap but above the indirect gap and is, thus, only a measure of the combined free-carrier, intervalence-band, and indirect processes. The incident excitation pulse irradiance was measured and the overlap of excitation and probe pulses was ensured employing techniques described in Ref. 4. The excitation pulse irradiance was determined by measuring the energy transmitted through a pinhole located at the focus of the excitation beam and coplanar with the germanium wafer using a calibrated detector. The probe beam was more tightly focused than the excitation beam to ensure complete spatial overlap with the excitation beam. The size of the pinhole was such that it transmitted 50% of the excitation pulse and 90% of the probe. Despite these precautions, we observed indications of day-to-day variations in excitation-beam and probe-beam overlap. We attribute these variations to "hot" spots in the focused multimode laser pulses.

The germanium sample was a high purity (ρ_{min} = 40 Ω cm) single crystal cut with the (111) plane as face. The sample was polished and etched with Syton to a thickness of 6 μm as determined by interferometric techniques.

V. RESULTS AND DISCUSSION

Here, we present and discuss the results of three separate measurements. (i) In the first of these, the sample is illuminated by an intense excitation pulse at a wavelength of 1.06 μm. The transmission of a weak probe pulse at 1.06 μm that arrives at a variable, delayed time after the excitation pulse is then monitored. We perform these measurements, which repeat those by Smirl *et al.*,[5] to ensure that the rise in probe transmission can be separated from any artifacts of the measurement technique. (ii) Next, the sample is irradiated by 1.06-μm-excitation pulses of various intensity that create electron-hole plasmas of varying density by direct band-to-band transitions. The change in absorbance at 0.80 and 1.17 eV, as a function of plasma density, is then measured by monitoring the transmission of weak probe pulses at 1.55 and 1.06 μm that arrive a short fixed delay after excitation. These 1.06-μm-probe transmission measurements will provide the absorbance versus density curve needed for investigation of the recombination model described in Sec. III. The 1.55-μm-probe measurements will give a measure of the importance of free-carrier, intervalence-band, and indirect absorbance as a function of carrier density. (iii) Finally, the transmission of a weak 1.55-μm-probe pulse is measured at various delays following an intense 1.06-μm-excitation pulse. The 1.55-μm-probe pulse monitors the temporal evolution of the change in the combined free-carrier, intervalence-band, and indirect absorbance following the photogeneration of a dense electron-hole plasma.

The results of experiments that measure the temporal evolution of the transmission of a thin germanium sample at a wavelength of 1.06 μm following the creation of a dense electron-hole plasma are shown in Fig. 4. The measurements were performed in the following manner (see insert, Fig. 4). The sample was irradiated by 1.06-μm-excitation pulses containing approximately 2×10^{15} quanta, and the transmission of each pulse was measured. Each excitation pulse was then followed

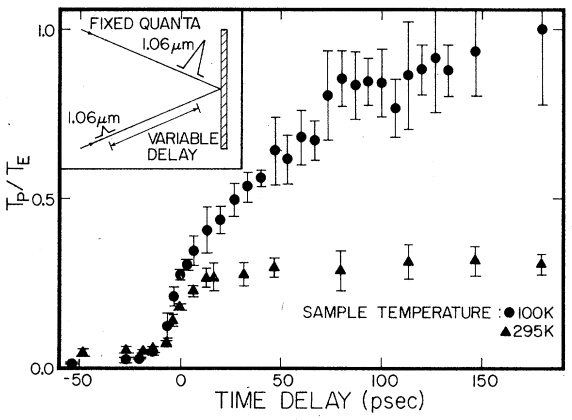

FIG. 4. Probe-pulse transmission vs delay between the excitation pulse at 1.06 μm and the probe pulse at 1.06 μm for sample temperatures of 100 and 295 K. The data are plotted as the normalized ratio of probe-pulse transmission to excitation-pulse transmission, T_P/T_E, in arbitrary units. The error bars represent one statistical standard deviation.

at various delays by a weak probe pulse at 1.06 μm. These measurements were performed for sample temperatures of 100 and 295 K. The data are plotted as the ratio of probe-pulse transmission T_P to excitation-pulse transmission T_E, in arbitrary units, versus time delay in picoseconds. The arbitrary units are chosen so that the peak of the probe transmission at 100 K is unity. The actual value of the ratio T_P/T_E was observed to be as large as six; however, this value strongly depends on the quality of the spatial overlap of the focused excitation and probe pulse on the sample surface. These measurements are identical to those performed by Smirl *et al.*, as presented in Fig. 2. However, when comparing the two sets of data, one must realize that the sample thickness and focused optical spot sizes are not identical.

The measurements of Smirl *et al.*[5] are repeated so that we can more carefully investigate the possibility that the rise in probe transmission follows the integrated optical energy. Specifically, we want to be assured that the rise in probe transmission is a real effect and that it is not an artifact of the excite-probe technique that can be attributed to the finite width of the optical pulses. For comparison, we have calculated the probe-pulse transmission by assuming a Drude model for the electron-hole plasma, calculating the optical polarization, and substituting into the wave equation. The details of such a procedure are published elsewhere,[3,18] and they are not repeated here. The calculated rise in the probe-pulse transmission, neglecting all decay processes, is simply proportional to the integral of the pulse autocorrelation function. The resulting theoretical integration curve assuming Gaussian-shaped optical pulses of 10-psec width [full width at half maximum (FWHM)] is shown as a solid line in Fig. 5. Experimental data from Fig. 4 are plotted on an expanded time scale for comparison. The authors conclude that the experimental rise in probe transmission at 295 K is indistinguishable from integration effects, in agreement with the original interpretation of the room temperature data by Shank and Auston.[3] However, the rise at 100 K cannot be attributed to such effects and represents a physical effect. It is this rise in probe transmission at 100 K that is the object of our investigation. Finally, we note that coherent coupling effects[3,18] are observed in these experiments as well; however, the delay increments of Fig. 5 are too coarse to resolve them.

The results of the measurement of the change in absorbance of the thin germanium crystal as a function of increasing carrier number (incident excitation pulse energy at 1.06 μm) are shown in Fig. 6 for photon energies of 1.17 and 0.8 eV. These data were obtained in the following manner.

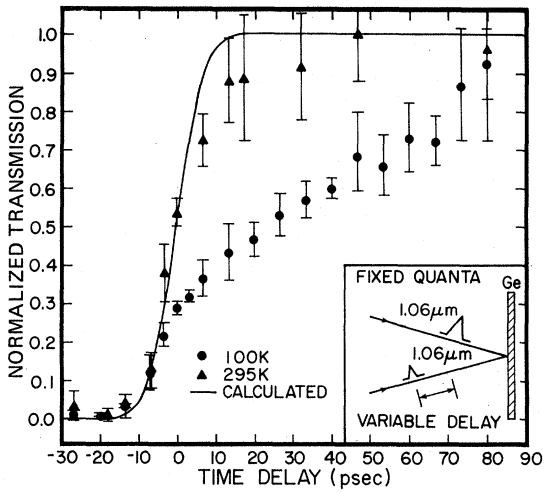

FIG. 5. Normalized probe-pulse transmission in arbitrary units vs delay between the excitation pulse at 1.06 μm and the probe pulse at 1.06 μm for sample temperatures of 100 and 295 K. The solid line represents a theoretical integration curve assuming Gaussian-shaped optical pulses of 10 psec width (FWHM).

The crystal was illuminated by variable energy pulses with a wavelength of 1.06 μm, and the transmission of each pulse was measured. Each pulse at 1.06 μm was followed immediately (at fixed delays of 17 and 26 psec) by pulses that monitored the absorbance of the crystal at wavelengths of 1.55 and 1.06 μm. The optical absorbance at 1.17 eV is seen to *decrease* by approximately 3.5 as the carrier number increases. This corresponds to a transmission *increase* by a factor of 30. By contrast, the absorbance at 0.8 eV *increases*

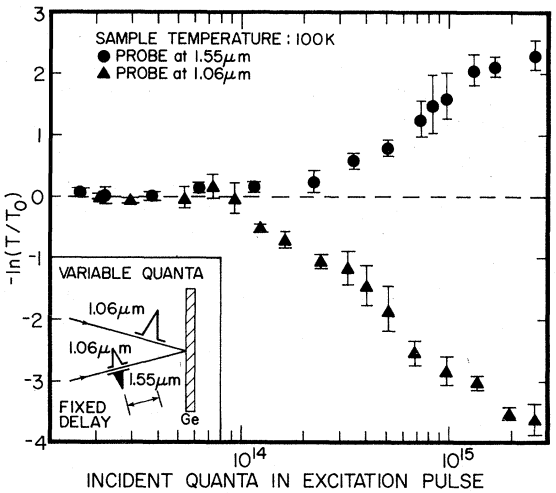

FIG. 6. Change in absorbance, $-\ln(T/T_0)$, of the germanium sample at 1.06 and 1.55 μm as a function of incident excitation-pulse energy at 1.06 μm where T_0 is the linear transmission of the sample at the wavelength under consideration.

roughly by 2.3, corresponding to a *decrease* in transmission by approximately an order of magnitude. Each datum point shown is the average of at least eight separate observations. The data were very reproducible within the error bars.

A striking feature of the data presented in Fig. 6 is that the absorbance of the crystal at 1.06 μm *does not decrease then increase* as required by the recombination model of Sec. III. In fact, as can be seen from Fig. 6, any *decrease* in carrier density with time caused by carrier recombination will be accompanied by an *increase* in the total absorbance at 1.06 μm. Thus, a temporal decay of carrier density alone cannot be combined with the absorption versus density relationship to account for the rise in probe transmission at 1.06 μm. The *total* change in absorbance of the crystal at 1.06 μm as the carrier density is increased is given by

$$-\ln\left(\frac{T}{T_0}\right)=\int_0^l \Delta\alpha_{\mathrm{DA}}(x)\,dx+\int_0^l [\Delta\alpha_{\mathrm{FC}}(x)+\Delta\alpha_{\mathrm{IB}}(x)+\Delta\alpha_{\mathrm{ID}}(x)]\,dx\,, \tag{1}$$

where T_0 is the linear transmission of the sample; $\Delta\alpha_{\mathrm{DA}}(x)$ is the change in the direct-absorption coefficient caused by the increased carrier number at the position x into the crystal; $\Delta\alpha_{\mathrm{FC}}(x)$, $\Delta\alpha_{\mathrm{IB}}(x)$, and $\Delta\alpha_{\mathrm{ID}}(x)$ are the changes in the absorption coefficient caused by free-carrier, intervalence-band, and indirect absorption, respectively; and l is the crystal thickness. The electron density and, consequently, the absorption coefficients are allowed to depend upon position. The last term on the right-hand side of Eq. (1) will be positive since free-carrier, intervalence-band, and Coulomb-assisted indirect absorption coefficients all increase with carrier density, and the first will be negative because of the partial saturation of the available optically coupled electronic states as the density increases. Since the overall absorbance at 1.17 eV is observed to monotonically decrease, we conclude that the saturation of the absorption is dominated by changes in the direct absorption coefficient. Although the free-carrier, intervalence-band, and indirect absorbance changes are smaller in magnitude and opposite in sign to those caused by saturation of the direct absorption, it is possible for them to significantly affect the overall magnitude of the total absorbance change. Inspection of Eq. (1) reveals that omission of these processes would result in a more rapid decrease in total absorbance with increasing carrier number than when they are included.

The measurement of the change in absorbance at 0.8 eV as the carrier number is increased by direct absorption of excitation pulses at 1.17 eV, as displayed in Fig. 6, tends to substantiate the arguments of the previous paragraph. That is, the change in absorbance at 0.8 eV, which is sensitive to free-carrier, intervalence-band, and indirect absorption effects, is slightly smaller in magnitude and opposite in sign to that measured at 1.17 eV, which is sensitive to direct absorption effects as well. Thus, if the results of the measurement of free-carrier, intervalence-band, and indirect absorbance at 0.8 eV could be extrapolated to 1.17 eV, we would conclude that the change in absorbance due to these processes is smaller in magnitude and opposite in sign to that caused by the saturation of direct absorption coefficient. However, we would also conclude that the change in the *combined* free-carrier, intervalence-band, and indirect absorbance is of sufficient magnitude to substantially slow the saturation of the total absorbance at 1.06 μm with the increasing carrier number. However, care must be taken when extrapolating absorbance measurements at 0.8 to 1.17 eV. Free-carrier and intervalence-band absorption coefficients are expected to decrease with increasing photon energy for a given (large) carrier density[17] while, according to Ref. 16, the Coulomb-assisted indirect absorption coefficient should increase.

The experiments shown schematically in the inset of Fig. 6 were repeated for a sample temperature of 295 K. Similar results were obtained. For the maximum carrier densities achieved at room temperature, the decrease in absorbance at 1.06 μm was 2.2 and the increase in absorbance at 1.55 μm was 1.8.

The results of excite-probe experiments that measure the temporal evolution of the change in absorbance at 1.55 μm are presented in Fig. 7. In this experiment, the sample was irradiated by

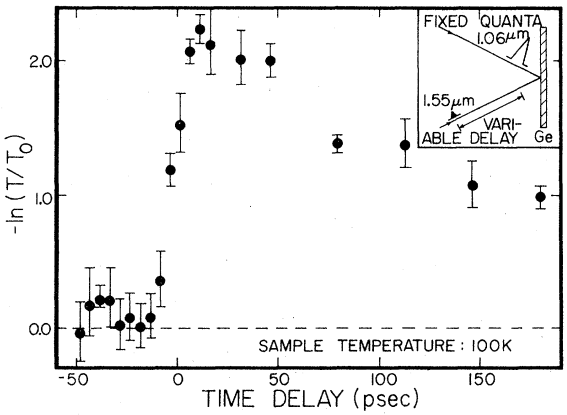

FIG. 7. Change in probe-pulse absorbance, $-\ln(T/T_0)$, vs delay between the excitation pulse at 1.06 μm and the probe pulse at 1.55 μm, where T_0 is the linear transmission of the probe pulse at 1.55 μm.

an optical pulse at 1.06 μm containing roughly 2×10^{15} quanta and was probed at various delays by a weak pulse having a wavelength of 1.55 μm. The results of the probe measurements at 1.55 μm are similar to those obtained by Auston *et al.*[4] However, these authors stated that they performed their measurements at excitation intensities such that the absorption of the excitation pulse was *linear*. Our experiments are clearly performed in the *nonlinear* region. In addition, the measurements of Auston *et al.*[4] were performed on a 300-μm-thick sample, our sample was 6-μm thick.

The measurements presented in Fig. 7 indicate that free-carrier, intervalence-band, and indirect absorption can be significant at the carrier densities encountered during the excite and probe experiments at 1.06 μm presented here. Auston *et al.*[4] attribute this decrease of the probe pulse absorbance at 1.55 μm with delay to a decrease in free-carrier absorption caused by a temporal decay in carrier density due to Auger recombination. The present experiments only allow the measurement of the change in the *combined* free-carrier, intervalence-band, and indirect absorbance, and they do not provide for a convenient separation of their individual contributions. These measurements were performed for a sample temperature of 295 K, as well. The results are similar to those of Fig. 7. It is important to note that we observe a strong temperature dependence in the rise in probe transmission at 1.06 μm (see Fig. 4 or 5); however, we do not observe a similar *strong* temperature dependence at 1.55 μm. We believe this is a further indication that indirect, free-carrier, and intervalence-band processes do not dominate the rise in probe transmission at 1.06 μm.

VI. SUMMARY AND CONCLUSIONS

The measurements by Smirl *et al.*[5] of the transmission of a 1.06-μm-probe pulse as a function of time delay after an intense 1.06-μm-excitation pulse have been carefully repeated for sample temperatures of 100 and 295 K. The rises in probe transmission for the two temperatures have been compared to a calculated integration curve, assuming an optical pulsewidth of 10 psec. We conclude from this comparison that the rise in probe transmission at 295 K is indistinguishable from the integration curve, but that the rise at 100 K is much slower than either the integration curve or the rise at 295 K and is not an artifact of the measurement technique.

The transmission of a thin germanium sample at 1.55 and 1.06 μm has been measured as a function of optically created carrier densities. Over the range of densities encountered in these experiments, the absorption versus density relationship at 1.17 eV *does not* exhibit a minimum. Thus, a temporal decay of carrier density alone cannot be combined with this absorption versus density relationship to account for the rise in probe transmission at 1.06 μm exactly as suggested in Sec. III. In addition, these measurements indicate that the *combined* free-carrier, intervalence-band, and indirect absorbance changes are opposite in sign and smaller in magnitude than the changes caused by saturation of the direct absorption. As a result, we believe that the decrease in absorbance at 1.06 μm with increasing carrier number is dominated by a saturation of the direct absorption coefficient; however, the rate of this decrease in absorbance is slowed by the contributions of these "other" processes that are opposite in sign.

In addition, the absorbance of a 1.55-μm-probe pulse has been measured as a function of time delay after an intense 1.06-μm-excitation pulse. The 1.55-μm-probe absorbance decays by approximately 0.8 in the first 100 psec following excitation, corresponding to a transmission increase of a factor of approximately 2. This represents a significant decay in the combined free-carrier, intervalence-band, and indirect absorbance during this period. Contrary, however, to measurements of the probe rise at 1.06 μm, the decay of probe absorbance at 1.55 μm exhibited no strong dependence on sample temperature.

As a result of the present measurements, the authors feel that free-carrier, intervalence-band, and Coulomb-assisted transitions combined with Auger recombination are not the mechanisms dominating the rise in 1.06-μm-probe transmission at 100 K. The contributions of these processes are significant, however, and they must be accounted for by any successful model. Unfortunately, the present measurements yield no *direct* information concerning carrier distribution temperatures or energy relaxation rates, and the question of attributing the rise in 1.06-μm-probe transmission to a cooling of a hot carrier plasma created by the excitation pulse remains unresolved.

Finally, we emphasize that we are aware that our measurements at 1.55 μm (0.8 eV) monitor the free-carrier, free-hole, and indirect absorption at an energy different from that of the experiments we are attempting to interpret (rise in probe transmission at 1.17 eV); however, we believe these experiments give the best available indication of the possible importance of these processes at the high optically created carrier densities encountered in excite and probe studies at 1.06 μm.

ACKNOWLEDGMENTS

The authors wish to acknowledge their debt to Dave Auston and Sigrid McAfee of Bell Laboratories for suggesting and sharing the recombination model presented in this paper and for their helpful discussions. This work was supported by the Office of Naval Research and the North Texas State University Faculty Research Fund.

[1]C. J. Kennedy, J. C. Matter, A. L. Smirl, H. Weichel, F. A. Hopf, and S. V. Pappu, Phys. Rev. Lett. 32, 419 (1974).

[2]D. H. Auston and C. V. Shank, Phys. Rev. Lett. 32, 1120 (1974).

[3]C. V. Shank and D. H. Auston, Phys. Rev. Lett. 34, 479 (1975).

[4]D. H. Auston, C. V. Shank, and P. LeFur, Phys. Rev. Lett. 35, 1022 (1975).

[5]A. L. Smirl, J. C. Matter, A. Elci, and M. O. Scully, Opt. Commun. 16, 118 (1976).

[6]H. M. van Driel, A. Elci, J. S. Bessey, and M. O. Scully, Opt. Commun. 20, 837 (1977).

[7]A. Elci, M. O. Scully, A. L. Smirl, and J. C. Matter, Phys. Rev. B 16, 191 (1977).

[8]H. M. van Driel, J. S. Bessey, and R. C. Hanson, Opt. Commun. 22, 346 (1977).

[9]J. S. Bessey, B. Bosacchi, H. M. van Driel, and A. L. Smirl, Phys. Rev. B 17, 2782 (1978).

[10]W. P. Latham, Jr., A. L. Smirl, and A. Elci, Solid State Electron. 21, 159 (1978).

[11]A. Elci, A. L. Smirl, C. Y. Leung, and M. O. Scully, Solid State Electron. 21, 141 (1978).

[12]D. H. Auston, S. McAfee, C. V. Shank, E. P. Ippen, and O. Teschke, Solid State Electron. 21, 147 (1978).

[13]This model was first discussed by D. H. Auston and S. McAfee at the International Conference on Hot Electrons in Semiconductors, July 6–8, 1977, Denton, Texas (unpublished). The possible importance of enhanced Coulomb–assisted indirect transitions to the interpretation of experiments at high optical excitations and the possibility of these indirect transitions introducing a minimum in the absorption versus density relationship was first discussed in Ref. 12 by D. H. Auston, S. McAfee, C. V. Shank, E. P. Ippen, and O. Teschke. The details of the model as presented here are courtesy of S. McAfee and D. H. Auston (private communication). This model was presented by Auston and McAfee in the spirit of illustrating that processes other than those considered by Elci *et al.* (Ref. 7) could be important in interpreting the rise in probe transmission. We thought the model so attractive as to deserve investigation. As a result of their informal remarks, the authors undertook the present studies.

[14]D. K. Ferry (unpublished).

[15]H. M. van Driel (unpublished).

[16]C. Haas, Phys. Rev. 125, 1965 (1962).

[17]R. Newman and W. W. Tyler, Phys. Rev. 105, 885 (1957).

[18]E. P. Ippen and C. V. Shank, in *Ultrashort Light Pulses*, edited by S. L. Shapiro, (Springer-Verlag, New York, 1977), p. 110.