An Introduction to Theory of Laser-Induced Ultrafast Structural Changes in Solids

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ABSTRACT: This paper introduces understanding and description of the response of solids to ultrafast optical excitations. In particular, we have studied structural changes induced in solids by the creation of a hot electron-hole plasma.

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INTRODUCTION

The study of the interaction of femtosecond laser pulses (pulse duration < 500f s) with solids has attracted considerable attention during the last decades [GDG83, SLFE87, BFI87, TABC88, KCL+ 88, LKJ+00, CTS+ 01, STBB+ 03, LLSTeA05, BBSS06, RTD+07, HEH+ 08]. Several studies were motivated by the fact that femtosecond laser excitation offers a novel tool for inducing new phenomena in solids, promising exciting potential applications. Most of the fundamental processes occurring in nature such as chemical reactions and phase transitions involve structural changes. By exciting solids appropriately, many different structural changes can be induced. In fact, depending on the laser characteristics (wavelength, pulse energy, pulse duration), laser solid interaction can result in a wide range of structural responses.

Among the different laser induced structural changes observed one can mention ultrafast melting [SAPF96a, JHL+03, LLSTeA05], solid-solid phase transitions [CTS+ 01, KTM03, RTD+07, KEH+07, CBRZ08], ablation [BBSS06, RSTvdLA04] and also generation of coherent phonons [PKKS92, SPK93, NHM+ 01, MMHK04, IKU06, ZTG06a]. The advantage of using ultra short laser pulse is that the different stages during the structural changes can be studied in a time-resolved way. For instance, melting, ablation and re-solidification phenomena take place on different time scales [BBSS06] (see figure 1.1) and therefore can be investigated separately.

A clear understanding of the mechanism for the structural response of solids to femtosecond laser excitation is therefore essential to take advantages of the huge technological applications possible.

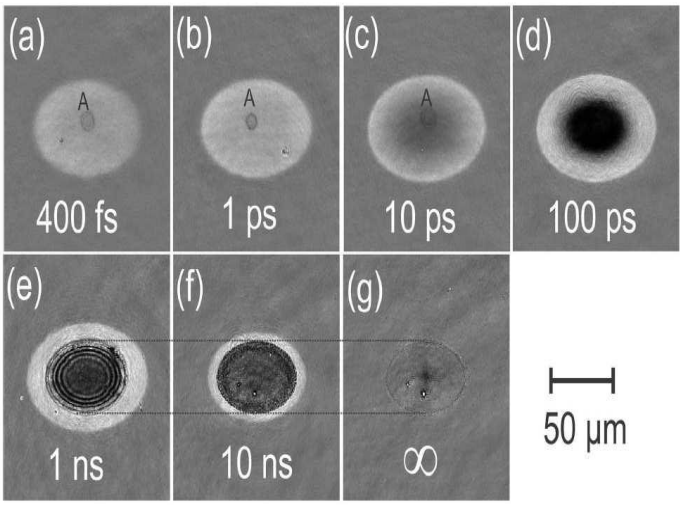

Figure 1.1: Images of a germanium surface at different times after the laser excitation (pump fluence 3.10 ± 0.08J/cm2, ablative regime). A denotes an imaging artifact which is not related to a modification of the sample surface. The image sequence is encoded in a linear gray scale with an optimized contrast. Figure reproduced from [BBSS06].

Since the development of techniques using ultra short laser pulses in the 1980s, a considerable number of applications have been found. For example, ultrafast laser techniques offer possibilities to shape tissues and skin for medical replacement and to manipulate and fabricate nano-sized materials which have direct applications in our everyday life. Despite the huge and technological applications in real world and the intense research investigations on the subject, a complete and exact understanding of the ultrafast dynamical processes which take place during and

after an intensive excitation of materials still remains a scientific and technological challenge.

New experimental techniques such as ultrafast x-ray diffraction [CTS+ 01, STBB+03, STBD+03, RTD+07] and time resolved reflectivity measurements [BBSS06, CBRZ08, HEH+ 08] allow to follow the detailed steps of matter transformation within the time scale on which the effect of a laser pulse is considered. Thus with the help of these techniques one can investigate the first steps in the laser driven phase transitions and transformations of materials. Up to the development of pump-probe techniques, it has not been possible to directly observe the atomic motion leading to a phase transformation in matter. For instance, while the first and last step of a chemical reaction was well established, it was not possible to probe the different intermediate steps of the elementary reactions. With the development of pump-probe techniques, structural changes are now measured in a time- resolved way. In the 1990s, Zewail and coworkers [Zew88, Zew92, PHP+92, Zew00] used ultra-short laser pulses to observe chemical reactions on the time scales they occur. The authors show that femtosecond laser pulses can be used as a mean to control the different processes occurring during chemical reactions [Zew88, KZ90] and structural changes in solids [KTM03, MMHK04, STBD+03, BBSS06]. The main outcome is the possibility to obtain the quantitative structural information's of physical, chemical and biological systems on time scales that are comparable with the natural periods of vibrations of atoms and molecules (10f s ≤ T ≤ 1ps).

Among the experimental studies regarding structural responses of solids to femtosecond laser excitation done so far, one can mention the following examples which attract our attention and are part of the motivations of this theoretical work:

1) The first example is the work from Kitagawa and coworkers [KTM03]. They used a femtosecond laser pulse to study a volume collapse phase transition which occurs in samarium sulfide. Kitagawa and coworkers performed Grazing incidence x-ray diffraction (GIXD) analysis of SmS (Fig. 1.2), and showed that by exciting samarium sulfide using femtosecond laser it is possible to induce the semiconductor (S-SmS) to metal phase transition (M-SmS). Ce and SmS exhibit phase transitions with the same characteristics at ambient conditions [JNM70, LLC83]. Therefore by exciting cerium, the same physical phenomenons can be expected. Up to now experiments regarding laser-induced transition in cerium have not been done.

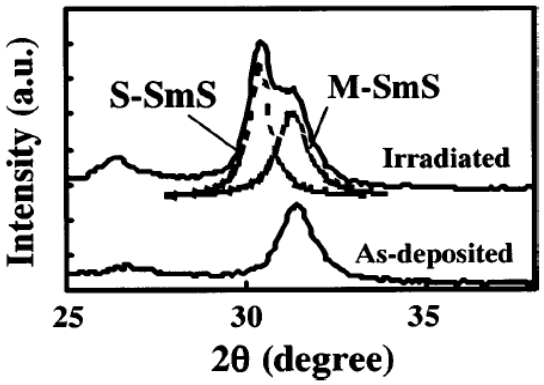

Figure 1.2: Grazing incidence x-ray diffraction (GIXD) analysis of the semiconductor samarium sulfide (S-SmS) to metal samarium sulfide (M-SmS) phase transition induced by femtosecond laser excitation. The figure shows the GIXD patterns of the as-deposited and irradiated film. Figure reproduced from [KTM03]

2) The second example concerns the structural response of bismuth to femtosecond laser excitation. Misochko and coworkers [MMHK04] report measurements of the reflectivity of bismuth during and after the femtosecond laser pulse. The authors used a pulse duration of 130f s less than a phonon period. Figure 1.3 shows the time derivative of the reflectivity in bismuth at different laser fluences. It was shown that the amplitude of co- herent A1g phonon oscillations vanishes and, at a later time, reappears when the fluence of the pump laser is above a certain threshold value. This phenomenon was explained as a quantum mechanical effect and was therefore referred to as "amplitude collapse and revival". The same phenomenon was observed in an independent experimental study by Hase and coworkers [HKNM02].

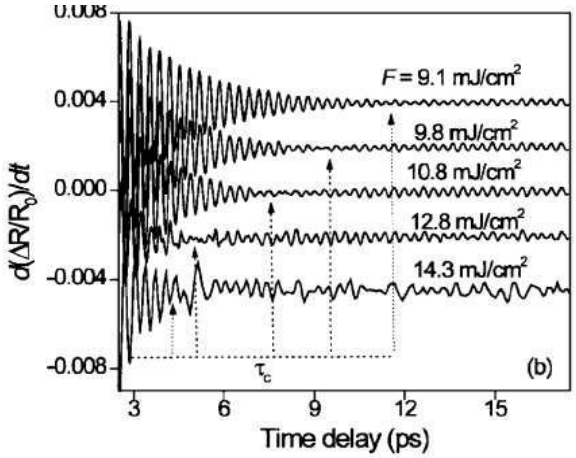

Figure 1.3: Time derivative of R/R0 as a function of the time delay demonstrating the collapse and revival in Bi at T = 10 K for different laser fluences with pulse duration of 130 fs (the transients are offset along the y axis and labeled with the fluence value). Arrows indicate the time collapse. Figure reproduced from [MMHK04]

3) The third and last example is related to the work from Sokolowski-Tinten and coworkers [STBB+ 03, STBD+ 03]. The authors report study of the non-thermal melting of germanium using ultrafast x-ray diffraction techniques. Non-thermal melting simply means that on the time scale on which the phase transition is observed, no thermal motions are involved (the lattice remains cold). The exchange energy between electrons and ions which causes the lattice heating, takes place usually in some picoseconds after the laser excitation peak. Therefore, the immediate change of the lattice structure after the laser excitation is entirely due to the presence of hot electron-hole plasma. The non- thermal melting can be seen from the loss of order indicated by the drop of the X-ray diffraction efficiency peak in figure 1.4. Another illustration of this non-thermal melting of germanium occurring in time scale less than half a picosecond is given in figure 1.1.

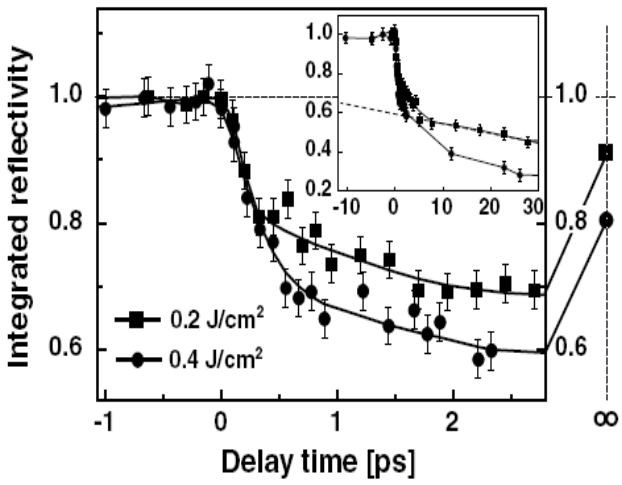

Figure 1.4: X-ray diffraction efficiency (integrated reflectivity) versus delay time. Infinity symbol: measurement a few minutes after the pump pulse. Inset: integrated reflectivity for an extended time span. Dashed line: melt from velocity of 850 m/s for rapid thermal melting. Figure reproduced from [STBD+03]

In an independent work Bonse and coworkers [BBSS06] studied the different stages of laser driven structural changes in germanium. The authors used time-resolved reflectivity measurements and show that the non-thermal melting take place at time t = 400f s after the laser peak. It was also shown in both experimental studies that after the laser excitation the system undergo several phases before ending to its almost initial phase at time t = ∞ (re-solidification), see figures 1.1 and 1.4.

Although the existing ultrafast x-ray diffraction techniques and time resolved reflectivity measurements allow monitoring of atomic motions in femtosecond time and angstrom spatial resolution, there are still a considerable uncertainty in the correspondence between the macroscopic quantities and the atomic scale properties for a given material. There- fore, there is need to go through the theoretical description of the response of materials to optical excitation.

A realistic theoretical description of laser heating solids must take into account explicitly the electronic as well as the atomic degrees of freedom. The reason is that, systems subjected to intense laser excitation will respond strongly to the modification of the interatomic potential or potential energy surface (PES) due to the significant electronic excitations. To calculate the potential energy surface which governs the atomic motion, several theoretical methods exist in various levels of sophistication: density functional theory, Hartree theory, tight binding approximations, empirical theory. Among these methods the most accurate and sophisticated ones so far are first principles (ab-initio) methods based on density functional theory [HK64, KS65].

However first principles methods are limited by the fact that they are computation- ally expensive. For this reason, theories based on simple empirical pair potential (for example Lennard-Jones-type potentials) are still in use for numerical study of dynamical properties of solids. In contrast to the other models, the empirical pair potentials do not include explicitly the electronic system and therefore are not suitable for the study of the dynamical processes which occur in excited systems. An intermediate possibility which combine a quantum mechanical treatment of electrons and classical treatment of ions is the tight binding theory. As discussed in section 2.4.1 the tight binding method is widely used because of its ability to treat different properties of solids in a reasonable way. The efficiency of tight binding formalism comes from the fact that the Hamiltonian can be parametrized. Consequently the electronic structure can be easily obtained. The tight binding Hamiltonian of solids are calculated from the hopping integral functions which are parameters and interatomic distance dependent. The difficulty of tight binding theory is to find an accurate and transferable model to study systems. Up to now only models for silicon [MS94a, BMP00], carbon [XWCH92] and germanium [MS98] exist.

Although many simulation methods of excited materials have been reported [VGCC96, SAPF96b, SP98], only few theoretical approaches which pay as much attention to the atomic as to the electronic system have been developed.

The starting point of the theoretical investigations was the work of Stampfli and Benne- man [SB90, SB92, SB94] regarding the study of structural responses of covalent materials (silicon, carbon, germanium) to femtosecond laser excitation. Stampfli and Benneman

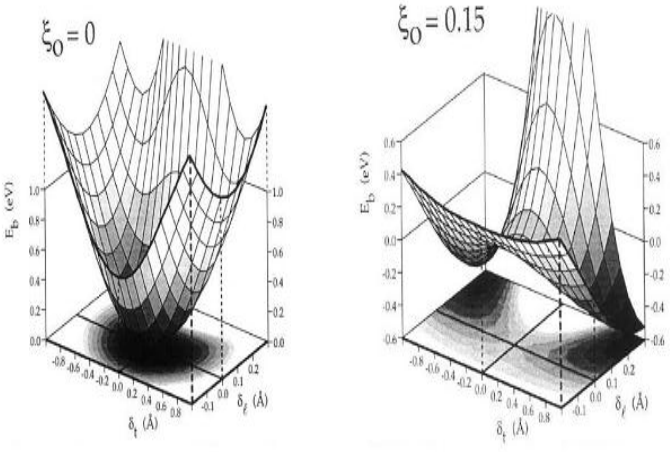

Figure 1.5: Cohesive energy of silicon in the absence of electron hole plasma (left figure) ξ = 0.0, and presence of hot electron-hole plasma of density ξ = 0.15 corresponding to the excitation of 15% of the valence electrons to the conduction band. δt and δl are respectively the transverse acoustic and longitudinal optic distortions (amplitude of the phonons). The ideal diamond structure (δt = δl = 0) becomes unstable in the presence of laser excitation (right figure) and corresponds to a stable minimum of the cohesive energy in the absence of excitation (left figure). Figures reproduced from [SB94] analysed the ultrafast laser-induced instability of the diamond structure of semiconduc- tors (Si,Ge,C). The cohesive energy of silicon was calculated [SB94] in function of trans- verse acoustic δt and longitudinal optic δl distortions (see figure 1.5). The time-dependent lattice instability of silicon was obtained and the results show that the softening of the tranverse acoustic modes is mainly responsible of the lattice changes. However due to the strong anharmonic interactions resulting from the laser-induced potential energy sur- face changes (figure 1.5), the longitudinal optical phonons are also affected. According to Stampfli and Benneman this lattice instability takes place within 120f s after the laser pulse and yields to rapid melting of the crystal. Same phenomenon was also observed for gallium arsenide (GaAs) [SB93].

Later on Jeschke and Garcia [JGB99a, JGB99b, JGB01, JG, GJ03, RGV+05] devel- oped a theory based on the approach proposed by Stampfli and Benneman to study the response of covalent materials to femtosecond laser excitation. In contrast to the model from Stampfli and Benneman, the model proposed by Jeschke and Garcia incorporated explicitly the time dependent non-equilibrium occupation of the energy levels (taking into account explicitly the time dependent changes of the electronic occupation during and after the laser pulse) in the calculation of the potential energy surface. They used MD simulation on the basis of an orthogonal tight binding Hamiltonian. This model was well applied for the description of structural responses of graphite and carbon nanotubes [JGL+02, GDJ04, DGJY04, RGV+05, DGJY06, JDG09] to femtosecond laser excitation.

In the 1990s, Parrinello and coworkers [SAPF96b] have used first principles molecular dynamics simulation to study the dynamical response of silicon to ultra-short laser excitation. Similar study has been performed to describe laser-induced melting of graphite [SP98]. The method proposed by Parrinello and coworkers are mainly based on the treatment of ions and electrons with density functional theory in the local density approximation. Within these model, an instant creation of electron hole plasma is assumed at time t = 0 so that the duration of laser pulse is set to zero (τ = 0). In fact the first principle methods do not allow an explicit time treatment of the laser pulse. We used a similar idea in the second purpose of this work, to calculate the potential energy surface of bismuth at high electronic temperatures (simulating laser excitation) and we proposed a model to include the time dependent laser parameters.

Figure 1.6 shows the observed isostructural phase transition [LLC83] (both phases are fcc structures) leading to a volume collapse of roughly 15% under ambient temperature and at a given critical external pressure. Same isostructural phase transition has been also observed for samarium sulfide [JNM70]. Regarding this fascinating behavior observed

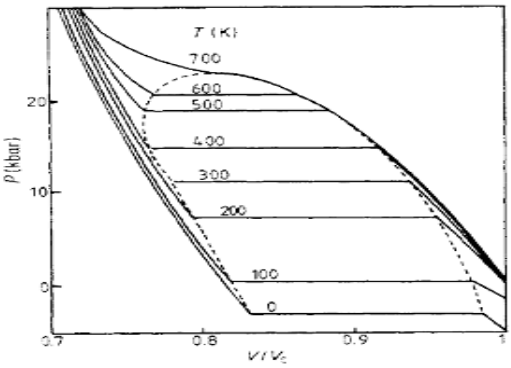

Figure 1.6: Time derivative of R/R0 as a Isotherm of cerium. Illustration of the volume collapse γ → α transition at ambient temperatures. Figure reproduced from [LLC83] in both systems cerium and samarium sulfide the questions which have no clear answer up to now are: how the microscopic quantities (electronic structure) are coupled to the macroscopic quantities (volume change during the phase transition)? What is the driving mechanism of the transition? And finally what is the role of the correlation between electrons and spd valence electrons in the transition? These fundamental questions are still under debate, and many experimental [vdEKvdM01, ea04] and theoretical studies [AM82, AL92, HOSK05] are devoted to this subject. We proposed an approach based on calculation of the potential energy surface from the model Hamiltonian proposed by Falicov [RF71] to study laser-induced phase changes in cerium. With a hydrodynamic simulation we estimate the time scale on which laser induced volume changes of cerium can occur and discuss about how the electronic structure changes are involved. We also investigated the structural properties of samarium Sulfide by means of first principle methods based on LDA+U. For this purpose we used LDA+U to study the equilibrium properties of SmS and discuss the possibility of laser induced the experimentally observed semiconductor-metal phase transition.

ii) Secondly we studied the dynamical response of bismuth to femtosecond laser ex- citation. A particular attention is given to the study of the experimentally observed amplitude collapse and revival of coherent A1g phonons. When femtosecond laser pulse interacts with bismuth crystal, due to the presence of hot electron-hole plasma large amplitude coherent phonons are excited [HWDK95]. These collective lattice vibrations, which usually involve only a few degrees of freedom, provide a useful system to study both laser-matter interactions and the physical processes related to the relaxation of the non-thermal state induced by the laser [HKNM02, JBM+08, BGR+08]. A question that has received relatively little attention is, whether the induced phonons behave classically as is usually assumed or whether some quantum effects may be detected [MSN00]. In this respect interesting observation has recently been made by Misochko and coworkers [MMHK04] in bismuth: The goal of this work is to clarify whether the origin of the observed amplitude collapse and revival of the coherent A1g phonon is classical or quantum mechanical. To this aim we have performed quantum dynamical simulations on time-dependent potential energy surfaces calculated using density functional theory and accurate full potential linearized augmented plane wave methods. The time dependent potential energy surface includes explicitly the laser pulse parameters (fluence, intensity, pulse duration).

iii) The third and last purpose of this thesis is the description of ultrafast phe- nomenons occurring in covalent materials upon ultrashort laser excitation. Particular interest has been given to the semiconductor germanium. The aim of our investigations was to understand on which time scale do laser-induced structural transitions occur in germanium, and identify the different processes involved in the experimentally observed changes [PKKS92, SPK93, NHM+ 01, STBD+03, BBSS06]. And finally look at whether these different processes can be controlled by laser parameters like fluences, duration, and intensity. In this last part of the work a theory which is mainly based on the model proposed by Jeschke and Garcia [JGB99a, JGB99b, JGB01, JG, GJ03] for the descrip- tion of laser induced electronic non-equilibrium states, will be developed and combine to MD simulations.

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