

# Time Evolution of Second Order Susceptibility in GaAs following a Fast Intense Laser Pulse

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## Abstract

Using the technique of tight-binding electron-ion dynamics, we have calculated the evolution of the nonlinear susceptibility  $\chi^{(2)}(\omega)$  in GaAs during the first few hundred femtoseconds following an ultrafast and ultra-intense laser pulse. Above a threshold fluence, our simulations show that  $\chi^{(2)}(\omega)$  drops to zero, in agreement with the experimental measurements. The results indicate a rapid nonthermal transition from the original tetrahedral structure to a disordered structure, and support the conclusion that structural changes following ultrashort pulses are a direct consequence of bond destabilization.

## 1 Introduction

The transformations that occur in a semiconductor subjected to intense laser radiation are of considerable interest, because one would like to understand the fundamental physical processes in the newly accessible regime of short time scales and high intensities. There have consequently been a number of previous experimental observations [1-5] and theoretical calculations [6, 7] of the behavior of semiconductors following ultrashort and ultra-intense laser pulses.

In recent experiments [3, 4], the time evolution of the second-order nonlinear susceptibility  $\chi^{(2)}$  has been measured in GaAs, using a 2.2 eV probe pulse after excitation with an intense 1.9 eV pump pulse. The observations show that the response of a semiconductor to an ultrafast laser pulse, with a duration of 100 femtoseconds or less, is fundamentally different from its response to a pulse with a duration of 1 picosecond or more. Whereas the longer pulses appear to produce ordinary heating of the sample by phonon emission, there is convincing evidence that ultrafast pulses induce a structural transition by directly destabilizing the atomic bonds [1-5,8].

The present paper complements previously published results [8] with a new study of the time evolution of  $\chi^{(2)}(\omega)$  in GaAs. As in Ref. 8, the simulations were performed with eight atoms and with a 50-attosecond time step. As in the experiments, the pulse duration was taken to be 70 femtoseconds and the photon energy to be 1.9 eV. Some key features of the method are reviewed in Section 2, and the main new results of our simulations are presented in Section 3.

## 2 Tight-Binding Electron-Ion Dynamics

Standard molecular dynamics techniques assume the validity of the Born-Oppenheimer approximation. The electrons are required to follow the motion of the nuclei adiabatically, remaining in a ground state configuration for which the one-electron states are determined by the time-independent Schrödinger equation

$$H(X) \psi_k(x, X) = \varepsilon_k(X) \psi_k(x, X). \quad (2.1)$$

The population of the one-electron states is thus assumed to remain invariant during the time evolution of the system. Clearly the Born-Oppenheimer approximation is not relevant to the present problem; in a system experiencing an intense laser pulse, a substantial fraction of the valence electrons are non-adiabatically promoted to excited states.

Tight-binding electron-ion dynamics (TED) is a method designed for nonadiabatic processes, and for interaction with a radiation field. Two coupled equations describe the dynamics:

$$i\hbar \partial \Psi_j / \partial t = \mathbf{H}(X, t) \cdot \Psi_j \quad (2.2)$$

$$M\ddot{X} = - \sum_j \Psi_j^\dagger \cdot \frac{\partial \mathbf{H}(X, t)}{\partial X} \cdot \Psi_j - \frac{\partial U}{\partial X}. \quad (2.3)$$

Here  $\mathbf{H}$  represents the usual tight-binding electronic Hamiltonian and  $U$  is the usual repulsive potential. Although  $\Psi_j$  is no longer an eigenstate of the Hamiltonian, the generalized Hellmann-Feynman theorem (3) is still valid [9]. The conjunction of the two above equations leads to a strongly interdependent picture: The electronic states determine the forces on the atoms, while the motion of the atoms (together with the applied electromagnetic field) determines the electronic states.

Coupling of the electrons to an arbitrarily strong electromagnetic field is included through a time-dependent Peierls substitution. No additional parameters are required, and the applied field enters the tight-binding Hamiltonian  $\mathbf{H}(X, t)$  only as an additional phase in the interatomic matrix elements [8, 10].

The second order equation (3) was solved with a velocity Verlet algorithm, which preserves phase space. The first order equation (2) was solved with a Cayley algorithm, which conserves probability (or more generally preserves the orthonormality of the one-electron wavefunctions  $\Psi_j(t)$ ). Further technical details can be found in Ref. 8.

When an ultrashort laser pulse is applied to a semiconductor, valence electrons are promoted to the conduction bands on a time scale which is short compared to that for atomic motion ( $\sim 10 - 100$  fs versus  $\sim 100 - 1000$  fs). Electronic relaxation subsequently occurs through a combination of phonon emission, Auger recombination, and carrier diffusion. Our model does not include any of these relaxation processes, so the occupancy of the states  $n_k$  remains constant after the end of the laser pulse [8]. However, this should not be a significant

limitation in the present work, which focuses on the initial electronic and structural response rather than the subsequent behavior at longer times.

Previous TED simulations [8] show that there is a structural change in GaAs above a threshold fluence that corresponds to promotion of about 10% of the valence electrons to conduction-band states, on a time scale of 100 fs. When 10% of the electrons are promoted from bonding to antibonding states, the effect is roughly the same as removing 20% of the bonds. There are consequently strong repulsive interactions in the initial atomic geometry, which produce massive disruption of this geometry on a time scale of a few hundred femtoseconds.

### 3 Second Order Susceptibility

Because of its sensitivity to the crystal symmetry, the second order susceptibility  $\chi^{(2)}(\omega)$  can provide direct information about structural changes in noncentrosymmetric materials like GaAs, for which  $\chi^{(2)}$  is nonvanishing in the usual bulk geometry.

We have previously developed a formalism for calculating  $\chi^{(2)}(\omega)$  with a tight-binding Hamiltonian [11]. Employing an  $sp^3s^*$  orbital basis, together with the analytical expression for  $\chi^{(2)}$  derived in Ref. 11, we obtained results that are in good agreement with the best available first-principles calculations and experimental measurements for the unperturbed GaAs crystal.

In the case of the present time-dependent simulations, the imaginary part of the second-order susceptibility tensor was calculated after each 25 fs during the first 650 fs of a run. Just as for the usual first-order susceptibility (or dielectric function  $\epsilon(\omega)$ ), a Kramers-Krönig transform relates the real and imaginary parts of  $\chi^{(2)}$ . It follows that a decrease in the imaginary part of  $\chi^{(2)}(\omega)$  over the whole frequency range also means a decrease in the real part.

Figs. 1, 2, and 3 show the evolution of the imaginary part of  $\chi^{(2)}(\omega)$  when a 70 fs pump laser pulse is applied to GaAs, at three distinct fluences. For relatively low fluences, we find that  $\chi^{(2)}$  exhibits no significant changes. This can be clearly seen in the results of Fig. 1, for a fluence corresponding to an amplitude  $A_0 = 0.5$  G cm. One can relate  $A_0$  to the fluence by using the conversion of Ref. 8: For a pulse with  $A_0 = 1.0$  G cm, and a full-width-at-half-maximum (FWHM) of 70 femtoseconds, the fluence is  $0.815$  kJ/m<sup>2</sup>. The intensity, or fluence for fixed pulse duration, then varies as  $A_0^2$ . It should be mentioned that the threshold value of  $A_0$  obtained in the present simulations is substantially higher than that obtained in the experiments, because the present method does not accurately predict absolute cross-sections for absorption [8, 10].

As the threshold fluence is approached, the material exhibits “elastic” behavior: A strong decrease in the imaginary part of  $\chi^{(2)}$  is followed by a rapid recovery, as can be seen in Fig. 2. The time at which  $\chi^{(2)}$  reaches a minimum (near 400 fs) corresponds to maximum departure from the original tetrahedral bonding. (This will be seen in Fig. 4.) The value of  $A_0$  in Fig.

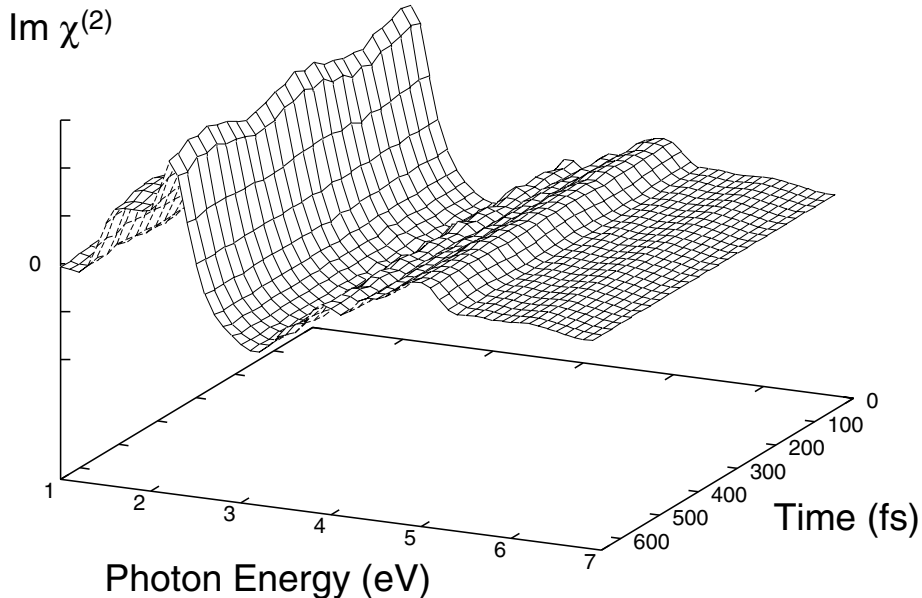


Figure 1:  $Im \chi^{(2)}(\omega)$  (in arbitrary units) as a function of the time  $t$  and photon energy  $\hbar\omega$ , well below threshold. The amplitude of the vector potential is  $A_0 = 0.5$  G cm. The laser pulse in all simulations begins at  $t = 0$  and has a FWHM duration of 70 fs with  $\hbar\omega = 1.95$  eV.

2 is 2.50 G cm, and it will be seen below that this corresponds to a fluence that is only very slightly below threshold.

Even slightly above threshold, on the other hand, there is an irreversible structural change. In Fig. 3, with  $A_0 = 2.51$  G cm, it is apparent that  $\chi^{(2)}$  is nearly zero over the whole frequency range after about 400 femtoseconds. This behavior indicates a change of symmetry in the material, and its persistence implies that a permanent structural change has occurred.

It is interesting that all three regimes represented by Figures 1-3 – no significant change in  $\chi^{(2)}$  at low fluence, large change followed by recovery at subthreshold fluence, and decrease to zero at large fluence – have been observed in the experiments [3, 4].

In order to obtain some microscopic insight into the nature of the reversible and irreversible transitions represented by Figs. 2 and 3, one can calculate the root-mean-square displacement of the atoms as a function of time. (This is the average over all atoms at a given time  $t$ .) The results are displayed in Fig. 4, for a range of values of  $A_0$ . There is a remarkably sharp transition from reversible to irreversible behavior for a critical intensity or fluence corresponding to  $A_0 \approx 2.5$  G cm. (As indicated above, the precise value of the

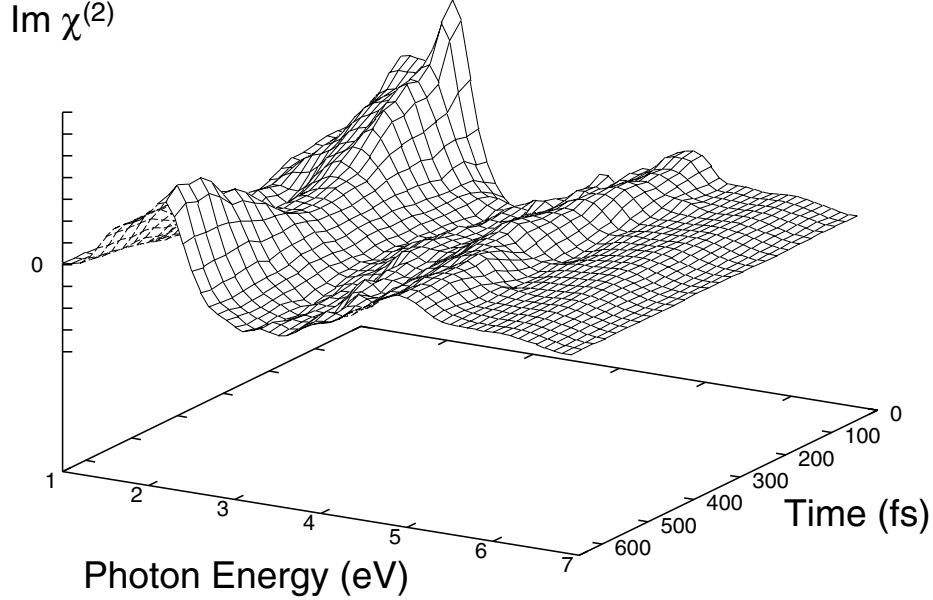


Figure 2:  $Im \chi^{(2)}(\omega)$  as a function of  $t$  and  $\hbar\omega$ , just below threshold, with  $A_0 = 2.50$  G cm.

threshold intensity is far from accurate, but the interesting feature is the existence of such a well-defined threshold.)

This abrupt transition in the behavior of the system suggests that a true phase transition occurs as the intensity of the pulse is varied.

In Fig. 4, notice that the thermal oscillations from equilibrium are continuously amplified in duration and magnitude as the intensity of the pulse is increased. For the subcritical value of  $A_0 = 2.50390$  G cm, there is a large departure from equilibrium, with  $R_{avg} \approx 0.12 \text{ \AA}$ , but the original structure is ultimately regained. On the other hand, a tiny increase to  $A_0 = 2.50393$  G cm results in sudden destabilization of the structure, after about 375 femtoseconds. The fact that the observed destabilization occurs *after* the maximum in  $R_{avg}$  suggests that the transition is not a collective phenomenon, but rather an initially local disruption that spreads to the whole structure on a short time scale.

Our calculations are complementary to those previously published [8], in which the first order susceptibility  $\epsilon(\omega)$  was found to evolve from semiconducting to metallic behavior, in agreement with the experimental observations. In the present paper we have obtained results which provide independent evidence for a structural transformation, from an ordered structure with a nonzero value of  $\chi^{(2)}$  to a disordered structure with  $\chi^{(2)} = 0$ . We have also determined the threshold intensity more carefully, and have found that there is a remarkably

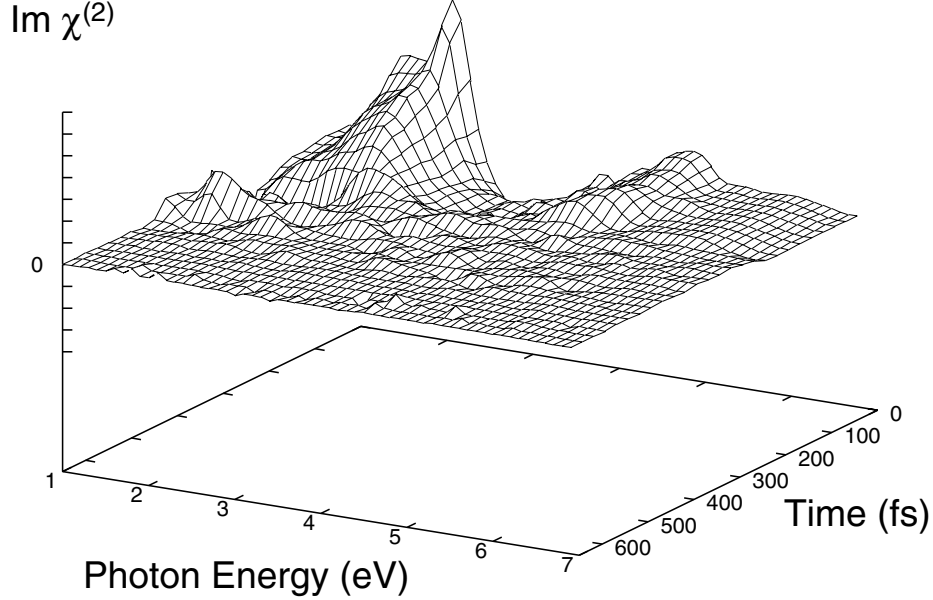


Figure 3:  $Im \chi^{(2)}(\omega)$  as a function of  $t$  and  $\hbar\omega$ , just above threshold, with  $A_0 = 2.51$  G cm.

abrupt transition from reversible to irreversible behavior as the intensity is varied, suggesting a true phase transition.

## 4 Conclusion

Using the method of tight-binding electron-ion dynamics [8], and an analytical expression for the second-order nonlinear susceptibility [11], we have simulated the interaction of ultra-short and ultra-intense laser pulses with GaAs and calculated the evolution of  $\chi^{(2)}(\omega)$  on a femtosecond time scale. Above a threshold fluence corresponding to excitation of about 10% of the valence electrons,  $\chi^{(2)}$  drops to zero on a time scale of 400 fs. This is the same threshold fluence, and same time scale, associated with the appearance of metallic behavior in the dielectric function  $\epsilon(\omega)$ . The time evolution of  $\chi^{(2)}$  indicates that the original symmetry of the GaAs crystal is lost, and the time evolution of  $\epsilon$  indicates that there is a loss of the original tetrahedral bonding. Both of these complementary results are consistent with the experimental measurements of  $\chi^{(2)}(\omega)$  and  $\epsilon(\omega)$ , and they independently support the conclusion that ultrashort laser pulses induce a nonthermal phase transition in this material.

## Acknowledgement

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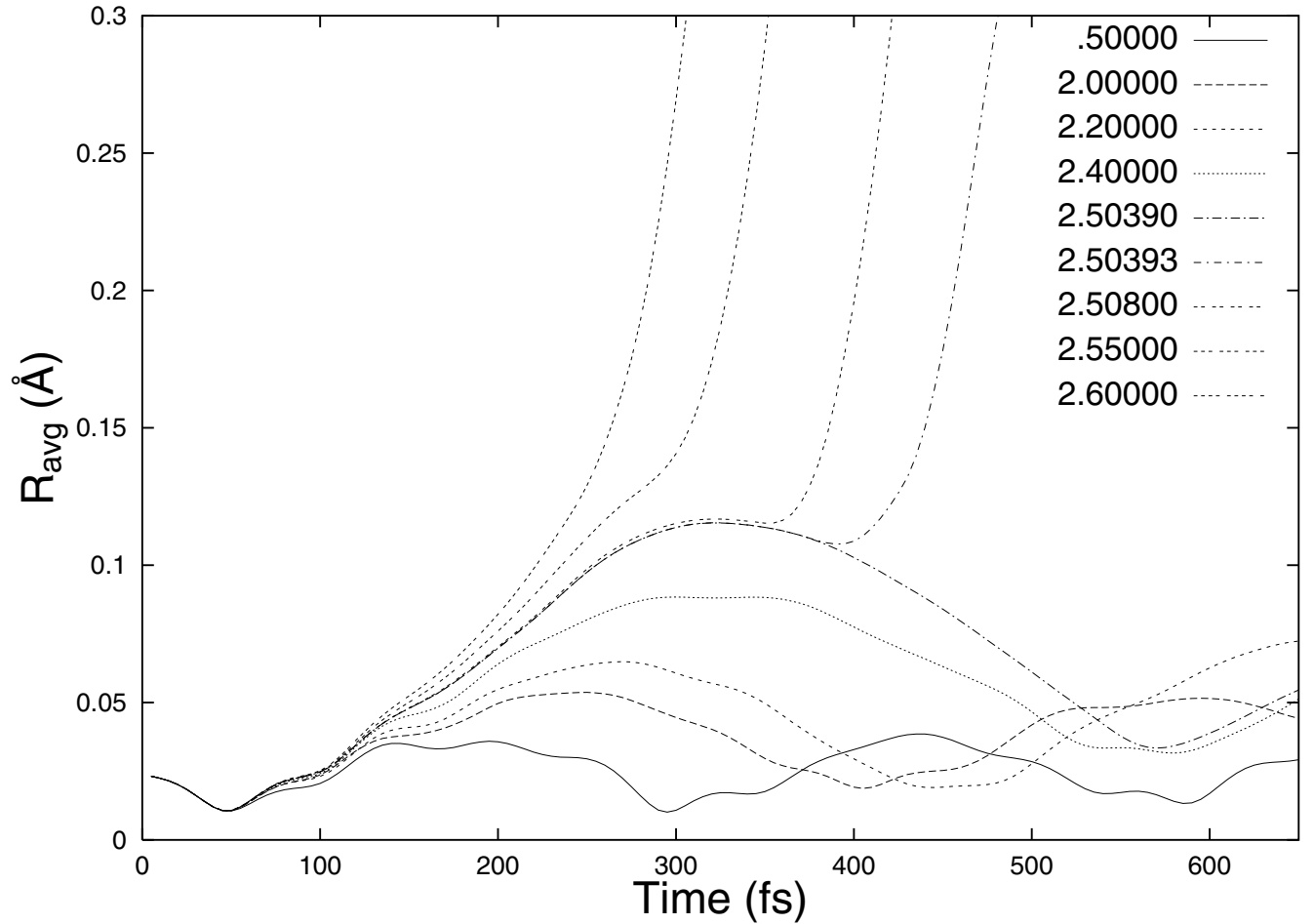


Figure 4: Root-mean-square displacement of atoms from their equilibrium positions for various intensities of the applied laser pulse.

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