Hot-Electron Recombination at Neutral Acceptors in GaAs: A cw Probe of Femtosecond Intervalley Scattering

R. G. Ulbrich,[a] J. A. Kash, and J. C. Tsang
IBM Research Division, Thomas J. Watson Research Center, Yorktown Heights, New York 10598
(Received 20 July 1988)

The rates at which hot electrons scatter from the Γ valley to the L and X valleys in GaAs have been measured as a function of electron energy. Scattering times are determined from the relative efficiency of recombination of hot electrons with neutral acceptors at low injected-carrier densities. Representative scattering times are $\tau_{\Gamma L}=540\pm120$ fsec for 0.48-eV electrons and $\tau_{\Gamma X}=180\pm40$ fsec for 0.58-eV electrons. Our results enable us to reconcile the large range of scattering rates reported in other experiments and demonstrate the power of this cw probe to study subpicosecond electron dynamics.

PACS numbers: 78.47.+p, 72.10.Di, 78.55.Cr

A quarter century after the first report of the Gunn effect[1] in GaAs, our knowledge of intervalley scattering rates greatly lags our understanding of hot-electron kinetics in the Γ valley. Most of the excess energy of a hot electron in the Γ valley is transferred to the lattice by the polar (Fröhlich) interaction[2] in a few picoseconds. If its initial energy is greater than about 300 meV, the electron may scatter to the satellite L and X valleys. If the carrier density is greater than about 10^{17} cm^{-3}, carrier-carrier scattering will further modify the relaxation kinetics. The recent activity in this field[3] underscores the complexity of the scientific and technical[4,5] interest in the problem. Unfortunately, there has not been a direct spectroscopic study of intervalley scattering at densities low enough (below 10^{16} cm^{-3}) that carrier-carrier scattering can be ignored. A spectroscopic probe is needed because intervalley scattering depends strongly on electron energy.[2] In this paper, we show that recombination luminescence between nonequilibrium electrons and neutral acceptors [hot (e,A^0) emission[6]] in GaAs at $T=2$ K provides such a tool. In essence, the known $\tau_{\text{po}}\simeq180$ fsec emission time[2,7,8] for polar optical phonons by hot electrons provides a built-in clock so that direct time resolution is not necessary. Thus we can measure femtosecond phenomena even when the emission is excited by a cw laser source. Detailed analysis of the hot luminescence as a function of excess electron energy provides two independent measures of intervalley scattering times relative to τ_{po}. The scattering-time ratios determine the fraction of electrons which scatter to the satellite valleys as a function of excitation energy. Our results show that the scattering time from the Γ valley to the L valley, $\tau_{\Gamma L}$, is about 3 times τ_{po} for electrons with 0.48-eV excess energy. This time has been reported to be anywhere from 34 fsec to over 4 psec from various experiments,[6,9-12] all at higher carrier densities. Similarly, while recent work has suggested that $\tau_{\Gamma X}$, the scattering time from the Γ valley to the X valley, is as short as 30 fsec,[13] our measurements demonstrate that the scattering time is substantially longer, about equal to τ_{po} for electrons with 0.58-eV excess energy. Our results allow us to correlate the many recent subpicosecond studies of electron kinetics in GaAs.

Luminescence measurements at $T=2$ K were made on acceptor-doped samples of [100] GaAs grown by Manasevit metalorganic chemical-vapor deposition technique. The results reported here were obtained on a layer 1.1 μm thick, doped with 1.2×10^{17}-cm^{-3} Mg. From other samples we verified that our results do not depend upon doping density, acceptor species (C, Mg, Zn), or the presence of confining layers of Al$_x$Ga$_{1-x}$As. For [100] GaAs and linear laser polarization, the luminescence was, as expected,[6] unpolarized. We polarized the laser along [100] and detected the (e,A^0) emission at 90° to the laser. The spectra, detected by an imaging photomultiplier, were excited using laser photon energies between 1.57 and 2.54 eV. The resulting excess electron energies ranged from 0.045 to 0.9 eV, i.e., from well below to well above the thresholds for scattering to the satellite L and X valleys. Injected-carrier densities were always below 3×10^{15} cm^{-3}, where the hot (e,A^0) spectral shape was unchanging and the intensity scaled linearly with laser intensity, demonstrating that carrier-carrier scattering is unimportant.

In Fig. 1 we show the hot (e,A^0) luminescence spectra for photon energies between 1.7 and the excitation energy for three different excitation energies. As discussed by several authors,[6,14] the spectra show three distinct sets of oscillations with periods close to the 37-meV zone-center LO phonon energy. The set denoted hh involves electrons excited from the heavy-hole valence band. A second set, denoted lh, involves electrons excited from the light-hole band. The spectra from these transitions, which will both be called direct spectra, track the laser excitation energy. A third set, denoted R for reentrant, is observed only for excitation energies greater than the threshold to create electrons that can scatter to the X and L valleys (i.e., curves b and c in Fig. 1). These spectra, which are fixed in energy, result from carriers which reenter the Γ valley from the L minima. For laser energies above 1.8 eV, a few (roughly 15%) of the electrons are excited from the split-off valence band. How-

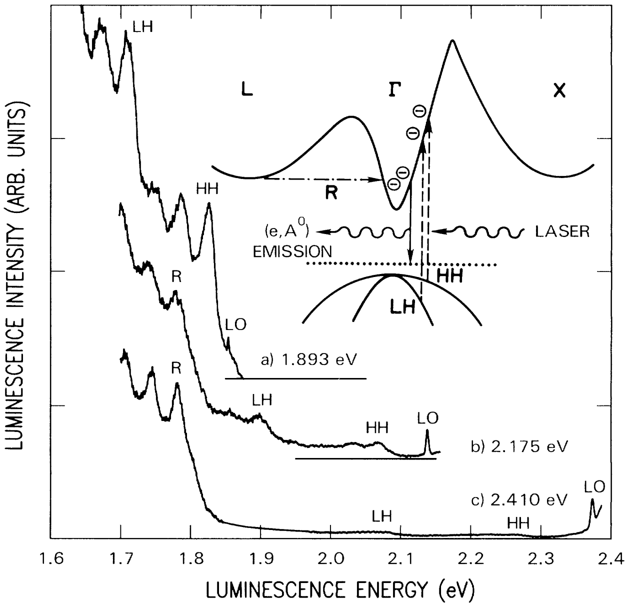

FIG. 1. Hot (e,A^0) luminescence spectra at $T=25$ K for GaAs:Mg, $p=1.2\times10^{17}$ cm^{-3}. The spectra were excited at 1.893 eV (curve *a*), 2.175 eV (curve *b*), and 2.410 eV (curve *c*). The intensities of the spectra are normalized to constant laser photon flux. Inset: Origins of the three sets of oscillations, as discussed in the text. The solid arrow indicates the recombination of a nonequilibrium electron with a neutral acceptor. The peaks marked LO are Raman scattering from LO phonons.

ever, the emission from these electron is unimportant in our analysis of the spectra. At excitation energies above 2.3 eV, warping of the valence and conduction bands broaden the hot-electron distributions so much that distinct LO phonon oscillations become hard to observe in the direct spectra, although the reentrant series remains sharp. The possible use of (e,A^0) emission for kinetic studies was noted by Fasol and Hughes.[14]

After correction for the laser photon flux and the throughput of the detection system, the intensity I (integrated area) of any of the (e,A^0) peaks is given by

$$I \propto |M(k)|^2 \tau p_e . \tag{1}$$

$M(k)$ is the Fourier component of the wave function of a hole bound to an acceptor at the wave vector k of the electron. From effective mass theory,[15]

$$|M(k)|^2 \propto (1+m_e^* E_e/m_A E_A)^{-4} . \tag{2}$$

Here m_e^* and E_e are the electron effective mass and energy, while m_A and E_A are the effective hole mass and acceptor binding energy, taken as $0.310 m_e$ and 27 meV.[16] We take E_e consistent with the work of Fasol and Hughes[14] (and confirmed by our measurements), while $m_e^* = 0.067 m_e$. Although m_e^* increases[17,18] with E_e, this has little effect on $M(k)$ since it is partially compensated by the valence-band nonparabolicity. The second factor in Eq. (1) is the electron lifetime τ at that energy. At the low densities in these experiments, $\tau=\tau_{\text{po}}$, the polar optic scattering time, for energies below the intervalley scattering threshold. (The recombination time for nonequilibrium electrons with the neutral acceptors is much longer than τ_{po} and can be ignored.) At the energies of interest in these experiments, τ_{po} is nearly constant.[2,8] Above the threshold for intervalley scattering, the electron lifetime will be reduced by scattering to the L valley, and at high enough energies, the X valley as well, so that

$$\tau^{-1} = \tau_{\text{po}}^{-1} + \tau_{\Gamma L}^{-1} + \tau_{\Gamma X}^{-1} . \tag{3}$$

The energy dependence of $\tau_{\Gamma L}$ is[17]

$$\tau_{\Gamma L} = \tau_{\Gamma L}^0 [(E_e - E_L - E_{\text{ze}})/E_{\text{ze}}]^{-1/2} , \tag{4}$$

with a similar expression for $\tau_{\Gamma X}$. [Equation (4) avoids the use of the deformation potential[17] $D_{\Gamma L}$ because uncertainties in the numerical values for quantities such as the effective mass of the L valley and the nonparabolicity of the Γ valley can produce substantial changes in the relationship between $D_{\Gamma L}$ and $\tau_{\Gamma L}$.] Here E_L is the energy of the L minimum with respect to the bottom of the Γ valley, and E_{ze} is the 28-meV average energy of the zone-edge phonons responsible for intervalley scattering. The third factor in Eq. (1), p_e, is the probability that an electron will actually pass through that energy in the conduction band. For the first hh or lh peak, this is just the fractional hh or lh absorption. For the reentrant peaks, this is just the total fraction of electrons which have transferred to the L valley at some time during their journey to the band edge, reentering the Γ valley from the L-valley minimum.

The open circles in Fig. 2(a) show the integrated area of the first hh direct peak versus laser photon energy. The data are given for constant laser photon flux and corrected for the throughput of the detection system. Contributions to the area from lower energy peaks were subtracted off. At the low densities used here, there is no background hot luminescence from recombination between free electrons and free holes. The dot-dashed curve is just the acceptor envelope $|M(k)|^2$ from Eq. (2). In order to show the data above the threshold for intervalley scattering more clearly, we do not display data for laser photon energies from 1.57 to 1.75 eV. For photon energies below the intervalley scattering threshold, the intensity of the first hh direct peak tracks precisely the calculated factor of 50 change in $|M(k)|^2$, showing the validity of Eq. (2). The other three curves include the effects of intervalley scattering through Eqs. (3) and (4). For all of these curves, we take $\tau_{\Gamma X}^0/\tau_{\text{po}} = 1.79$, while $\tau_{\Gamma L}^0/\tau_{\text{po}} = 7.14$, 3.175, and 0.595 for the solid, dashed, and dotted curves, respectively. The solid curve, which corresponds to $\tau_{\Gamma L} = 3\tau_{\text{po}}$ for a 0.48-eV electron and $\tau_{\Gamma X} = \tau_{\text{po}}$ for a 0.58-eV electron, accounts

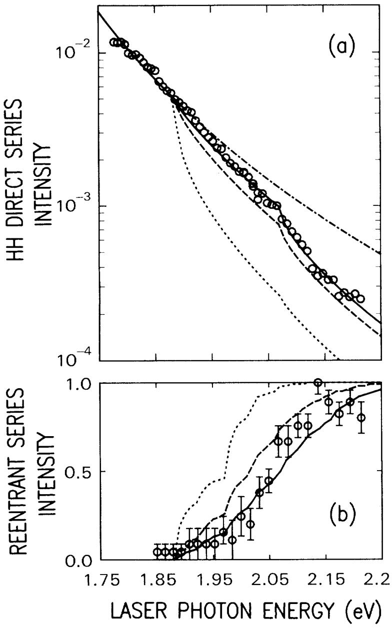

FIG. 2. The dependence of the intensity (integrated area) of hot (e,A^0) luminescence in GaAs on the laser photon energy. (a) Open circles give the integrated area of the highest-energy hh direct series peak, normalized to unity at the band edge. Errors are 10% or smaller. (b) Open circles with error bars give the intensity of the reentrant spectra normalized to unity at high energies. The simple model which gives the curves is described in the text.

best for the data.

To independently confirm $\tau_{\Gamma L}$, we show in Fig. 2(b) the intensity of the reentrant spectra versus laser wavelength. This intensity is proportional to the total fraction of carriers which return to the Γ valley from the L minimum. Corrections due to the changing absorption depth of the laser light[19] can be shown to be less than 25%; carrier diffusion during the several psec before the carriers return to the Γ valley makes this correction even smaller. Because of the large density of states in L and X as compared to Γ, electrons which scatter to L or X will almost always return to Γ from the bottom of L.[6] Thus, the data in Fig. 2(b) directly give the total fraction of electrons which undergo intervalley scattering from Γ to either L or X. The data are normalized to unity at the highest laser energy (2.54 eV), where essentially all electrons contribute to the reentrant spectrum. A photon energy of about 2.1 eV is required before half the carriers scatter from the Γ valley. Using Eqs. (2) and (3), with the additional assumption[20] that half the absorption is heavy hole and half is light hole, we obtain the three curves in Fig. 2(b) using the same intervalley scattering rates as in Fig. 2(a). The data are consistent with only the longer scattering times. If more than half of the excited carriers come from the heavy-hole band or if this fraction decreases with increasing energy, even longer scattering times would be required to fit the data in both Figs. 2(a) and 2(b). The data in Fig. 2(b) are obtained independently of those in Fig. 2(a), and their interpretation does not require Eqs. (1) and (2). Each measurement gives the same ratio for the intervalley to polar optical scattering rates. Thus, the largest source of error in our determination of absolute intervalley rates is the uncertainty[2,7,8] in τ_{po} about 20%, divided evenly between the magnitude and the energy dependence of τ_{po}.

Further support for these intervalley scattering rates is obtained by measuring the linewidth of the first hh direct peak. We have measured the half width at half maximum (HWHM) on the high-energy side of the first hh direct peak to avoid the need to deconvolve the lower energy peaks (see Fig. 1). At the lowest laser energy (1.57 eV), the HWHM of 5 meV corresponds to 150 fsec, quite close to τ_{po}. At this energy, the spread in initial electron energies due to warping of the valence bands is only about 1.5 meV,[18] and can be ignored. As the laser photon energy increases, warping broadens the peak to 8 meV at 1.85 eV. Above the threshold for intervalley scattering (1.86 eV) there is additional lifetime broadening due to intervalley scattering. Estimating the warping from $\mathbf{k}\cdot\mathbf{p}$ theory[18] the extra linewidth is consistent with $\tau_{\Gamma L} > 200$ fsec for 0.5-eV electrons. Because $\mathbf{k}\cdot\mathbf{p}$ theory loses accuracy at these high energies, we cannot make a more precise statement than this, but completely ignoring the warping and assuming that *all* the broadening is due to lifetime gives an *absolute* lower limit $\tau_{\Gamma L} > 100$ fsec for laser photon energies around 2.0 eV.

Our value for $\tau_{\Gamma L}$ is much shorter than that obtained by Collins and Yu,[12] somewhat longer than those suggested by Shah *et al.*[10,21] (Fig. 2, dashed curves), and considerably longer than those obtained by Tang, Wise, and Walmsley[9] (Fig. 2, dotted curves) and Mirlin and co-workers.[6,13] Collins and Yu were unable to see any effect of Γ-L scattering on nonequilibrium phonon generation, and deduced from this fact that $\tau_{\Gamma L} > 4$ psec for $E_e < 0.5$ eV. However, Collins and Yu neglected phonons generated by the electrons which contribute to the lh direct series and the reentrant series, which makes the total nonequilibrium phonon population insensitive to Γ-L scattering. The results of Shah *et al.* and Tang, Wise and Walmsley may be perturbed by their high carrier densities which imply rapid carrier-carrier scattering. The absorption measurements of Tang, Wise, and Walmsley are sensitive to the shortest time, which will be the carrier-carrier scattering rate. The simulation of Shah *et al.* is sensitive to the total fraction of carriers which scatter to L, as well as the time they remain there, and not on the scattering rate from the Γ valley. At high densities, many electrons will gain energy by carrier-carrier scattering; those that obtain enough energy can scatter to the X valley, which, as we have shown, is faster than scattering to the L valley. Thus the results of Shah *et al.* may reflect a weighted average of X and L valley scattering times. It is also possible that their intervalley scattering rates are directly affected by the presence of high carrier densities. Finally, from depolarization studies Mirlin and co-workers[6,13] derived $\tau_{\Gamma L}=250$ fsec for 0.385-eV electrons and $\tau_{\Gamma X}=30$ fsec for 0.57-eV electrons. Their model requires knowledge of the cyclotron mass for 0.385- and 0.57-eV electrons and assumes that electron scattering times are independent of magnetic field. The sub-60-fsec intervalley scattering times suggested in Refs. 9 and 13 can directly be ruled out from our linewidth measurements. Our results also reconcile time-resolved Raman scattering data[7] with subpicosecond luminescence studies[10] in GaAs. The present results show that at laser photon energies around 2 eV, roughly half the electrons transfer to the L valley. The Raman results are sensitive to those carriers which come directly down the central valley, while the near band-gap luminescence is strongly perturbed by the energetic carriers slowly returning from the L valley.

In summary, we have measured the intervalley scattering rate as a function of excitation energy in GaAs. The LO phonon emission process makes is possible to use cw spectroscopy to study events occurring within a fraction of $\tau_{\mathrm{po}} \simeq 180$ fsec. The technique used here allows us to spectroscopically demonstrate that carrier-carrier scattering is unimportant, greatly simplifying the analysis. The hot (e,A^0) emission intensity gives us two independent and consistent measures of intervalley scattering. The linewidths provide further corroboration of these rates. A comparison of hot (e,A^0) luminescence with Raman scattering from nonequilibrium phonons will be interesting, as will time-resolved hot (e,A^0) luminescence.

We thank T. F. Kuech for the samples used in this study, G. D. Pettit for the loan of equipment, and Professor E. Burstein for helpful discussions.

---

[a] Permanent address: Institut für Physik der Universität Dortmund, 46 Dortmund 50, Federal Republic of Germany.

[1] J. B. Gunn, Solid State Commun. **1**, 88 (1963).

[2] E. M. Conwell and E. O. Vassel, IEEE Trans. Electron Devices **13**, 22 (1966).

[3] For a recent review, see S. A. Lyon, J. Lumin. **35**, 121 (1986).

[4] M. Heiblum, D. C. Thomas, C. M. Knoedler, and M. I. Nathan, Appl. Phys. Lett. **47**, 1105 (1985).

[5] J. R. Hayes, A. F. J. Levi, and W. Weigmann, Phys. Rev. Lett. **54**, 1570 (1985).

[6] D. N. Mirlin, I. Ja. Karlik, L. P. Nikitin, I. I. Reshina, and V. F. Sapega, Solid State Commun. **37**, 757 (1981).

[7] J. A. Kash, J. M. Hvam, and J. C. Tsang, Phys. Rev. Lett. **54**, 2151 (1985).

[8] A. F. J. Levi, J. R. Hayes, and R. Bhat, Appl. Phys. Lett. **48**, 1609 (1986).

[9] C. L. Tang, F. W. Wise, and I. A. Walmsley, Solid State Electron. **31**, 439 (1988).

[10] Jagdeep Shah, Benoit Deveaud, T. C. Damen, W. T. Tsang, and P. Lugli, Phys. Rev. Lett. **59**, 2222 (1987).

[11] M. C. Nuss, D. H. Auston, and F. Capasso, Phys. Rev. Lett. **58**, 2355 (1987).

[12] C. L. Collins and P. Y. Yu, Phys. Rev. B **30**, 4501 (1984).

[13] D. N. Mirlin, E. Ja. Karlik, and V. F. Sapega, Solid State Commun. **65**, 171 (1988).

[14] G. Fasol and H. P. Hughes, Phys. Rev. B **33**, 2953 (1986).

[15] W. P. Dumke. Phys. Rev. **132**, 1998 (1963).

[16] A. Baldereschi and Nunzio O. Lipari, Phys. Rev. B **8**, 2697 (1973); D. Bimberg, in *Festkörperprobleme XVII,* edited by J. Treusch, Advances in Solid State Physics (Vieweg, Braunschweig, 1977), p. 195.

[17] W. Fawcett, A. D. Boardman, and S. Swain, J. Phys. Chem. Solids **31**, 1963 (1970).

[18] U. Rössler, Solid State Commun. **49**, 943 (1984).

[19] D. E. Aspnes and A. A. Studha, Phys. Rev. B **27**, 985 (1983).

[20] Evan O. Kane, J. Phys. Chem. Solids **1**, 249 (1957). This assumption is also consistent with our measured intensities of the hh and lh direct series.

[21] Since the occupation of these zone-edge phonons increases to about 0.5 at room temperature, intervalley scattering times are temperature dependent, doubling from 2 K to room temperature. We thank Dr. M. V. Fischetti for this point.