

Femtosecond carrier dynamics in Ge measured by a luminescence up-conversion technique and near-band-edge infrared excitation

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The luminescence at the direct band edge of bulk intrinsic and p -type Ge ($p \sim 2 \times 10^{19} \text{ cm}^{-3}$) samples was measured in a two-wavelength up-conversion experiment with $\lambda = 1.25\text{--}1.35 \mu\text{m}$ excitation and at lattice temperatures 20 and 300 K. The near-band-edge carrier dynamics, measured with 100-fs temporal resolution and at carrier densities of $5 \times 10^{16}\text{--}2 \times 10^{18} \text{ cm}^{-3}$, are dominated by electron-phonon intervalley scattering and electron thermalization. Thermalization governs the initial rise of the luminescence in the first 500 fs and is studied as a function of energy and electron density. With excitation photon energy 100 meV greater than the direct band gap, the thermalization time of electrons was measured to decrease with increasing density as $n^{-0.55 \pm 0.1}$. Degeneracy has a strong influence on the thermalization rate with 50 meV excess energy. The L -electron cooling through the electron-hole interaction, as well as hole screening and degeneracy in p -type Ge, is discussed.

The ultrafast properties of germanium have attracted renewed interest, both fundamentally and technologically (e.g., SiGe alloys for high-speed electronics). But, only recently, developments in femtosecond infrared pulse generation have allowed a wider range of experiments to be made in Ge.¹⁻⁴ These previous experiments have shown that with an indirect band-gap structure (see Fig. 1) and nonpolar bonding, Ge is an interesting alternative semiconductor for studying ultrafast carrier dynamics. Electron-phonon intravalley scattering near the bottom of the Γ valley is weak because there is no strong polar Fröhlich coupling and the optical deformation-potential mechanism is symmetry forbidden. The subpicosecond, density-independent intervalley scattering time at the Γ point⁵ is comparable to the electron-electron scattering mediated thermalization time,² which suggests a way to study electron scattering using the intervalley scattering as a temporal clock.

In previous experiments, the electron dynamics in Ge were studied at 300 K with a wavelength degenerate pump-probe technique near the direct band edge.² The transmission changes of the probe beam are dominated by the electron dynamics because the electron mass is eight times smaller than the heavy-hole mass. These experiments could only study the behavior of electrons at the photoexcited energy. The electron distribution function can be more easily studied using luminescence up-conversion techniques.⁶ Previous experiments³ used high photon-energy excitation $E_{\text{gd}} + 0.7$ eV (where E_{gd} is the direct band gap; 0.89 eV and 0.81 eV, at 20 K and 300 K, respectively). At this high photon energy, the intervalley scattering to the L and X satellite valleys is extremely fast (< 100 fs) and the electrons in each valley reach a quasiequilibrium with each other within a few hundred femtoseconds. Thus, the band-edge luminescence describes only the cooling behavior of the thermalized carriers on a picosecond time scale.

We also use luminescence up-conversion techniques in this work but excite the sample only up to 100 meV above the direct band edge (E_{exc} in Fig. 1) with a tunable infrared

optical parametric oscillator. Close to the band edge, it takes ~ 1.6 ps for the Γ electrons to reach particle equilibrium with the L electrons, as calculated by detailed balance.³ In this time, the L -electron average energy has dropped significantly below the Γ -electron band edge and the L electrons do not scatter back into the Γ valley in significant numbers. Therefore, we can resolve the rise of the luminescence at the direct band edge (E_{lum} in Fig. 1) as being due to electron scattering and the subsequent decay as being due to intervalley scattering, rather than the cooling behavior of L electrons. Measurements as a function of excitation photon energy, luminescence wavelength, photoexcited carrier density, and sample temperature are presented. Crystalline Ge samples with heavy p doping were used to isolate the electron dynamics⁷ and were compared to an intrinsic sample.

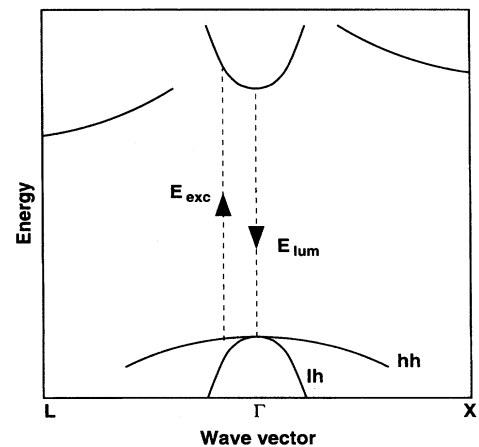


FIG. 1. Schematic band-structure diagram of Ge at 300 K. The approximate excitation photon energy of the optical parametric oscillator pulses (E_{exc}) and the measured band-edge luminescence (E_{lum}) are also shown.

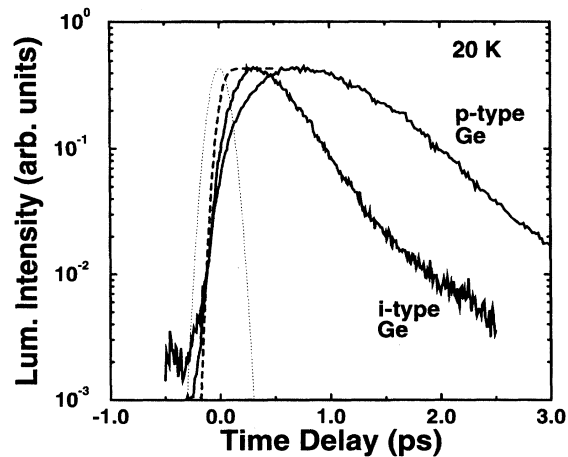


FIG. 2. The temporal evolution of the band-edge luminescence in *p*-type and *i*-type Ge samples with $1.32\text{-}\mu\text{m}$ excitation ($E_{\text{gd}}+50\text{ meV}$). The dotted curve is the cross correlation between the optical parametric oscillator and Ti:sapphire pulses. The dashed curve is the calculated evolution of the initial photoexcited electron population.

The luminescence up-conversion experiments used an optical parametric oscillator (Spectra Physics Opal) pumped by a 82-MHz femtosecond Ti:sapphire laser. The bulk crystalline germanium samples were held in a He flow cryostat at either 20 K or 300 K, and excited with the 130-fs infrared pulses from the oscillator. The luminescence from the sample was up-converted with part of the Ti:sapphire pump pulses at 775 nm with a temporal resolution of 130 fs. The spectral resolution was 15 meV. This two-wavelength geometry maximizes the parametric oscillator power, available for luminescence excitation, and limits as well the stray light, since the non-phase-matched frequency doubled Ti:sapphire pulses are not at the same wavelength as the up-converted luminescence. This attains particular importance when exciting and measuring close to the band edge. The samples were either *p* type ($p\sim 2\times 10^{19}\text{ cm}^{-3}$) or intrinsic Ge. Neutron-irradiated samples with subnanosecond carrier lifetimes were also measured to ascertain that carrier accumulation effects were minimal.

The general features of the transient luminescence of the *p*-type Ge sample are shown in Fig. 2 (*p*-type Ge curve) where the band-edge luminescence intensity as a function of time delay between the parametric oscillator and Ti:sapphire pulses (at the up-conversion crystal) is plotted. The sample temperature is 20 K, the photoexcited carrier density is

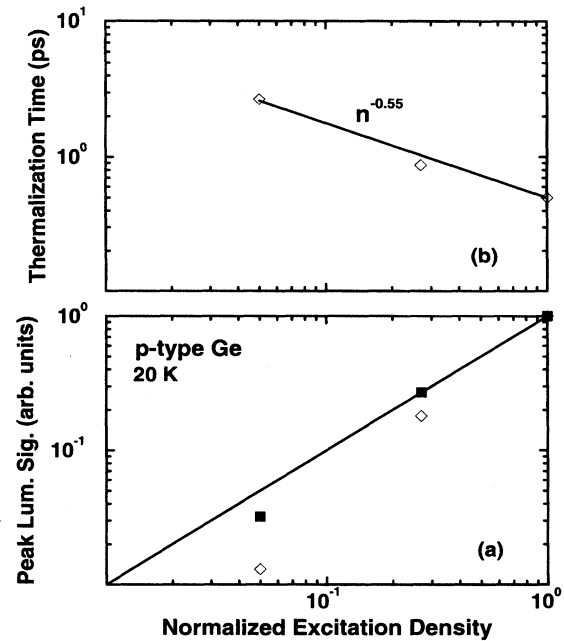


FIG. 3. (a) The normalized peak luminescence at the band edge (*p*-type Ge) as a function of photoexcitation density with $1.32\text{-}\mu\text{m}$ excitation (solid squares) and $1.25\text{-}\mu\text{m}$ excitation ($E_{\text{gd}}+100\text{ meV}$; diamonds). The solid line has a slope 1. (b) Thermalization time from the two-parameter model ($1.25\text{ }\mu\text{m}$).

width and an assumed Gaussian pulse shape. The luminescence then decays as the electrons are scattered from the Γ to the satellite *L* valleys, emitting LA and TA intervalley phonons. The $\Gamma\rightarrow L$ intervalley scattering time near the band edge, at 20 K, is $570\pm 50\text{ fs}$ (measured up to a delay time of 4.5 ps, and confirming that the measurement is not excitation wavelength dependent).

The luminescence rise time, that is to say, the thermalization time of electrons generated in the initial photoexcited states and then scattered to the band edge, was studied by changing the excitation wavelength (the initial energy) and the carrier density. In particular, a change in the peak luminescence strength with density is a relatively sensitive indication of a change in the thermalization time, since the intervalley scattering time is density independent. The density-dependent temporal evolution of the band-edge luminescence was studied with an excitation wavelength of $1.25\text{ }\mu\text{m}$ ($E_{\text{gd}}+100\text{ meV}$) and $1.32\text{ }\mu\text{m}$ ($E_{\text{gd}}+50\text{ meV}$) and at a lattice temperature of 20 K. The results for the peak

$$\frac{dn_i}{dt} = -\frac{n_i}{\tau_r} - \frac{n_i}{\tau_{\Gamma L}} + g(t), \quad (1)$$

$$\frac{dn_f}{dt} = +\frac{n_i}{\tau_r} - \frac{n_f}{\tau_{\Gamma L}}, \quad (2)$$

where $\tau_{\Gamma L}$ is the intervalley scattering time, τ_r describes the redistribution time from the initially excited electron state i to the final (band-edge) state f , and $g(t)$ is a Gaussian generation function. Finally, $n_f(t)$ is convoluted with another Gaussian pulse function and compared with the experimental data. Since $\tau_{\Gamma L}$ is known, τ_r is determined by fitting the full width at half maximum of the temporal response.

The relaxation time approximation implied by Eqs. (1) and (2) is very good for describing intervalley scattering; the intervalley scattering time is not very sensitive to the carrier density, nor to the intervalley phonon occupation number, nor to the electron distribution function, under our experimental conditions. In contrast, for carrier-carrier scattering, this approximation is a poor one because it is not possible to ascribe a single time constant to the evolution of nonthermal electron distributions to thermal ones. The scattering time τ_r should be considered an average scattering time. Furthermore, these equations certainly do not represent a rigorous microscopic description of the particle dynamics. A first-principles treatment of the carrier dynamics necessarily includes a quantum kinetic treatment including many-body effects (see, e.g., Ref. 10), since our experiments are carried out at rather high densities, and perhaps with coherent effects considered.¹¹ The high doping density of our samples requires that the impurity band tailing be taken into account in any realistic description of the band structure.¹²

The thermalization time as a function of density, extracted from this simple two-parameter model, for 1.25- μm excitation is shown in Fig. 3(b). The density dependence $n^{-0.55 \pm 0.1}$ is similar to that seen in previous experiments, which measured hot-electron thermalization times in GaAs mediated by electron-electron interactions¹³ ($n^{-0.58 \pm 0.1}$). (Theoretical considerations¹⁴ point to a thermalization time scaling as $n^{2/3}$.) The similarity is surprising because the electron-hole interaction, which plays a role in the electron thermalization, should be independent of the electron density (at least at low electron densities). The thermalization times shown in Fig. 3(b) are longer than one would expect from a comparison with previous experiments in GaAs (Ref. 15) at similar densities, which showed a fast *redistribution* of electrons within ≈ 100 fs due to electron-electron scattering. Aside from excitation differences in those experiments (five times larger excess electron energy and a density far from degeneracy), which could offer a partial explanation, fundamentally, the initial redistribution time is usually much shorter than the time for full thermalization,¹⁶ which we measure. A faster initial decay time for luminescence *above* the band edge evolving to $\tau_{\Gamma L}$ after 1–1.5 ps also shows that complete thermalization is achieved on a ≈ 1 -ps time scale (see also the discussion of Fig. 5).

The density dependence is nearly linear for the case with 1.32- μm excitation. At lower excess energies and high carrier densities, electron degeneracy¹⁷ plays an important role and has the opposite effect on the density dependence of the scattering time; it tends to make the density dependence less

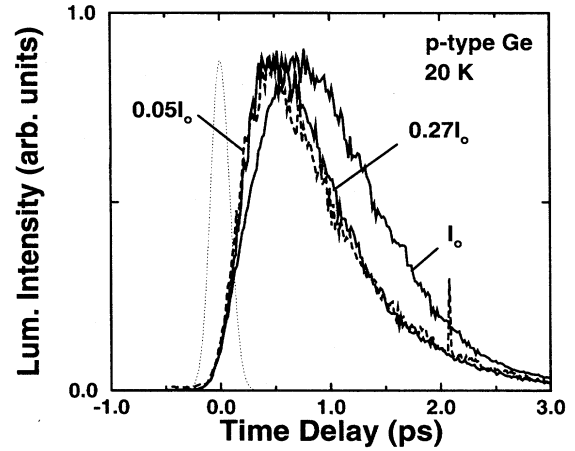


FIG. 4. The temporal evolution of the band-edge luminescence in p -type Ge as a function of excitation density with 1.32- μm excitation.

sublinear. This degeneracy also implies that the absorption can be nonlinear. Evidence for the former interpretation can be seen directly in the time domain. Figure 4 shows the normalized time-resolved luminescence at various excitation densities corresponding to the data in Fig. 3. At lower densities the rise time is noticeably faster, indicating that degeneracy cannot be ignored. In agreement with the reduced degeneracy with 1.25- μm excitation, the maximum temporal shift of the peak luminescence with decreasing density is five times smaller than that shown in Fig. 4.

We return to consider the electron-hole interaction. Previous studies^{7,9} as well as our own measurement of an i -type

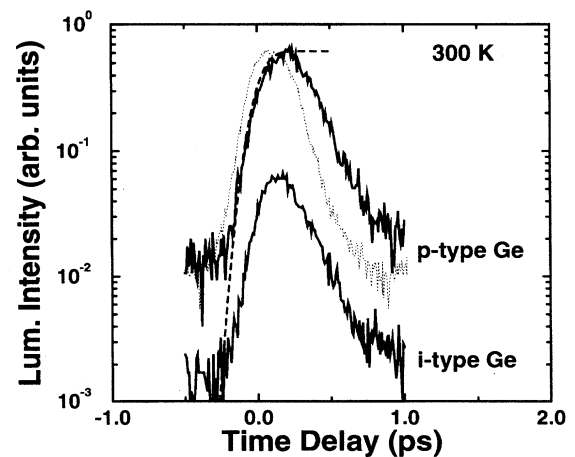


FIG. 5. Comparison of the band-edge luminescence for p -type and i -type Ge samples at 300 K. The excitation wavelength is 1.32 μm ($E_{\text{gd}} + 130$ meV). The dotted curve is the luminescence measured above the band edge at $E_{\text{gd}} + 65$ meV photon energy (p -type Ge sample only). The dashed curve is the calculated evolution of the initial photoexcited electron population. The curves have been offset for clarity.

Ge sample at 20 K (Fig. 2) illustrate the efficiency and magnitude of the electron cooling through the e - h interaction. In the i -type Ge sample, the temporal evolution of the band-edge luminescence is determined by the product of the photogenerated carrier distribution functions $f_e f_h$. The hole distribution is not degenerate and is strongly influenced by heating from the scattered hot L electrons (with initial temperature ≈ 1200 K). The electron-hole cooling is very efficient because of the similar L -electron ($0.22m_0$) and heavy-hole ($0.34m_0$) mass and the higher initial L -electron temperature compared with the Γ electrons. The heating of the holes results in the faster initial decay of the luminescence in the i -type Ge sample. The approximate initial energy-loss rate is 0.2 eV/ps, and is similar to recent measurements,⁹ taking the different mass ratio into account. Beyond 1.2 ps, the luminescence decay is again dominated by the intervalley scattering of Γ electrons.

The efficient Γ -electron cooling through e - h interactions, as fast as 100 fs (extrapolated from the L -electron-hole cooling rate), is of the same magnitude as the electron-electron scattering time. However, our experimental measurement of the L -electron cooling in the i -type Ge sample and previous experiments^{7,9} have not considered the effect of a cold, degenerate hole plasma found in the p -type Ge sample.

Screening by the cold holes and the hole degeneracy should also have a strong effect on the Γ -electron-hole cooling and electron-electron scattering.¹⁷ The reduced hole cooling due to electron degeneracy in n -type modulation-doped quantum wells at 5 K was previously reported.¹⁸ The stronger screening of cold carrier populations, as expected from a simple Debye screening model, has been recently shown.¹⁹

We intentionally reduce the effect of screening by the cold holes and reduce the degeneracy by repeating the measurements at 300 K. The time-resolved band-edge luminescence for the i -type and p -type Ge sample [excitation wavelength

$1.32 \mu\text{m}$ ($E_{\text{gd}}+130$ meV)] is plotted in Fig. 5. The electron density is approximately $2 \times 10^{18} \text{ cm}^{-3}$. Both curves are remarkably similar²⁰ even though the hole density is ten times smaller in the i -type Ge sample. The rise time of the luminescence is as fast as the carrier accumulation; the electron thermalization is faster than with a cold hole population. (Note, the faster thermalization is not due to a difference in the excitation conditions. The rise time of a p -type Ge sample at 20 K with $E_{\text{gd}}+100$ meV excitation is only somewhat faster than that shown in Fig. 2 for $E_{\text{gd}}+50$ meV excitation.)

The overall thermalization time is also shortened, as seen in the luminescence response above the band edge (dotted curve in Fig. 5). The signal is measured at a wavelength halfway between the excitation wavelength and the band-edge luminescence wavelength ($E_{\text{gd}}+65$ meV). As discussed before, the luminescence rises sooner (≈ 60 fs) and initially decays faster due to incomplete thermalization. After 500 fs, the thermalization seems mostly complete. Transient heating of the holes is not seen in the luminescence decay of the i -type Ge sample because the holes are strongly coupled to the lattice at 300 K.²¹

In conclusion, the up-converted luminescence from p -type and i -type Ge samples was studied with femtosecond resolution and infrared excitation. Thermalization and cooling, due to electron-electron and electron-hole scattering, were measured using the electron intervalley scattering time (or rate) as a reference. These experiments offer an alternative viewpoint for theoretical calculations, especially at high carrier densities and with a cold hole plasma, complementing previous experiments at low and moderate densities.¹³

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¹G. Mak and H. M. van Driel, Appl. Phys. Lett. **66**, 763 (1995).
²G. Mak and H. M. van Driel, Phys. Rev. B **49**, 16 817 (1994).
³X. Q. Zhou, H. M. van Driel, and G. Mak, Phys. Rev. B **50**, 5226 (1994).
⁴T. Rappen *et al.*, Phys. Rev. B **48**, 4879 (1993).
⁵Screening of the intervalley scattering involving a large- k zone-boundary phonon is weak. At high carrier densities ($>10^{18} \text{ cm}^{-3}$) the screening distance is approximately the interparticle distance, which is still smaller than the lattice constant. Lack of screening of the deformation potential in intervalley scattering was also seen in previous experiments (Ref. 3).
⁶J. Shah, IEEE J. Quantum Electron. **24**, 276 (1988).
⁷T. Furuta and A. Yoshii, Appl. Phys. Lett. **59**, 3607 (1991); U. Hohenester *et al.*, Phys. Rev. B **47**, 13 233 (1993).
⁸With this excitation density, the total hole temperature directly after photoexcitation, i.e., including the photoexcited holes, is heated to ≈ 30 K but the band-edge hole occupancy is unchanged because the holes are very degenerate (and remain so up to 100 K).
⁹R. Rodrigues *et al.*, Semicond. Sci. Technol. **9**, 456 (1994); R. A. Höpfel, J. Shah, and A. C. Gossard, Phys. Rev. Lett. **56**, 765 (1986).

¹⁰H. Haug and S. W. Koch, *Quantum Theory of the Optical and Electronic Properties of Semiconductors*, 2nd ed. (World Scientific, Singapore, 1993).
¹¹T. Kuhn, S. Haas, and F. Rossi, Phys. Status Solidi B **188**, 369 (1995).
¹²M. Takeshima, Phys. Rev. B **40**, 3090 (1989).
¹³J. A. Kash, Phys. Rev. B **48**, 18 336 (1993).
¹⁴D. W. Snoke, Phys. Rev. B **50**, 11 583 (1994).
¹⁵T. Elsaesser *et al.*, Phys. Rev. Lett. **66**, 1757 (1991).
¹⁶D. W. Snoke *et al.*, Phys. Rev. B **45**, 10 979 (1992).
¹⁷See, e.g., M. Combescot and R. Combescot, Phys. Rev. B **35**, 7986 (1987).
¹⁸A. Tomita *et al.*, Phys. Rev. B **48**, 5708 (1993).
¹⁹J. A. Kash, Phys. Rev. B **51**, 4680 (1995).
²⁰The shorter intervalley scattering time (≈ 170 fs) at room temperature (Refs. 2 and 22) originates from the temperature-dependent effective intervalley deformation potential (Ref. 23).
²¹X. Q. Zhou, K. Leo, and H. Kurz, Phys. Rev. B **45**, 3886 (1992).
²²G. Mak, Ph.D. thesis, University of Toronto, 1994.
²³S. Zollner, S. Gopalan, and M. Cardona, Solid State Commun. **76**, 877 (1990).