Ab initio Method for Calculating Electron-Phonon Scattering Times in Semiconductors: Application to GaAs and GaP

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We propose a fully *ab initio* approach to calculate electron-phonon scattering times for excited electrons interacting with short-wavelength (intervalley) phonons in semiconductors. Our approach is based on density functional perturbation theory and on the direct integration of electronic scattering probabilities over all possible final states with no *ad hoc* assumptions. We apply it to the deexcitation of hot electrons in GaAs, and calculate the lifetime of the direct exciton in GaP, both in excellent agreement with experiments. Matrix elements of the electron-phonon coupling, and their dependence on the wave vector of the final state and on the phonon modes, are shown to be crucial ingredients of the evaluation of electron-phonon scattering times.

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The interaction of excited electrons with phonons plays a central role in nanoelectronics [1]. When electrons are promoted to the conduction band (CB) of a semiconductor (SC) by an interband absorption process, only a small portion of the excited electrons can return into the valence states, giving rise to emitted radiations. Rather, the finite lifetime of the excitation is due to nonradiative scattering mechanisms such as collisional processes with surfaces, impurities, and phonons [2]. The nature of the scattering depends on the excitation energy with respect to the bottom of the CB. In a relatively pure sample, at energies lower than the band gap energy, electron-phonon interaction is the dominant process limiting the excitation lifetime, while above a threshold energy larger than the band gap, carrier-carrier scattering yields an additional limiting mechanism known as inverse Auger or impact ionization [3].

Despite its importance, only few works have been devoted to the *ab initio* study of electron-phonon coupling in SCs. Theoretical works based, in particular, on density functional theory (DFT) have addressed deexcitation mechanisms like impact ionization [3] or the scattering by impurities [4]. Contrastingly, a reliable approach within DFT is still lacking for phonon interaction with CB carriers. Moreover, the coupling of excitons with phonons has only been calculated through a semiempirical approach [5,6], notwithstanding the great progress made by *ab initio* methods in the understanding of the excitonic effects in optical absorption spectra [7]. On the other hand, ultrafast optical spectroscopy now provides an efficient tool for detailed investigations of the microscopic scattering processes related to hot carriers [8], and, in particular, of their deexcitation through phonon scattering [9]. Numerical simulations of ultrafast processes lack precision as many parameters enter the calculations [2,8,10]. This leads to difference among experimental deformation potentials as large as 100% [11]. The theoretical interpretation of time-resolved spectroscopy results without fitting parameters is thus still in its infancy.

To bridge this gap, we study in this Letter the electron-phonon scattering time (EPST) for collisions with short-wavelength phonons in semiconductors. The EPST is of crucial importance in SCs with different minima (valleys) in the CB, since, e.g., the transfer to a valley with a high effective mass drastically affects the carrier mobility [12], limits the transport at high field, and controls the dynamics of deexcitation [2]. Our fully *ab initio* approach for the interaction of an electronic state in the CB with short-wavelength phonons is based on Density Functional Perturbation Theory (DFPT) [13]. The electronic relaxation rate (ERR) is evaluated with Fermi's golden rule, its inverse yielding the EPST. No *ad hoc* assumptions are made concerning relative energies of the CB valleys, carrier effective mass, phonon spectrum, or carrier-phonon coupling matrix elements. We compare our results to various experimental situations:

(i) In GaAs, hot electrons at Γ rapidly cool down by intervalley scattering, which is more efficient than intravalley relaxation. Thus, the promotion of photoelectrons at 0.5 eV above the direct band gap by a laser excitation results in a thermalized distribution of hot carriers at L. The EPST τ_L from L to the zone center valley has been measured by various time-resolved spectroscopy experiments and ranges from 1.4 to 2.7 ps [9,14,15]. According to our calculations, most of these values are overestimated.

(ii) In GaP, the EPST τ_Γ corresponds to the lifetime of the direct exciton [5]. In this indirect gap SC, emission or absorption of short-wavelength (intervalley) phonons transfer the electron from Γ to the neighboring CB minima (Fig. 1, upper panel). The corresponding linewidth of the excitonic peak measured by spectroellipsometry [5] and transmission experiment [16] was found to strongly disagree with calculated ERRs [5,6]. Our method is able to explain quantitatively the excitonic linewidth.

GaAs and GaP are described within density functional theory using the local density approximation. Phonon frequencies and the corresponding perturbations of the self-

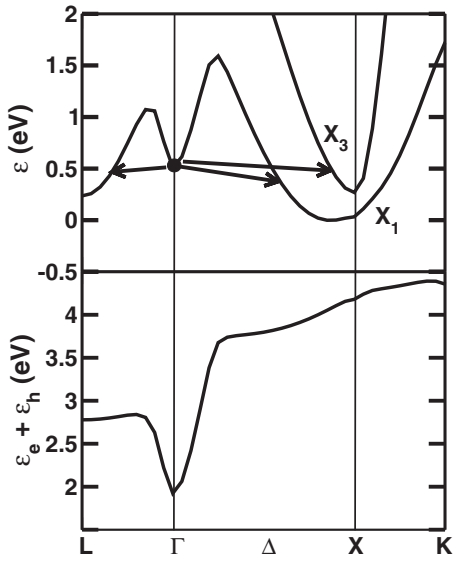

FIG. 1. GaP. Upper panel: Lowest CBs in DFT-LDA and schematic representation of diffusion channels available from the Γ point. The energy (eV) is referred to the CB bottom. Lower panel: uncorrelated electron-hole (e-h) energy $\varepsilon_e + \varepsilon_h$ (eV) within DFT-LDA.

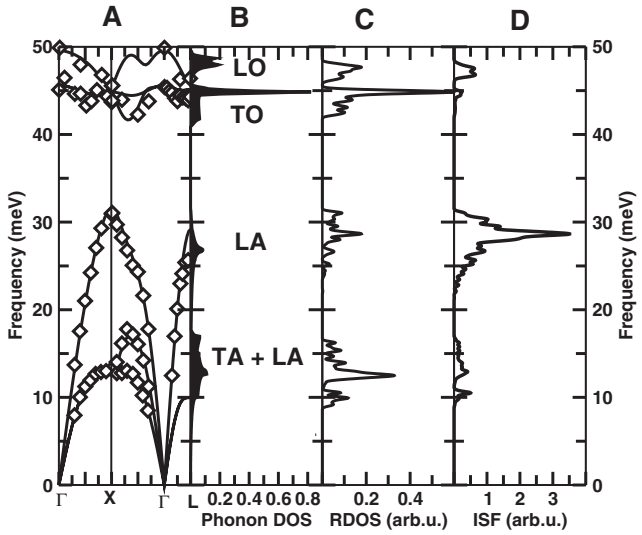

FIG. 2. GaP. (a) Phonon dispersion. Solid lines: this work. Diamonds: experiment [23]. (b) calculated phonon density of states (DOS). (c) restricted intervalley phonon density of states (RDOS) (Eq. (7)). (d) intervalley spectral function (ISF) [Eq. (4)].

consistent crystal potential are calculated within DFPT [13]. For GaAs, details of the calculations and results on the CB topology and on the phonon properties have been reported in Ref. [17]. For GaP [18], our results are close to previous theoretical works [21,22]. The relative energies at the high-symmetry points of the CB are found in extremely good agreement with experiment [23], the differences lying within experimental uncertainty. Calculated phonon dispersion curves and experimental ones [23] are also in excellent agreement for this SC (Fig. 2, panel A).

In this Letter, we consider the transfer of an electron excited at a given $\mathbf{k}$ point of the nth CB to another valley, due to emission or absorption (plus and minus in the following) of short-wavelength phonons. These intervalley transitions must verify energy and momentum conservation conditions:

$$\mathbf{k}' = \mathbf{k} \pm \mathbf{q}, \qquad \varepsilon_{n'\mathbf{k}'} = \varepsilon_{n\mathbf{k}} \pm \hbar\omega_{\mathbf{q}}^{\lambda}. \tag{1}$$

Here, n' and $\mathbf{k}'$ are the band number and wave vector of the final electronic state; λ and $\mathbf{q}$ are phonon mode index and wave vector; ε is the energy of the electronic state; and ω the phonon frequency. As phonon energies are always much smaller than electronic ones, in what follows we shall concentrate on *horizontal* transitions where energies of the initial and final electronic states are equal.

The transition amplitude is given by the electron-phonon matrix elements, which read in DFPT

$$\langle n, \mathbf{k}|\Delta W_{\mathbf{q}}^{\lambda}|n', \mathbf{k} \pm \mathbf{q}\rangle, \tag{2}$$

where $|n, \mathbf{k}\rangle$ and $|n', \mathbf{k} \pm \mathbf{q}\rangle$ are unperturbed Kohn-Sham electronic states, and $\Delta W_{\mathbf{q}}^{\lambda}$ is the variation of the Kohn-Sham self-consistent crystal potential with respect to the displacement pattern of the scattering phonon. The electron-phonon matrix elements have been widely studied in metals because of the superconductivity arising at low temperature [24].

If we neglect coherent processes, the probability $P_{n\mathbf{k},n'\mathbf{k}\pm\mathbf{q}}^{\lambda}$ of an intervalley transition is given by Fermi's golden rule:

$$P_{n\mathbf{k},n'\mathbf{k}\pm\mathbf{q}}^{\lambda} = \frac{2\pi}{\hbar}|\langle n, \mathbf{k}|\Delta W_{\mathbf{q}}^{\lambda}|n', \mathbf{k} \pm \mathbf{q}\rangle|^2 \delta(\varepsilon_{n'\mathbf{k}'} - \varepsilon_{n\mathbf{k}}). \tag{3}$$

By integrating over available states in the final valley, one obtains the phonon-frequency-dependent spectral function $F_{n\mathbf{k}}(\omega)$:

$$F_{n\mathbf{k}}(\omega) = \sum_{n'}\sum_{\lambda}\int_{BZ} d^3\mathbf{q} P_{n\mathbf{k},n'\mathbf{k}\pm\mathbf{q}}^{\lambda}\delta(\omega_{\mathbf{q}}^{\lambda} - \omega). \tag{4}$$

Further integration of $F_{n\mathbf{k}}$ over the frequency of possible scattering phonons yields the ERR of initial state $\Gamma_{n\mathbf{k}}$:

$$\Gamma_{n\mathbf{k}} = 2\int d\omega F_{n\mathbf{k}}(\omega)\left(N(\omega, T) + \frac{1}{2}\right), \tag{5}$$

which now depends on temperature through $N(\omega, T)$, the Bose-Einstein distribution function for phonons at thermal equilibrium. The factor of 2 in front of the integral comes from the emission and absorption of phonons that are treated together. Finally, the EPST is defined as the inverse of the ERR:

$$\tau_{n\mathbf{k}} = \hbar\Gamma_{n\mathbf{k}}^{-1}. \tag{6}$$

We have first applied Eqs. (2)–(6) to the transfer from L to the Γ valley in the first conduction band of GaAs. Our

ab initio value of the EPST is 1.5 ps (Table I). This is very close to the value obtained by a direct fit of the transient absorption spectrum in a pump-probe experiment [14]. It is also in agreement with time-resolved spectroscopy measurements of Refs. [9,15], whose interpretation is less straightforward and relies on the solution of Boltzmann equation for charge carriers. Resulting EPST are somewhat overestimated (Table I). At variance with previous theoretical data [25,26], our approach is parameter free. Our error bar of ± 0.2 ps comes from the density of final states, which depends on the precision of the dispersion of the CB in Kohn-Sham framework. For GaAs, important quantities are the relative Kohn-Sham energies at L and Γ, and the curvature of $\varepsilon(\mathbf{k})$ —the effective mass— at Γ.

Turning to gallium phosphide, our value of the ERR $\hbar\tau_\Gamma^{-1}$ at low temperature is 9.2 meV. The width of the direct exciton is found to be 12 meV [16] or 16 meV [5]. Three hypotheses underlie the direct comparison of these experimental values with our calculation of the EPST for a KS orbital. (i) The perturbation by the phonon of the correlation part of the excitonic Hamiltonian can be neglected [27]. (ii) The perturbation of the uncorrelated part of the excitonic Hamiltonian consists of the scattering of the electron plus the scattering of the hole [6,27]. But in GaP, the valence band dispersion is such that the energy conservation rule (1) forbids the phonon + hole decay channels, and thus the electron scattering described by Eq. (2)–(6) is the dominant contribution to the EPST [6]. (iii) In Eq. (2), the initial state should be an excitonic wave function, described by the mixing of wave functions of independent electron-hole pairs whose energies are close to each other. However, the dispersion of the uncorrelated electron-hole energy is such that only states very close to Γ can be mixed (Fig. 1, lower panel). As a result, the Kohn-Sham orbital at Γ is preponderant in the excitonic wave function, and can be chosen as the initial state for the electron-phonon scattering.

Taking 12 meV as an upper limit for the fundamental experimental [16] ERR due to exciton-phonon coupling, and comparing to our theoretical value, we show that our hypotheses are valid within 23%. Experimental resolution as well as surface and electron-electron scatterings are present in the measurements and not in our theoretical value and this further strengthens the agreement between theory and experiment. Our *ab initio* result quantitatively improves over previous theoretical works [5,6], which yielded an upper value of $\hbar\tau_\Gamma^{-1} = 4$ meV. A detailed investigation shows that variations of the screening potential with respect to atomic displacements induced by phonons are the main source of improvement.

Our theoretical value, $\tau_\Gamma = 71$ fs (Table II), is due to the intervalley scattering from Γ point to X_1, X_3 and L valleys (Fig. 1, upper panel). Scattering to the X_1 valley is the fastest, due to the high density of final electronic states available in this valley (Table II). Note however that the scattering time to the L valley is comparable, and that scattering to the X_1 valley can not be considered as the only dominant mechanism, at variance with a previous suggestion [5].

The calculated EPST is drastically reduced at ambient temperature, by a factor of 2 (Table II). The experimental width of the excitonic line [5] is accordingly twice larger at ambient temperature than at 10 K. Moreover, the order of magnitude of the EPST for $\Gamma \rightarrow X_3$ scattering, 1 ps at 300 K, is consistent with the experimental result of time-resolved IR-absorption spectroscopy [28]. In the later (indirect) experiment, the electron population in the X_3 valley was found to peak 2 ps after the pumping into Γ valley had started.

Longitudinal acoustic (LA) phonons provide the main contribution to the EPST as shown by the intervalley spectral function (Fig. 2, panel D). This result is important, as it shows that the transversal acoustic (TA) phonons are less important than previously believed [5].

To understand the role of expression (2) in this last finding, we define a "restricted phonon DOS" $R_{n\mathbf{k}}$ as

$$R_{n\mathbf{k}}(\omega) = \sum_{n'} \sum_{\lambda} \int_{\mathrm{BZ}} d^3\mathbf{q}\, \delta(\varepsilon_{n'\mathbf{k}\pm\mathbf{q}} - \varepsilon_{n\mathbf{k}})\delta(\omega_{\mathbf{q}}^{\lambda} - \omega) \tag{7}$$

which is a DOS restricted to phonons which enter the intervalley scattering process and thus verify the energy and momentum conservation laws of Eq. (1). This amounts to set electron-phonon matrix elements to a constant in Eq. (4). There is a one-to-one correspondence between peaks of $R_\Gamma(\omega)$ and those of the phonon DOS (Fig. 2, panels C and B, respectively). Yet, relative heights of the peaks are strongly modified. $R_\Gamma(\omega)$ is similar to the DOS only for optical phonons. This is due to the flatness of the optical branches (panel A).

TABLE I. GaAs: electron-phonon scattering time τ_L (ps) from the L point to the Γ valley in the first CB at 300 K.

	This work	Theory	Exp.
τ_L (ps)	1.5 ± 0.2	2.2 ± 0.5 [25]	≈ 2.7[a]
		1.3 ± 0.3 [26]	2 ± 0.5[b]
			1.4[c]

[a]Time-resolved four wave mixing experiment [15].
[b]Time-resolved luminescence [9].
[c]Pump-probe measurement of the transient optical absorption [14].

TABLE II. GaP. Theoretical electron-phonon scattering time τ_Γ (fs) from the Γ point of the first conduction band into energetically lower valleys, at low and ambient temperature.

T (K)	τ_Γ (fs)	Total	$\Gamma \rightarrow X_1$	$\Gamma \rightarrow X_3$	$\Gamma \rightarrow L$
10		71	123	1900	186
300		32	55	894	97

At variance with $R_\Gamma(\omega)$, $F_\Gamma(\omega)$ (Fig. 2, panel D) shows an unexpectedly small contribution coming from optical phonons. The difference between the intervalley phonon spectral function F_Γ and the restricted DOS R_Γ arises from the presence in the former of the electron-phonon coupling matrix elements of expression (2) which, for optical phonons, are found either very small or null because of selection rules [29]. Expression (2) is thus a crucial ingredient of the EPST.

Comparison of $F_\Gamma(\omega)$ and $R_\Gamma(\omega)$ for GaP unveils the strong dependence of the electron-phonon coupling matrix elements on the wave vector of the final electronic state and on the phonon mode. This important result, already pointed out for GaAs [25,30], is nevertheless neglected in most of today's descriptions of the collisional deexcitation processes [10,31]. The integration over all final electronic states required by Eq. (4) is a crucial ingredient and the most cumbersome part of our calculation [32]. The numerical cost of such a procedure is heavy because the calculation of several hundreds of phonons is necessary to achieve convergence.

In conclusion, we have performed a fully *ab initio* study of the electron relaxation via emission or absorption of short-wavelength phonons in GaAs and GaP. The method we propose to evaluate the electron-phonon scattering time provides insight into the electronic deexcitation by intervalley phonons, allowing us to distinguish efficient scattering phonon branches and dominant valleys from first principles. Our results illustrate the potential of density-functional-based method for the study of electron-phonon coupling in semiconductors, in particular, for the interpretation of time-resolved spectroscopy experiments and for the lifetime of excitons. It is directly applicable to nanostructures such as superlattices and nanowires.

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