Invited Paper

Intervalley scattering times from the rigid-pseudoion method

Stefan Zollner[a], Sudha Gopalan[b], and Manuel Cardona[a]

[a] Max-Planck-Institut für Festkörperforschung, Heisenbergstr. 1, D-7000 Stuttgart 80, FRG
[b] The University of Western Ontario, Department of Physics, London, Ontario, Canada N6A 3K7

ABSTRACT

We have used the rigid-pseudoion method (with q-dependent matrix elements and a realistic non-parabolic band structure) to calculate the lifetimes of electrons at the L- and X-points in GaAs as a function of temperature (L: 2.2±0.5 ps, X: 130±20 fs at room temperature). The contribution of the TA phonons to $L\Gamma$-scattering explains the discrepancy between the experiments of Shah and Kash, performed at two different temperatures. About 80% of the carriers at X scatter into the L-valleys. The intervalley scattering times in the Γ-valley for electrons with an energy of 165 meV above the L-point are found to be 750±100 fs at helium temperatures (100 fs for electrons with an energy of 270 meV). These results compare favorably with recent femtosecond and CW laser experiments.

1. INTRODUCTION

Progress in ultrafast laser and detection techniques[1] has made possible direct measurements of intervalley scattering (IVS) times in GaAs. [2] The groups of Shah[3] (using femtosecond luminescence with up-conversion detection) and Alfano[4,5] (four-wave mixing and visible pump-infrared probe) have found the room temperature lifetimes of electrons in the L_6- and X_6-valleys to be 2 ps and 700±500 fs, respectively. IVS scattering times for the reverse process, i. e., for carriers in the Γ_6-valley with very high energies to the subsidiary L_6- and X_6-valleys have been determined with CW hot-electron luminescence. [6-10] Visible pump-and-probe measurements[11-13] are more difficult to interpret, as carrier-carrier scattering makes the IVS times density- and even time-dependent. [14-16]

2. THEORY

In a 3-D elemental or binary compound semiconductor without impurities, the dominant IVS mechanism is the deformation-potential electron-phonon interaction. [17] In the common theoretical model, [17] one assumes a q-independent coupling constant, the intervalley deformation potential (IDP) D (which theory predicts to be about 3 eV/Å for ΓL- and ΓX-scattering in GaAs and InP[18,19]), proportional to the electron-phonon matrix element, and a band structure with spherical valleys around the Γ-, L-, and X-points. Then Fermi's golden rule can be integrated analytically over all final states to yield Conwell's formula for the IVS time. [17,20]

We have shown previously, however, that the intervalley deformation potentials for GaAs[20] and GaP[21] do depend on the phonon wave vector q. This makes Conwell's formula a poor approximation. A better model uses a realistic pseudopotential band structure for the conduction band and q-dependent electron-phonon matrix elements and performs the integration over all possible final states numerically, e. g., with the tetrahedron method. This procedure has been described in detail in Ref. 20. The IVS time $\langle \tau_k(T) \rangle$ for an electron with wave vector $\vec{k}$ as a function of (lattice) temperature T is found to be

$$\langle \tau_{\vec{k}}(T) \rangle^{-1} = \frac{2}{\hbar} \int_0^\infty d\Omega \; g^2 B\left(\vec{k}, \Omega\right) \left(N_\Omega(T) + \frac{1}{2} \right), \tag{1}$$

where the dimensionless intervalley phonon spectral function $g^2 B\left(\vec{k}, \Omega\right)$ is a phonon density of states weighted with the electron density of final states and the strength of the appropriate electron-phonon coupling. Both emission and absorption processes are considered. The small phonon energy Ω in the δ-function of the golden rule (energy conservation) has been neglected. The latter approximation simplifies the numerical procedure and only causes a small error near the onset of IVS.

Throughout this paper, we study the intervalley scattering probabilities for a *single* electron in the crystal, i. e., for the zero-density limit. At higher carrier densities, the intervalley scattering times may be modified, mainly because of partially filled final states (Pauli principle), see Ref. 16. Screening of the intervalley electron-phonon interaction is of minor importance, as the momentum transfer of a zone-boundary phonon to the electron is much larger than the screening wave vector.

3. RESULTS

3.1. Lifetimes of electrons at the L- and X-points

The intervalley spectral functions for electrons at the L- and X-points, calculated with local empirical pseudopotential form factors from Ref. 22, interpolated as in Ref. 23 with a cutoff[24] of E_1=E_2=13, and a 10-parameter valence-overlap shell model for the phonons, [25,26] are shown in Fig. 1. The lifetimes as a function of temperature are given by the solid lines in Fig. 2. From Fig. 1 (a) it can be seen that the TA, LA, and LO phonons contribute to $L\Gamma$-scattering, whereas the contribution of the TO phonons is very small. At low temperatures, the IVS time is inversely proportional to the area under the peaks, therefore the contribution of the TA phonons will be moderate. At room temperature, however, the TA phonons will have a larger occupation factor than the LA and LO phonons, therefore they will give the largest contribution. This explains the discrepancy between the CW hot-luminescence experiment of Kash and coworkers[7] ($D_{\Gamma L}$=3.85 eV/Å at 2 K) and the femtosecond luminescence measurement by Shah and coworkers[3] ($D_{L\Gamma}$=6.5 eV/Å at 300 K). The low-temperature result of Kash gives the correct value, in very good agreement with the theoretical result[19] $D_{\Gamma L}$=2.6±0.3 eV/Å, for the combined IDP for the LA and LO modes (as the TA mode is not important), whereas the neglection of the TA mode at room temperature in the analysis of Shah's experiment leads to an overestimate of the IDP. For the same reason, Kim and Yu[28] also overestimate the $D_{\Gamma L}$ deformation potential in their subpicosecond Raman experiment performed at room temperature. The lifetime of an electron at the L-point as a function of temperature is given by the solid line in Fig. 2 (a) (6.6±1.0 ps at 10 K and 2.2±0.5 ps at 300 K, in agreement with the result of Shah, [3] the errors given are the standard deviations of ten calculations with different pseudopotential interpolations and phonon models). The dotted line in Fig. 2 (a) gives the lifetime when the interaction of the electron with the TA phonons is switched off. This leads to an increase of only 35% at 10 K; but more than doubles the lifetime at 300 K. Therefore the TA phonons must be taken into account in a Monte-Carlo analysis of hot-carrier experiments at room temperature. (Alternatively, an unphysically high value of about 7 eV/Å has to be used for the IDP at 300 K.[3,16]) At low temperatures, it is a reasonable approximation to omit TA phonon scattering and use an IDP of about 3.5 eV/Å as in Ref 6. We stress that Fig. 2 (a) gives the return times at the L-point. The return times at other points in the L-valley (with higher energies) may be shorter, as pointed out by Kann *et al.* [16]

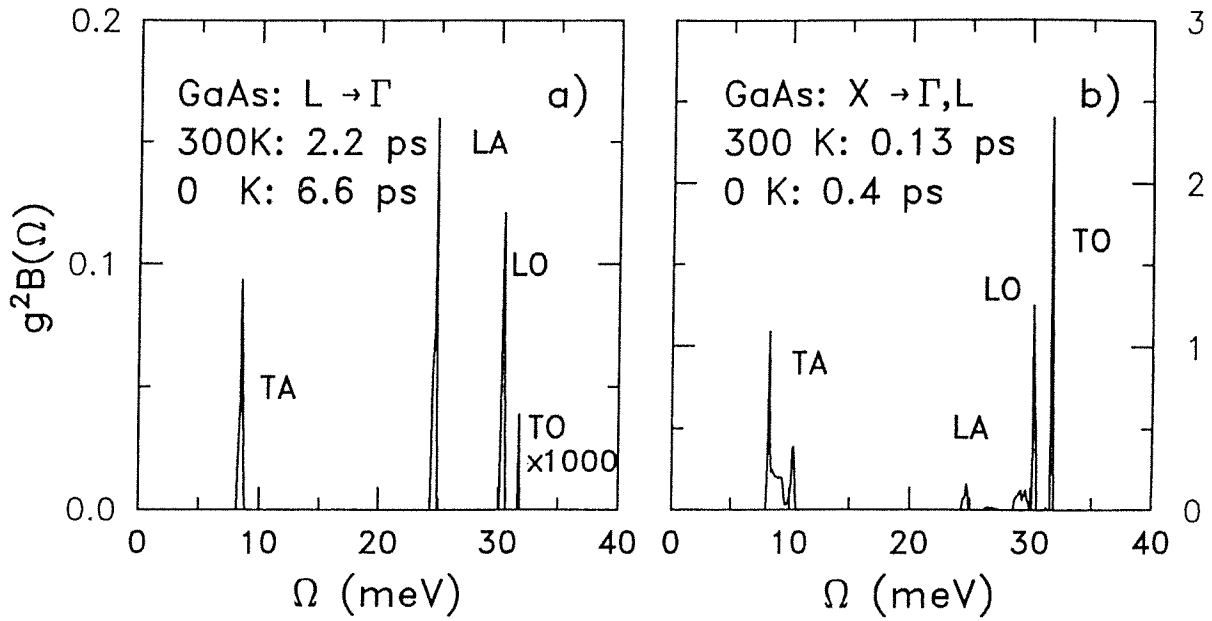

Figure 1: Temperature-independent, dimensionless intervalley phonon spectral function $g^2B(\Omega)$ for the lifetime of an electron at (a) the L-point and (b) the X-point. The abscissa is the energy Ω of the intervalley phonon. This spectral function has to be multiplied with the Bose–Einstein factor $N_\Omega(T)$ and integrated over all phonon energies in order to obtain the (zero carrier-density) lifetimes of the electrons as a function of temperature.

An electron at X_6 can scatter to the L_6-minima (by emission or absorbtion of an L-phonon) as well as to the Γ_6 minimum (with an X-phonon). Its intervalley phonon spectral function is given in Fig. 1 (b). It can be seen that the TA contribution is even larger than for $L\Gamma$-scattering, a consequence of the dispersion curves of Ref. 20. This means that the interaction with the TA phonons is the dominant mechanism for XL- and $X\Gamma$-scattering. As the TA (L) phonon peak (8.1–9.5 meV for our phonon model) is much larger than the TA (X) peak (9.6–10.3 meV), most carriers at X_6 will rather scatter to the L_6- than to the Γ_6-valley. The small peaks at about 27, 29, and 31.1 meV are the contributions of the LA (X), LO (X), and TO (X) phonons, respectively, whereas the large peaks at 24.8, 30.5, and 31.7 meV are due to the LA (L), LO (L), and TO (L) phonons, respectively. The importance of the TA phonons for $X\Gamma$-scattering proves that the commonly used[16,28] value of $D_{\Gamma X}$=10 eV/Å for the LO phonons is an overestimate, the actual value is much lower, in agreement with our previous results.[19] The lifetime of an electron at X_6 as a function of temperature is given by the solid line in Fig. 2 (b) (400±90 fs at 10 K and 130±20 fs at RT). These rates are somewhat shorter than the experimental X_6-lifetime of 700±500 fs at 300 K reported in Ref. 5, but agree well with the Monte-Carlo results of Kann *et al.* [16] The dashed line shows the lifetime when scattering from X_6 to the Γ-valley is switched off, i. e., when only scattering to the L-valleys is considered. This means that about 80% of the carriers at X_6 scatter to the L-valleys, only about 20% to the Γ-valley. This number is almost independent of temperature. Our calculation for $X\Gamma$-scattering is less accurate than for $L\Gamma$-IVS, since the effective mass in the Γ-valley 500 meV above its minimum is enhanced by nonparabolicity and thus not so well known. We have checked, however, that our pseudopotential model gives energies very close to those obtained from a $\vec{k}\cdot\vec{p}$-calculation used to interpret recent magneto-Raman data. [29]

3.2. Intervalley scattering times for electrons in the Γ-valley at different energies

The same numerical integration method can be used to calculate the lifetimes of electrons in the Γ-valley for any given initial k-point, see Figs. 3 and 4. We note, however, that this may require a finer mesh of phonon q-vectors in the integration. For numerical reasons it is desirable that both the initial electron wave vector and the minima of the valleys in question should be part of the mesh, especially for electrons just slightly above or below the onset of IVS. Because of storage and CPU-time limitations we used a mesh with 505 points in the irreducible wedge of the Brillouin zone with which this condition could not always be satisfied, hence our IVS rates carry some numerical noise, which decreases with increasing carrier energy. An additional source of error is the linear interpolation scheme used in

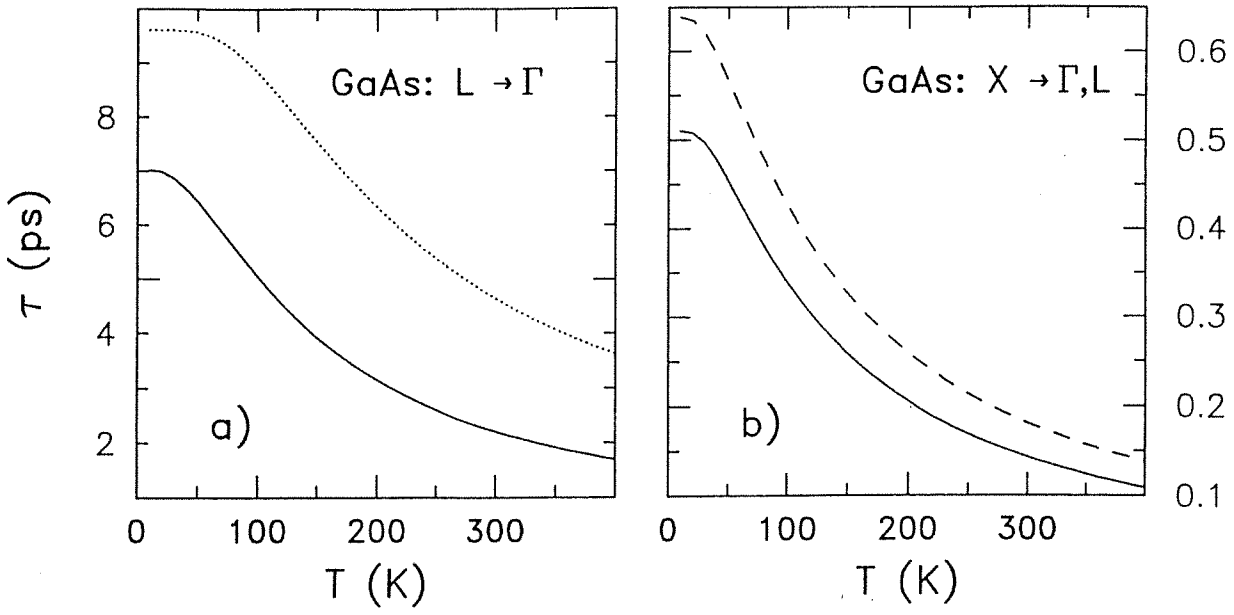

Figure 2: Lifetimes (return times) of electrons at the (a) L_6- and (b) X_6-points as a function of lattice temperature T in the zero carrier-density limit. The dotted line in Fig. 2 (a) gives the lifetime at L_6 when the interaction with the TA phonons is switched off. The dashed line in Fig. 2 (b) gives the scattering time from X_6 to the L_6-valleys only.

the tetrahedron method. We find, however, that the bare electronic densities of states obtained in one L-valley can be described well with an effective mass of m=0.24m_0 for energies of more than 100 meV above the L-minimum. Therefore our rates are reliable for carrier energies between 400 and 600 meV above the Γ minimum. In the same energy range, hot-electron luminescence measurements are most accurate. [10,7,8]

The intervalley phonon spectral functions [used to calculate the IVS rates with Eq. (1)] for electrons along the (100) direction with energies just below the X-point and 100 meV above the X-point, calculated with the same set of parameters as in the previous section, are given in Figs. 5 (a) and (b), respectively. For case (a), where only scattering to the L-valley is possible, we find that the optical phonons give the largest contribution, in qualitative agreement with the results of the groups of Mirlin[10] and Kash. [27] The other phonon modes (TA and LA) also contribute, as observed in the experiment by Mirlin and co-workers. [10] It is difficult, however, to estimate experimentally the exact ratios of the TA, LA and LO contributions to ΓL-scattering.[10] In Fig. 5 (a) it can be seen that the dominant intervalley phonon peak (LO) has a finite width Γ of about 1 meV (corresponding to a time $\tau = \hbar/\Gamma$=600 fs) caused by the dispersion of the LO phonons. The peak widths are even larger for ΓX-scattering, see Fig. 5 (b). This dispersion, however, should not have an influence on the lifetime broadenings of the *initial* states, but will broaden the final states in the satellite valleys.

We obtain IVS times of about 0.2 ps and 0.7 ps at room and zero temperature, respectively, in very good agreement with the experiment of Ref. 7. For case (b), IVS to the X-valley is also possible. In this case, we find IVS times of 25 fs and 100 fs, respectively, in reasonable agreement with the experiment of Ref. 7 (180 fs at 2 K). We note that the TA phonons give the dominant contribution to ΓX-scattering. This case is more difficult than case (a), as little is known about the possible camelback structure near the X-point in GaAs.

In Fig. 3 we show the IVS rates of electrons in the Γ-valley as a function of energy at zero temperature. The zero-point on the energy scale is taken to be the energy E_L of the L-point. The symbols give the results of our calculation along the (100), (110), and (111) directions, whereas the solid line was fitted by Kash and co-workers[7] to their hot-electron luminescence data with Conwell's formula (Eq. (3) of Ref. 7), assuming a constant electron-phonon matrix element and parabolic bands. The dotted and dashed lines give the IVS rates with the intervalley

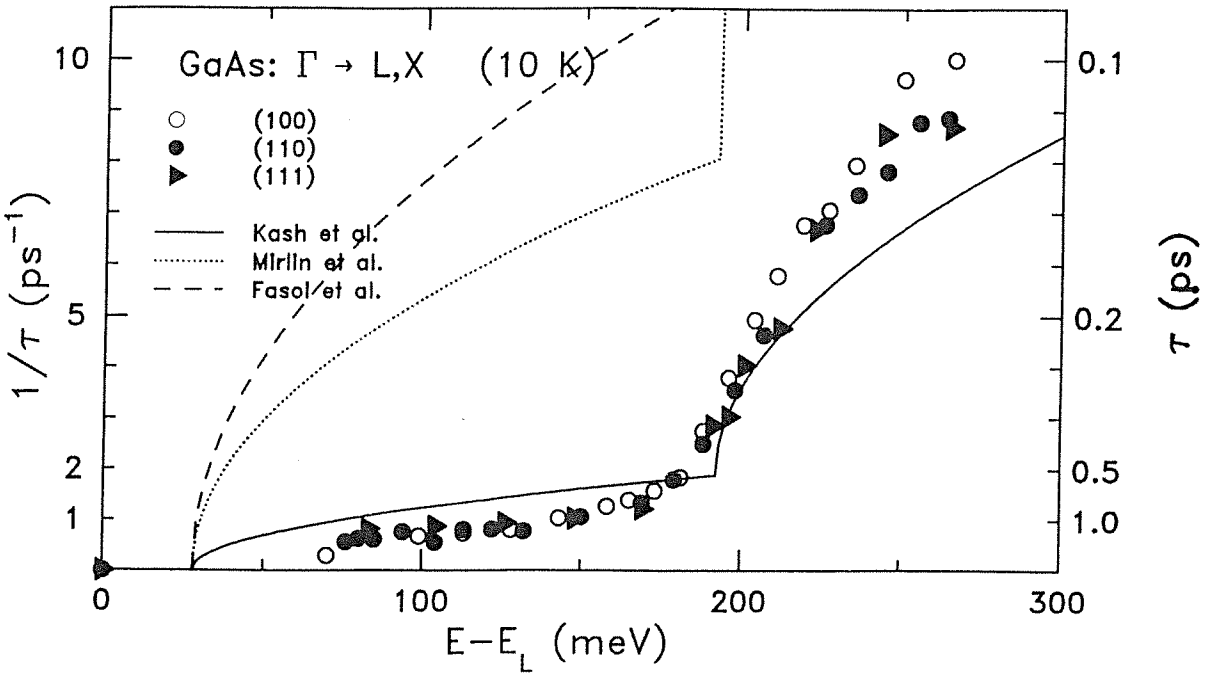

Figure 3: Lifetimes of carriers in the Γ-valley as a function of electron energy at 10 K (zero carrier-density limit). Symbols: IVS times for electrons with wave vectors along the (100), (110), and (111) directions, calculated as described in the text. The solid, dotted, and dashed lines give the fits with Conwell's formula to the experimental data of Refs. 7, 9, and 8, respectively.

deformation potentials of Refs. 9 and 8, respectively. No significant difference is seen in our calculation between the three directions, i. e., the IVS process is isotropic. The agreement with the experiment of Ref. 7 in the energy range from 150 to 250 meV above the L-point (where both the numerical procedure and the experiment are most accurate) is good. Below $E - E_L$=150 meV our theory gives somewhat longer times than expected from Conwell's formula. This may be due to non-parabolicity effects, the dispersion of the electron-phonon matrix elements, or the numerical integration procedure, as the minima in the band structure near L are linearly interpolated.

In Fig. 4 we give the IVS rates at room temperature as a function of electron energy. The solid, dotted, and dashed lines represent the IVS rates with the deformation potentials given in Refs. 7,9 and 8, respectively. The extrapolation of the experiment of Ref. 7 to room temperature overestimates the IVS times, because the TA phonons were not considered, just as in the case of $L\Gamma$-scattering discussed in Sec. 3.1. A direct comparison of our room temperature results with *femtosecond videos* (i. e., visible pump-and-probe measurements[11–13]) is not possible, as carrier-carrier scattering will generate a broad energy distribution of the electrons in the Γ-valley.[15]

3.3. Intervalley scattering-induced lifetime broadenings of hot-electron luminescence peaks

While our results agree very well with the hot-electron luminescence experiments of Kash, Ulbrich, and Tsang, [7] they disagree with those of Fasol and co-workers. [8] A possible explanation for this discrepancy could be that the peak-height analysis of Ref. 7 measures only the IVS times, whereas the analysis of the broadenings by Fasol *et al.*[8] is also affected by other scattering mechanisms, e. g., acoustic phonon scattering.

In order to investigate other possible scattering mechanisms, we have calculated the spectral function for deformation-potential intravalley scattering for an electron in the (100)-direction with an energy of 420 meV above the Γ-point, see Fig. 6. Both longitudinal and transverse acoustic phonons contribute, and also the optical phonons. We find intravalley scattering times of 5.3 ps and 550 fs at 10 and 300 K, respectively (compared to IVS times of 1.2 ps anf 350 fs), which are too long to affect the measured broadenings considerably. An estimate of the acoustic deformation potential (ADP) time with the equation[30]

$$\frac{1}{\tau_{\mathrm{ADP}}} = \frac{\pi E_1^2 q}{Mc}\left(N_q + \frac{1}{2} \pm \frac{1}{2}\right)\delta\left(E_f - E_i\right) \tag{2}$$

(and the parameters ADP constant E_1=8 eV, phonon wave vector $q = 0.2\pi/a$, lattice constant a=5.65 Å, mass of

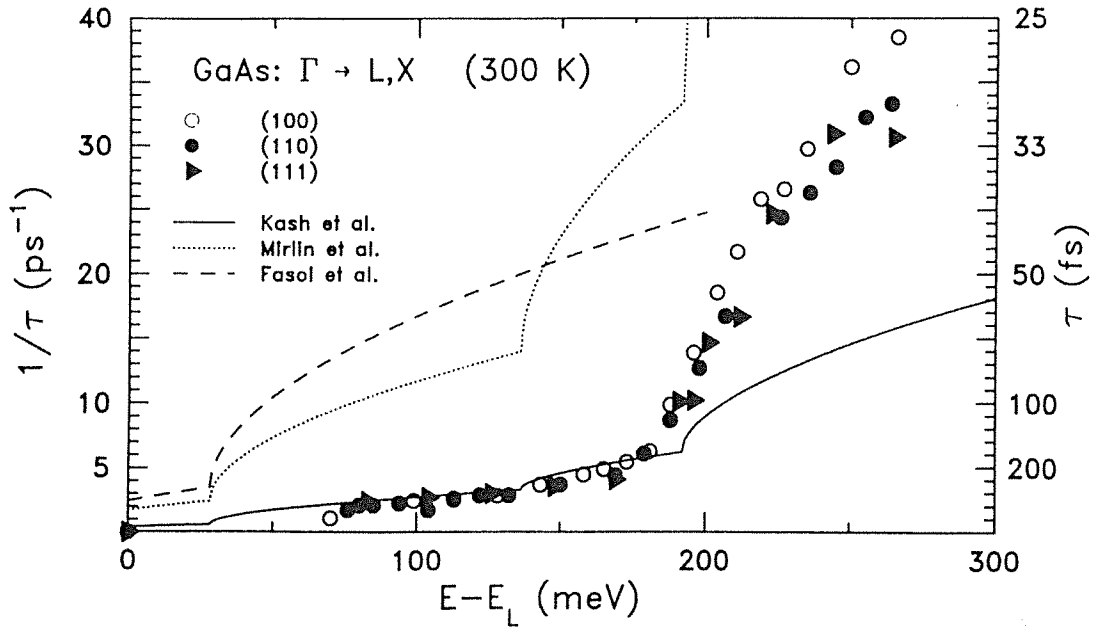

Figure 4: As Fig. 3, but at room temperature.

the unit cell $M = 2.4 \times 10^{-23}$ kg, speed of sound c=5 km/s) gives τ_{ADP}=3 ps at low temperatures, in reasonable agreement with our result.

4. CONCLUSION

We have found that the simple model of Ulbrich and Kash[7] is sufficient to model the intervalley electron dynamics at low temperatures. At room temperature and for ΓX-scattering, however, the contribution of the transverse acoustic phonons calls for a more detailed description. We have been able to explain several available experiments under different conditions (which at first sight seem to contradict each other) with a self-consistent model that is free of adjustable parameters for the electron-phonon coupling.

5. REFERENCES

1. J. D. Simon, "Ultrashort light pulses", *Rev. Sci. Instrum.*, vol. 60 (12), 3597-3624, 1989.
2. J. Shah, "Photoexcited hot carriers: From cw to 6 fs in 20 years", *Solid-State Electron.*, vol. 32 (12), 1051-1056, 1989.
3. J. Shah, B. Deveaud, T. C. Damen, W. T. Tsang, A. C. Gossard, and P. Lugli, "Determination of intervalley scattering rates in GaAs by subpicosecond luminescence spectroscopy," *Phys. Rev. Lett.*, vol. 59 (19), pp. 2222-2225, 1987.
4. A. Katz and R. R. Alfano, "Intervalley scattering rates in GaAs measured by time–resolved four–wave mixing spectroscopy," *Appl. Phys. Lett.*, vol. 53 (12), pp. 1065-1067, 1988.
5. W. B. Wang, N. Ockman, M. Yan, and R. R. Alfano, "The intervalley $X_6 \rightarrow \Gamma_6, L_6$ scattering time in GaAs measured by ultrafast pump-probe infrared absorption spectroscopy," *Solid-State Electron.*, vol. 32 (12), 1337-1345, 1989. See also the following paper of this conference.
6. R. G. Ulbrich, J. A. Kash, and J. C. Tsang, "Hot-electron recombination at neutral acceptors in GaAs: A *cw* probe of femtosecond intervalley scattering", *Phys. Rev. Lett.*, vol. 62 (8), 949-952, 1989.
7. J. A. Kash, R. G. Ulbrich, and J. C. Tsang, "Quantitative measurements of intervalley and carrier-carrier scattering in GaAs with hot (e,A^0) luminscence", *Solid-State Electron.*, vol. 32 (12), 1277-1281, 1989.

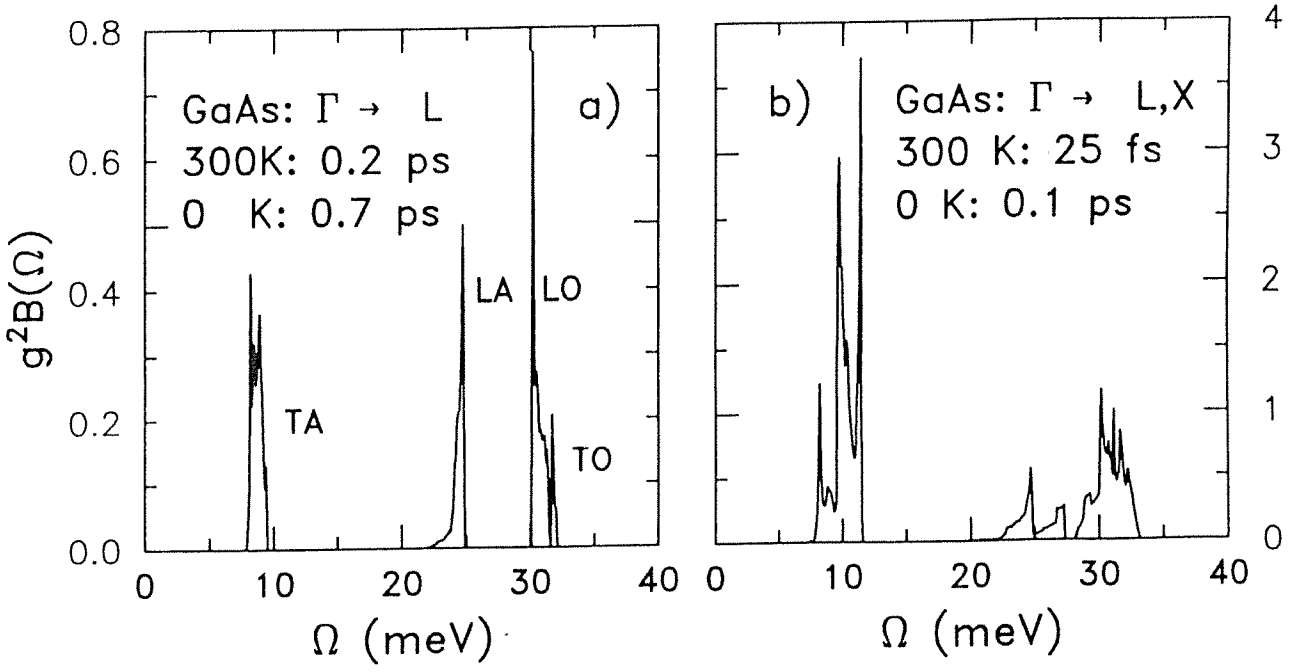

Figure 5: Dimensionless intervalley phonon spectral functions for electrons in the Γ-valley with energies just below (a) and 100 meV above (b) the X-point. The IVS times at zero and room temperatures are given.

8. G. Fasol, W. Hackenberg, H. P. Hughes, K. Ploog, E. Bauser, and H. Kano, "CW spectroscopy of femto-second carrier scattering in GaAs," *Phys. Rev. B.*, vol. 41 (3), 1461-1478, 1990. See also the preceding paper of this conference.
9. M. A. Alekseev, I. Ya. Karlik, D. N. Mirlin, and V. F. Sapega, "Spectroscopy of hot luminescence of semiconductors (review)", *Sov. Phys. Semicond.*, vol. 23 (5), 479-490, 1989.
10. D. N. Mirlin, I. Ja. Karlik, L. P. Nikitin, I. I. Reshina, and V. F. Sapega, "Hot electron photoluminescence in GaAs crystals", *Solid-State Commun.*, vol. 37, 757-760, 1981.
11. M.J. Rosker, F. W. Wise, and C. L. Tang, "Femtosecond optical measurements of hot-carrier relaxation in GaAs, AlGaAs, and GaAs/AlGaAs multiple quantum well structures", *Appl. Phys. Lett*, vol. 49 (25), 1726-1728, 1986.
12. W.-Z. Lin, R. W. Schoenlein, J. G. Fujimoto, and E. P. Ippen, "Femtosecond absorption saturation studies of hot carriers in GaAs and AlGaAs," *IEEE J. Quantum Electron.*, vol. 24 (2), pp. 267-275, 1988.
13. X. Q. Zhou, K. Seibert, W. Kütt, K. Wolter, and H. Kurz, "Hot carrier relaxation in InP and GaAs on a subpicosecond time scale," *Solid-State Electron.*, vol. 32 (12), 1591-1595, 1989.
14. D. W. Bailey, C. J. Stanton, M. A. Artaki, K. Hess, F. Wise, and C. L. Tang, "Ensemble Monte Carlo simulations of femtosecond energy relaxation of photoexcited electrons in bulk GaAs", *Solid-State Electron.*, vol. 31 (3/4), 467-470, 1988.
15. L. Rota and P. Lugli, "Energy exchange via electron-electron scattering in many-valley semiconductors," *Solid-State Electron.*, vol. 32 (12), 1423-1427, 1989.
16. M. J. Kann, A. M. Kriman, and D. K. Ferry, "Role of electron-electron scattering on ultrafast probe phenomena of photoexcited carriers in GaAs", this conference.
17. E. M. Conwell, *High-field transport in semiconductors*, Solid State Physics, Suppl. 9, Academic Press, New York, 1967, pp. 149.
18. W. Fawcett and D. C. Herbert, "High-field transport in gallium arsenide and indium phosphide", *J. Phys. C*, vol. 7, 1641-1654, 1974. We feel that the screened values for the intervalley deformation potentials of this paper are relevant for the problem under investigation.
19. S. Zollner, Sudha Gopalan, and M. Cardona, "Intervalley deformation potentials and scattering rates in zinc blende semiconductors," *Appl. Phys. Lett.*, vol. 54 (7), pp. 614-616, 1989. The IDPs given in this paper have to divided by $\sqrt{2}$ to be consistent with Conwell's notation.

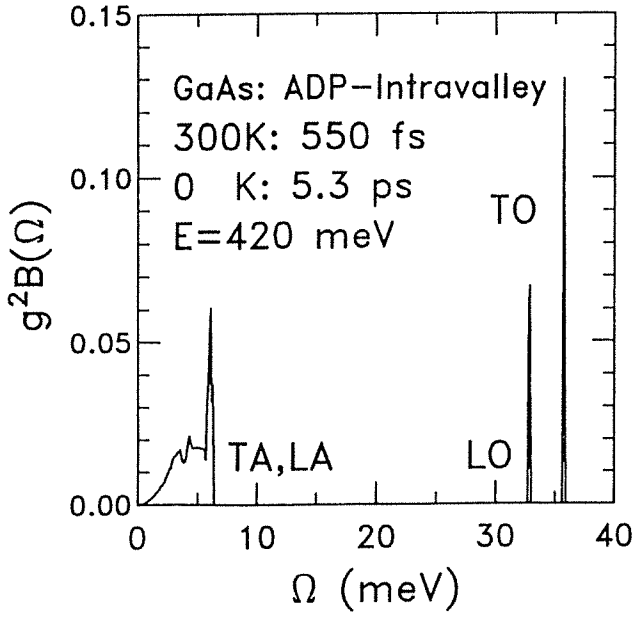

Figure 6: Dimensionless spectral function of an electron with E=420 meV for deformation-potential assisted intravalley scattering (zero-density limit).

20. S. Zollner, Sudha Gopalan, and M. Cardona, "Microscopic theory of intervalley scattering in GaAs: k-dependence of deformation potentials and scattering rates," to appear in *J. Appl. Phys.*
21. S. Zollner, J. Kircher, M. Cardona, and Sudha Gopalan, "Are transverse phonons important for Γ-X-intervalley scattering ?," *Solid-State Electron.*, vol. 32 (12), 1585-1589, 1989.
22. E. Caruthers and P. J. Lin-Chung, "Pseudopotential calculations for $(GaAs)_1$-$(AlAs)_1$ and related monolayer heterostructures," *Phys. Rev. B*, vol. 17 (6), pp. 2705-2718, 1978.
23. Sudha Gopalan, P. Lautenschlager, and M. Cardona, "Temperature dependence of the shifts and broadenings of the critical points in GaAs," *Phys. Rev. B*, vol. 35 (11), pp. 5577-5584, 1987.
24. M. L. Cohen and T. K. Bergstresser, "Band structures and pseudopotential form factors for fourteen semiconductors of the diamond and zinc-blende structures," *Phys. Rev.*, vol. 141 (2), pp. 789-796, 1966.
25. K. Kunc and H. Bilz, "Local approach to polarizabilities and trends in the Raman spectra of semiconductors," *Solid State Commun.*, vol. 19, pp. 1017-1030, 1976.
26. K. Kunc and O. H. Nielsen, "Lattice dynamics of zincblende structure compounds. II. Shell model," *Computer Physics Commun.*, vol. 17, pp. 413-422, 1979.
27. J. A. Kash, (private communication).
28. D.-S. Kim and P. Y. Yu, "Phonon temperature overshoot in GaAs excited by subpicosecond laser pulses," *Phys. Rev. Lett.*, vol. 64 (8), pp. 946-949, 1990.
29. T. Ruf and M. Cardona, "Nonparabolicity of the conduction band in GaAs", submitted to *Phys. Rev. B.*
30. L. Reggiani, "General theory" in *Hot-electron transport in semiconductors*, ed. by L. Reggiani, Springer, Berlin, 1985, p. 66.

Stefan Zollner

PROCEEDINGS

SPIE—The International Society for Optical Engineering

Ultrafast Laser Probe Phenomena in Bulk and Microstructure Semiconductors III

Robert R. Alfano
Chair/Editor

18-19 March 1990
San Diego, California

Sponsored by
SPIE—The International Society for Optical Engineering

In cooperation with the
Society of Vacuum Coaters

Published by
SPIE—The International Society for Optical Engineering
P.O. Box 10, Bellingham, Washington 98227-0010 USA

SPIE P PROCEEDINGS SERIES

Volume 1282