# Determination of Intervalley Scattering Rates in GaAs by Subpicosecond Luminescence Spectroscopy

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We report a slow rise of luminescence in GaAs following subpicosecond photoexcitation and show that it results from a slow return of electrons from the $L$ to the $\Gamma$ valley. By fitting our data with an ensemble Monte Carlo calculation, we determine the $\Gamma$-$L$ deformation potential to be $(6.5 \pm 1.5) \times 10^8$ eV/cm. We show that the electrons returning to the $\Gamma$ valley act as a source of heating for the photoexcited plasma. We further show the importance of electron-electron scattering and inadequacy of a simple phonon-cascade model, even at a density as low as $5 \times 10^{16}$ cm$^{-3}$.

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Scattering of electrons between the various valleys of the conduction band in a semiconductor plays an important role in the determination of high-field transport properties of semiconductors and is of significant interest in hot-electron physics. These intervalley scattering processes also govern the physics of many high-speed devices and may play an important role in the initial relaxation of carriers excited by ultrafast lasers, an area of intense current interest.[1-7] In spite of their importance, one lacks a quantitative understanding of intervalley scattering processes. Even for an important semiconductor such as GaAs, values for $D_{\Gamma L}$ (deformation potential which governs the intervalley scattering rate) range from $1 \times 10^9$ eV/cm (fits to $I$-$V$ curves[8]), to $7 \times 10^8$ eV/cm (nonlinear optical studies[9] at 10.6 $\mu$m, to $1.5 \times 10^8$ eV/cm (time-resolved Raman scattering studies[10]).

We present results on subpicosecond luminescence spectroscopy in GaAs which clearly demonstrate the important role of intervalley scattering in electron relaxation and which determine the intervalley scattering rates in GaAs. These experiments provide results in the time range 0.5 to 15 ps, which has remained unexplored in spite of the intense current interest in relaxation of photoexcited carriers in semiconductors. Our most important finding is that, following excitation by a $<0.5$-ps pulse, the luminescence intensity in GaAs increases very slowly, taking approximately 10 ps to reach its maximum value. This behavior is in stark contrast to the relatively fast rise of luminescence ($\simeq 2$ ps) in InP, in which there is no significant intervalley transfer of electrons for our excitation energy. We show that the slow rise in GaAs luminescence is a result of the slow return of electrons from the $L$ to the $\Gamma$ valley and determine $D_{\Gamma L}$ by comparing our experimental results with an ensemble Monte Carlo calculation. We further demonstrate that intervalley scattering also plays an important role in plasma relaxation by acting as a source of heating and thus slowing down the cooling of the electron gas, an effect not considered before. We also show the importance of electron-electron scattering and the inadequacy of a simple phonon-cascade model even at a density as low as $5 \times 10^{16}$ cm$^{-3}$.

The GaAs sample was a 460-nm-thick GaAs active layer clad by AlGaAs layers.[4] The InP sample was a single 2-$\mu$m-thick layer grown on InP substrate.[11] The samples (at 300 K) were excited by $<500$-fs pulses from a dye laser operating at 2.04 eV. Luminescence spectra with subpicosecond time resolution were measured with use of a recently developed system which provides the zero time delay with high accuracy.[12]

Figure 1 shows typical luminescence spectra of GaAs for three different delays. At 1, 2, and 10 ps, the spectra can be well fitted by thermalized (Fermi-Dirac–type) distribution functions with temperatures larger than the lattice temperature. Even at earlier times, 0.5 ps, the observed spectra peak close to the band-gap energy (1.425 eV) and are qualitatively similar to those expected for thermalized distribution functions with high effective temperatures ($>600$ K).

The most remarkable aspect of the data in Fig. 1 is that the luminescence intensity near the band-gap energy as well as the integrated luminescence intensity shows significant increase for nearly 10 ps after the end of the excitation pulse. This is shown most clearly in Fig. 2(a) where we have plotted the time evolution of the luminescence intensity at 1.45 eV for GaAs. The curve in Fig. 2(b) shows the rise in more detail; the filled circles show the integrated luminescence intensity. Essentially identical rise curves have also been obtained at excitation densities from $5 \times 10^{16}$ cm$^{-3}$ to $1 \times 10^{18}$ cm$^{-3}$ (see also Ref.

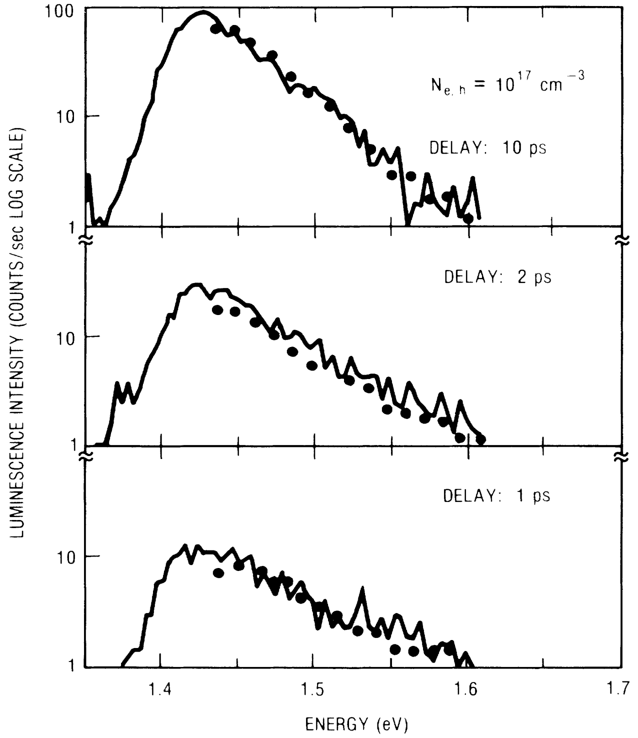

FIG. 1. Luminescence spectra of GaAs at 300 K excited by < 0.5-ps pulses at 2.04 eV for three different delays after excitation. Zero delay corresponds to the center of the excitation pulse. Circles are calculated with ensemble Monte Carlo method with $D_{\Gamma L} = 6 \times 10^8$ eV/cm and parameters from Ref. 13. There are no adjustable parameters, except that the peaks of the calculated and measured spectra were matched at 10 ps.

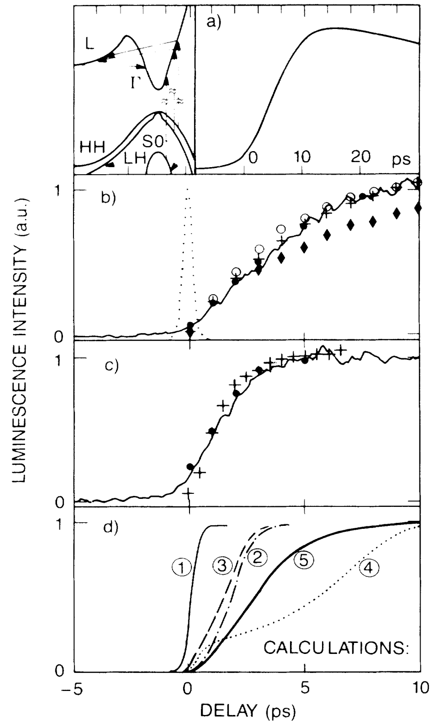

FIG. 2. Luminescence intensity at 300 K vs delay. (a) GaAs at 1.45 eV; (b) same as (a) on expanded scale; the filled circles show the spectrally integrated intensity; (c) InP, same as (b); and (d) different calculations, curves 1 to 5, as explained in the text. Results of ensemble Monte Carlo calculations are also shown: (b) $D_{\Gamma L} = (4, 6, \text{ and } 8) \times 10^8$ eV/cm for GaAs (lozenges, crosses, and open circles, respectively) and (c) InP. Parameters for the calculations are given in Ref. 13.

4) and from unconfined GaAs samples. For comparison, we have shown our data for InP in Fig. 2(c). Note that the rise of luminescence is considerably faster in InP and that the intensity at zero delay is essentially zero for GaAs but about 20% of the peak for InP.

This large difference between InP and GaAs is quite remarkable in view of the fact that the two semiconductors have similar characteristics. The major difference between the two as far as our experiments are concerned is that the Γ-*L* separation in InP is much larger (0.61 eV)[14] than in GaAs (0.29 eV).[15] Thus in GaAs, a substantial fraction of the photoexcited electrons may transfer rapidly to the *L* valley (where they cannot contribute to the luminescence) but return to the Γ valley rather slowly because of the smaller effective mass in the Γ valley. In InP, on the other hand, the photoexcited electrons remain in the Γ valley all the time. *We conclude from these arguments that the primary cause of the slow rise in GaAs is the slow return of the electrons from the L to the* Γ *valley.* This conclusion is further supported by our observations that the rise of luminescence is slow in semiconductors in which intervalley transitions are possible (GaAs, InGaAs, InGaAsP) but fast in semiconductors in which they are not possible (InP, CdSe, AlGaAs) for our excitation energy.

The initial relaxation of photoexcited carriers is governed by electron-electron, hole-hole, electron-hole, and carrier-phonon interactions. The process is further complicated by the presence of heavy-hole, light-hole, and split-off valence bands, by subsidiary valleys in the conduction bands, and by the density dependence of the scattering processes. In order to take these complexities into account, we have performed an ensemble Monte Carlo calculation[16] and determined the intervalley scattering rate by comparing the calculation and the data. However, before discussing these calculations, we consider some simple models which give physical insight into the important processes.

Figure 2(d) shows the results of calculations for two very simple models: (i) instant thermalization and cooling of carriers (curve 1) and (ii) a simple phonon-cascade model in which electrons relax by successively emitting LO phonons (curve 2, calculated[13] for InP). Both models assume that the holes are at 300 K (see discussion below). Clearly, neither model agrees with the data. The disagreement of the second model with the data and the observation that, at 0.5 ps (end of the pulse), the carrier distribution function is essentially thermalized with an effective temperature considerably higher than $\hbar\omega_0/k$ ($\hbar\omega_0$=optical-phonon energy) show the inadequacy of a simple cascade model, even at a density as low as $5\times10^{16}$ cm$^{-3}$.

A better model is to assume that the carrier-carrier collisions lead to thermalized distribution functions for electrons and holes with characteristic temperatures determined by energy input from photoexcitation and energy loss to the lattice. A calculation using this model[17] shows that the holes cool to the 300-K lattice temperature very quickly (essentially within the excitation pulse) whereas the electrons cool in about 3 ps. Since the integrated luminescence intensity depends on the carrier temperatures, there will be a corresponding rise time for the luminescence. The calculated curve for InP, shown as curve 3 in Fig. 2(d), gives a good agreement with the data for InP, showing that this model reasonably approximates the actual conditions in InP.

A repetition of the calculation for GaAs[13] gives a curve which is very close to the InP curve but far from the experimental curve for GaAs. Since slow cooling of photoexcited carriers has been observed[17] in GaAs for long (tens of picoseconds) times, we have attempted fits to the data using the electron coupling to the lattice as an adjustable parameter. We find that we need to reduced the coupling by about a factor of 3 to reproduce the measured electron temperature (from the luminescence spectra) at 10 ps. However, such a reduction leads to calculated electron temperatures which are too high and to calculated integrated intensities [curve 4, Fig. 2(d)] which are too low compared to the data at intermediate delays (2 to 8 ps). *We conclude that the slow rise of luminescence in GaAs is not simply due to a slowed cooling of electrons and that physical phenomena other than those considered above play an important role in GaAs.*

As a final model, we take the electron-lattice coupling as a constant given by the known parameters[13] but consider the effect of intervalley scattering. Physically, this introduces three effects: The rapid initial transfer of electrons to the $L$ valley results in lower initial electron temperatures, the number of electrons in the $\Gamma$ valley is a function of time, and finally, the electrons returning to the $\Gamma$ valley from the $L$ valley act as a *source of heating* of the electrons in the $\Gamma$ valley so that the net cooling is slower, in agreement with the experimental observations. The results of such a calculation, for an $L$-$\Gamma$ return time constant of 2.5 ps, are shown as curve 5 in Fig. 2(d). We see that this curve gives reasonable agreement with the data of Fig. 2(b), supporting the conclusion that intervalley scattering plays an important role in these experiments.

In order to obtain a quantitative fit to the data and determine $D_{\Gamma L}$, we have used an ensemble Monte Carlo approach.[16] We consider that the photoexcitation couples all three valence bands to the conduction band, so that three broadened distributions of electrons and holes (see the inset in Fig. 2) are produced. The calculation includes electron-electron interactions, electron interactions with polar optical and acoustic phonons, intervalley scattering through deformation coupling, and hot-phonon effects. This simulation directly gives the electron distribution function $f_e$ at various times. We assume that the holes relax to a thermal distribution with temperature equal to the lattice temperature within the pulse width; electron-hole interactions are not included.[18] Integrated luminescence intensity as a function of time is calculated for different values of $D_{\Gamma L}$ by integration of the product $f_e f_h$ over all $k$ values. The calculations were performed for both GaAs and InP.

The results of Monte Carlo calculations for InP [Fig. 2(c)] agree well with the experimental data and with the simplified electron-temperature model [curve 3, Fig. 2(d)]. In Fig. 2(b) we show the results of the calculation for GaAs for three different values of $D_{\Gamma L}$. The best fit is obtained with $6.5\times10^8$ eV/cm with an estimated error of about ±20%.[19] This gives an average $\Gamma$-$L$ transfer time of about 100 fs for electrons with 500-meV kinetic energy in the $\Gamma$ valley and an average return time of about 2 ps from $L$ to $\Gamma$ for electrons at the bottom of the $L$ valley.

We emphasize that the rise of the integrated luminescence intensity results from the time dependence of *both* the electron density in the $\Gamma$ valley and the electron distribution function, whereas the spectral shape is determined only by the distribution function. Comparison of the measured and the calculated (Monte Carlo) spectra shows excellent agreement (Fig. 1) and *provides an important independent test of the validity of the model.* The ability to measure spectra is thus an invaluable strength of the technique.

Raman-scattering measurements of phonon populations by Kash, Tsang, and Hvam[3] show that the population of LO phonons is maximum at about 2 ps after excitation. While the simple cascade model proposed to explain these results appears to be inadequate as discussed above, our results indicate that the density of electrons between 100 and 200 meV above the bottom of the conduction band peaks about 2 ps after the excitation pulse. This is entirely consistent with the Raman data.[3] Nuss, Auston, and Capasso[20] have recently measured the mobility of photoexcited GaAs with subpicosecond time resolution. They see a long rise time for mobility and explain it with a qualitative model similar to ours.

In summary, luminescence spectroscopy with subpicosecond time resolution shows that the integrated luminescence intensity in GaAs rises very slowly after the end of the excitation pulse. We demonstrate that the slow return of the electrons from the $L$ to the $\Gamma$ valley is responsible for this behavior. In addition to making the density of electrons in Γ valley time dependent, the returning electrons act as a source of heating and slow down the cooling of the photoexcited plasma. By comparing our data with Monte Carlo calculations, we determine that $D_{\Gamma L}$ in GaAs is $(6.5 \pm 1.5) \times 10^8$ eV/cm. We show the importance of carrier-carrier scattering and inadequacy of a simple phonon cascade model at low densities. Our results thus provide new insight into the initial relaxation of carriers in semiconductors.

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[13] Parameters for GaAs (InP): $E_g = 1.42$ (1.34) eV, $\Delta_{\Gamma L} = 0.29$ (0.61) eV, $m_e^\Gamma/m_0 = 0.063$ (0.075), $m_e^L/m_0 = 0.22$ (0.44), $m_{hh}/m_0 = 0.57$ (0.6), $m_{eh}/m_0 = 0.082$ (0.12), $m_{so}/m_0 = 0.154$ (0.11), $K_\infty = 10.92$ (9.52), $K_0 = 12.9$ (12.35), $D_{\Gamma L} = 2.5 \times 10^8$ eV/cm, $T_{\text{int}} = 357$ (492) K [(intervalley phonon energy)/$k$], and $T_{\text{pop}} = 427$ (498) K [(polar optical-phonon energy)/$k$ in Γ valley]. The light- and heavy-hole bands are assumed to be separated by 140 meV at the photon energy of interest (2.04 eV). $\Delta_{\Gamma X} = 0.48$ eV so that transfer to $X$ valley is expected to be very weak. This is confirmed by three-valley Monte Carlo calculations. Nonparabolicity and $X$ valley produce opposing effects so that the calculated results are not affected significantly.

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[18] Our calculations show that because of the strong coupling between holes and lattice, the photoexcited holes cool to the lattice temperature of 300 K within the pulse width. Electron-hole interactions are estimated to be small at $\simeq 1 \times 10^{17}$ $\text{cm}^{-3}$ and are not expected to affect hole or electron temperatures significantly for the lattice at 300 K. This is in contrast to what is expected at lower lattice temperatures [M. A. Osman, U. Ravaioli, R. Joshi, W. Potz, and D. K. Ferry, in *Proceedings of the Eighteenth International Conference on the Physics of Semiconductors,* edited by O. Engstrom (World Scientific, Singapore, 1987), p. 1310].

[19] We estimate that approximately half the error arises because of experimental uncertainty and the rest from an uncertainty in band-structure parameters. Note that the experimental curves cannot be fitted with $D = 1.5 \times 10^8$ eV/cm (Ref. 10) or $2.5 \times 10^8$ eV/cm used to calculate $I$-$V$ curves [J. Pozhela and A. Reklaitis, Solid State Electron **23**, 927 (1980)].

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