Anharmonic Noninertial Lattice Dynamics during Ultrafast Nonthermal Melting of InSb

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We compute the potential energy surface of femtosecond-laser-excited InSb along the directions in which the crystal becomes soft. Using dynamical simulations the time dependence of the atomic coordinates is obtained. We find that at high excitation densities the anharmonicity of the potential energy surface becomes significant after ~100 fs. On the basis of our results we explain recent time-resolved x-ray diffraction experiments. We point out that an alternative model for ultrafast melting [A. M. Lindenberg *et al.*, Science **308**, 392 (2005)] is inconsistent with our calculations.

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Femtosecond lasers create extreme nonequilibrium conditions in solids [1]. The reason is that the electrons, which interact strongly with light and are heated by the laser, have no time to thermalize with the lattice vibrations during the subpicosecond pulse duration. The possibility to induce a state of matter in which the electrons are hot and the ions are cold opens pathways that would not be accessible under normal thermodynamic conditions and leads to qualitatively new physical phenomena. Examples are laser-induced solid-to-solid phase transitions [2,3], laser-excited large-amplitude coherent phonons [4], and laser-induced nonthermal melting. In the latter case the kinetic energy of the electrons is transferred to the ions in 100's of fs, where a thermal process would at least require 1000's of fs. Ultrafast melting was first unambiguously observed in Si in 1983 [5,6] and in GaAs in 1991 [7–9]. In contrast to these early measurements, which were optical, recent time-resolved x-ray diffraction experiments on InSb [10–12] as well as an electron diffraction study on Si [13] provide direct information about the atomic pathways followed during ultrafast melting. Still, there exist conflicting physical explanations for this important phenomenon [10,14]. To clarify the current confusing situation, in this Letter we present state-of-the-art computations that reveal what really happens during the first stages of nonthermal melting of InSb.

In [10] a new theoretical model of ultrafast melting is proposed, which assumes that a femtosecond-laser pulse with a sufficiently high fluence erases all interatomic potentials. After a laser pulse the atoms would then continue their motion inertially, i.e., without being restrained by any crystal potential. Although this model provides an explanation of experimental facts, it ignores previous theoretical calculations of the atomic pathways involved in nonthermal melting of Si [14–16] and rather than clarifying the physical picture it appears to have created confusion [11–13]. In this Letter, we compute the response of InSb to intense laser excitation on the basis of density functional theory with emphasis on anharmonic contributions. We find that our calculations are consistent with all important experimental data. In addition, our results imply that the initial stages of ultrafast melting of InSb cannot be described by the inertial dynamics of atoms on flat potential energy surfaces as proposed in [10].

Before turning to a description of our computations, we briefly summarize the basic theory of ultrafast melting of materials that crystallize in the diamond and zinc blende structures as put forward by Stampfli and Bennemann in a series of papers, which appeared in the early 1990s [14–16]. Here we wish to stress that although the findings of Stampfli and Bennemann have sometimes been challenged, they have never been refuted. Therefore, we feel that they provide the best starting point for the theoretical background, which we need in this Letter. In the first paper [15], Stampfli and Bennemann use tight-binding theory to study the effect of a dense electron-hole plasma resulting from a short, intense laser pulse on the stability of Si, Ge, and diamond. They find that the transverse acoustic phonons become soft if more than about 8% of the valence electrons are excited to the conduction band. Neglecting anharmonicity this is shown to lead to an exponential increase of the average atomic displacement in time.

In the second paper [14], Stampfli and Bennemann extend their previous theory by including anharmonic effects. The resulting computed average atomic displacement is now roughly linear in time. In the third paper [16], Stampfli and Bennemann also include longitudinal optical phonon distortions. They demonstrate that these enhance the instability of the transverse acoustic phonons, increasing the kinetic energy of the atoms and the final lattice temperature. They use this result to visualize the detailed pathways followed by the atoms during the first stages of ultrafast melting. This last paper thus provides a graphic explanation supported by solid computations of how the energy of the electrons can be transferred to the lattice in several 100's of fs. The average displacement of the atoms as a function of time (our main concern in this Letter) appears, however, to be not very much influenced by the longitudinal optical distortions as can be seen by comparing Fig. 4(a) in [14] with Fig. 5(a) in [16]. For this reason, in this Letter we will take into account the anharmonicity of the transverse acoustic phonons in InSb, but we do not include their coupling to the longitudinal optical phonons. Notice that the group III-V semiconductors GaAs and InSb and the group IV semiconductors Si, Ge, and C crystallize basically in the same structure (the diamond and zinc blende structures are closely related) and exhibit the same type of electronic bonding. Therefore, we expect that the results that Stampfli and Bennemann have obtained for Si are also applicable to GaAs and InSb (we expect that the laser-induced changes in the ionicity of GaAs and InSb are small compared with the changes in the covalent bonding).

We now summarize the main findings of the above-mentioned recent time-resolved x-ray diffraction experiments on InSb, which were published in three papers [10–12]. In the first work, Lindenberg and co-workers [10] report how the reflected intensities of two x-ray diffraction peaks evolve in time after intense femtosecond-laser irradiation. Using a time-dependent Debye-Waller model these data are analyzed in terms of the average atomic displacements in real space. Four important results are obtained: (i) In the first 400 fs after intense laser excitation the root-mean-square atomic displacement changes linearly with time; (ii) this change is the same in the [111] and [110] directions; (iii) the slope of the curve showing the root-mean-square displacement versus time equals 2.3 Å/ps, which happens to be very close to the thermal root-mean-square velocity of the ions in InSb at room temperature, 2.5 Å/ps; (iv) these observed effects show little variation when the fluence is varied between 50 and 100 $\mathrm{mJ/cm^2}$. To explain these four results the authors postulate that a sufficiently strong femtosecond-laser pulse erases the interatomic potentials in InSb. The atoms would then continue their thermal movements from before the laser excitation without being restrained by the harmonic potential of the crystal. Note that this interpretation is in stark contrast with the explanation of ultrafast melting of Stampfli and Bennemann [14,16], who have found that only the transverse acoustic phonons soften (instead of all modes as proposed by Lindenberg and co-workers) and have predicted that anharmonicity becomes important on the relatively short time scale of ~100 fs.

In the second paper about femtosecond time-resolved x-ray diffraction experiments [11], Gaffney and co-workers extend the previous study [10] to longer delay times and laser fluences up to 130 $\mathrm{mJ/cm^2}$. As in the previous work, the root-mean-square displacements of the atoms are obtained from the measured x-ray intensities using a time-dependent Debye-Waller model. For the sake of clarity of presentation we will limit our discussion to these real-space data, as we have done above. The two main results obtained by Gaffney and co-workers are as follows. (i) During the first 400 fs after the laser excitation, the slopes of the curves showing the root-mean-square displacement of the atoms versus time equal 1.1 and 1.6 Å/ps when the fluences are, respectively, 50 and 130 $\mathrm{mJ/cm^2}$. This first result, which can straightforwardly be derived from Fig. 2 in [11], is in obvious contradiction to the inertial dynamics model proposed by Lindenberg and co-workers [10]. Surprisingly, the authors try to reconcile their data with this model by limiting their comparison to a fitted time constant of a Gaussian component to the measured intensity decay of the x-ray diffraction peaks. This is misleading because the main prediction of the inertial dynamics model [10] is that the aforementioned slope should be 2.5 Å/ps independent of the fluence as long as it exceeds a certain threshold value. Sadly, this also casts some doubt on the way in which (at least part of) the same data has been analyzed in [10]. (ii) At later times, the root-mean-square displacement of the atoms increases more slowly and this change of behavior occurs first in the [110] and then in the [111] direction. This second result, which is in fact the main focus of [11], is interpreted as a sign of structural anisotropy and the onset of diffusive atomic motion. Here we want to mention a recent study by Wark [17], which shows that the observed difference is not due to an asymmetry in the mean-square displacement of the atoms. On the basis of a molecular dynamics simulation using a hard sphere model, Wark [17] has computed time-dependent structure factors of InSb. By inverting the structure factors following the same procedure as in [10,11], a flattening of the curves derived from the (111) and (220) peaks is observed at different times, even though the atoms move isotropically. Wark [17] attributes the observed effect to the fact that the (220) Bragg peak looses information about the structure at smaller atomic displacements than the (111) peak.

In the third paper about time-dependent x-ray diffraction experiments [12], Hillyard and co-workers extend the previous measurements up to a fluence of 160 $\mathrm{mJ/cm^2}$. Under the same assumptions as used in [11], the authors claim that for all fluences of 44 $\mathrm{mJ/cm^2}$ or more but less than 160 $\mathrm{mJ/cm^2}$, the ultrafast melting can be described by the inertial dynamics model of [10]. The 160 $\mathrm{mJ/cm^2}$ data are interpreted as accelerated disordering. It should be stressed that this interpretation relies heavily on the validity of the inertial dynamics model [10].

Another recent time-resolved experiment that we wish to mention is [13], where Harb and co-workers use electron diffraction to study ultrafast melting of Si. They try to explain their results with the inertial dynamics model of [10], but they find that the initial atomic velocities they have to assume are about 3 times smaller than the estimated room-temperature root-mean-square velocity of the Si atoms.

Summarizing the current state of affairs, there are now two competing but mutually exclusive models that can potentially describe ultrafast melting of semiconductors that crystallize in the diamond and zinc blende structures. The first model has been put forward by Stampfli and Bennemann in the early 1990s. Their calculations show that ultrafast melting occurs due to the softening of transverse acoustic phonons. The alternative model has been proposed almost 15 years later to explain time-resolved x-ray diffraction experiments. It assumes that a femtosecond laser erases all interatomic potentials. The atoms then move freely with the velocities that they had before the laser excitation. To clarify the present confusing situation and to determine which of the two proposed models realistically describes ultrafast melting, we have performed state-of-the-art all-electron density functional theory calculations of the laser-induced lattice softening of InSb.

In a first step, we have computed potential energy surfaces using WIEN2K [18]. We chose to work with this code because it is very accurate and relies on no other approximation than the local density approximation [19]. In the electronic structure part of our calculations, we sampled the first Brillouin zone with $10 \times 10 \times 10$ k points and we included linearly augmented plane waves with energies up to 387 eV in our basis set. The excitation due to a femtosecond intense laser pulse was treated on the basis of the following physical picture [20]: Initially, the laser creates electron-hole pairs. However, due to rapid dephasing and frequent collisions, the electrons and holes thermalize on a time scale much shorter than the typical time of ionic motion. In other words, the thermalization of the electrons and holes occurs for all practical purposes instantaneously. The laser excitation can then be characterized by a single electronic temperature T_e and the forces on the ions are the first derivatives of the electronic free energy. It is important to note that a formal justification for this approach within density functional theory was already given in 1965 [21].

Our computed phonon frequencies, which are proportional to second derivatives of the potential energy surface, are shown in Fig. 1 for the Γ, X, and L points. Our results clearly indicate that of all calculated lattice vibrations only the transverse acoustic phonons at the X and L points become soft upon intense laser excitation. This falsifies the inertial dynamics model of Lindenberg and co-workers [10], which assumes that the interatomic potentials are erased in all directions, and supports the theory developed by Stampfli and Bennemann [14–16]. It is astonishing that the harmonic level of theory already distinguishes so clearly between the two models proposed for ultrafast melting. The inadequacy of the inertial dynamics model of [10] is the first important result of this Letter.

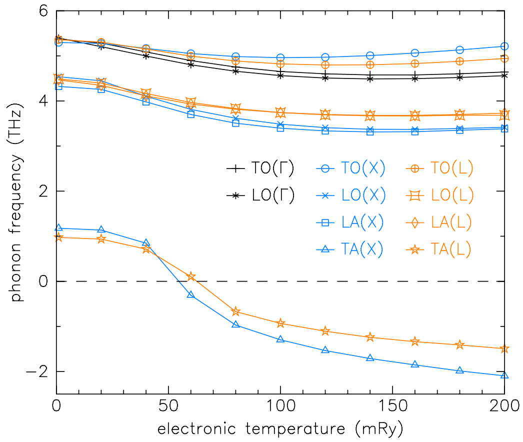

FIG. 1 (color online). Phonon frequencies at the Γ, X, and L points as a function of the electronic temperature. The labels indicate whether the phonons are longitudinal (L) or transverse (T) and optical (O) or acoustic (A). Negative frequencies represent repulsive potentials. The lines are a guide to the eye.

Our second important result is that anharmonicity cannot be ignored for times greater than ~100 fs. To arrive at this conclusion we have computed the potential energy of laser-excited InSb as a function of the atomic displacements in the directions of the transverse acoustic phonons at the X and L points. The X point describes the direction that shows the strongest laser-induced lattice instability and which can thus be expected to mainly determine the atomic displacements at larger times [14]. Computed potential energy surfaces (data points and 12th order polynomial fits) are shown in Fig. 2.

We now develop the dynamical theory for ultrafast melting of InSb. Toward this goal we have performed dynamical simulations on the potential energy surfaces of Fig. 2. We will not say much about our method because it is a direct generalization of the approach followed in [14] for Si. One complication is that in InSb the directions of the transverse acoustic and transverse optical motions at the X point are not fixed by symmetry and depend on the electronic temperature. This results in slightly more complicated initial conditions for the laser-excited transverse acoustic phonons, which now have contributions from both the electronic ground state transverse acoustic and transverse optical modes. In addition, it is worth mentioning that our calculations are based on all-electron density functional theory and involve no free parameters nor do they rely on unnecessary (but often useful) approximations, such as pseudopotentials.

On the basis of our dynamical simulations we have computed the average root-mean-square displacements of

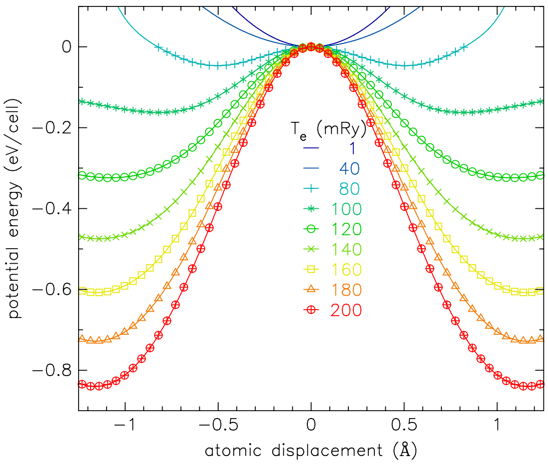

FIG. 2 (color online). Potential energy of laser-excited InSb in the directions of the transverse acoustic phonons at the X point for selected electronic temperatures T_e. The horizontal axis shows the displacement of the In atoms. For each temperature, the displacement of the Sb atoms is proportional to that of the In atoms. The proportionality constant varies between 0.81 for the electronic ground state and 0.94 for the highest excited state.

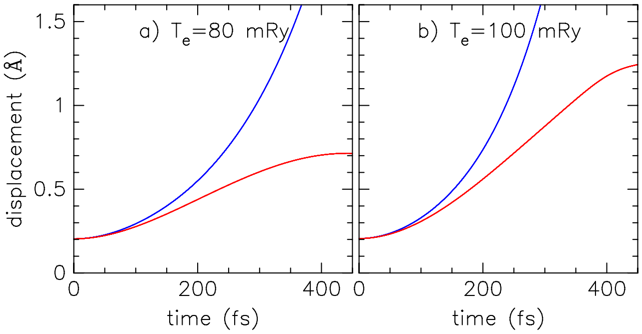

FIG. 3 (color online). Root-mean-square atomic displacement versus time for two laser-induced electronic temperatures T_e. Whereas the top (blue) curves show results within the harmonic approximation, the bottom (red) curves include anharmonic effects. The discrepancies between both approaches demonstrate the importance of anharmonicity for times greater than ~100 fs. The anharmonicity leads to a deceleration of the atoms.

the atoms, as shown in Fig. 3 for two laser-induced electronic temperatures. We wish to stress that our model predicts that the atomic motion is uniform in all directions as can be easily derived by taking into account the symmetry of the crystal (there are three X points and four L points in the first Brillouin zone). This is not inconsistent with experiment, because, as we have mentioned above, the discrepancies in the experimental information obtained from the (111) and (220) Bragg peaks are not related to any physical process involved in the nonthermal melting of InSb [17]. The main conclusions that can be drawn from Fig. 3 are as follows. (i) For times greater than ~100 fs, anharmonic effects dominate the atomic motions. (ii) The curves including anharmonicity are roughly linear in time, in agreement with experiment [10–12]. (iii) The slopes of the curves equal 1.1 [Fig. 3(a)] and 2.3 Å/ps [Fig. 3(b)]. These values appear realistic. They reproduce the 50 mJ/cm^2 data of [11] and the data presented in [10] (the fluence is not given), respectively [the 130 mJ/cm^2 curve of [11] has a slope intermediate between those of Figs. 3(a) and 3(b)]. Based on the computed absorbed laser energies (0.165 and 0.259 Ry/cell, respectively) and tabulated optical properties of InSb at a wavelength of 800 nm (the reflectivity equals 41% and the penetration depth is 91 nm [22]), we estimate that the incident fluences needed to reach the electronic temperatures of 80 and 100 mRy at the sample surface are 83 and 130 mJ/cm^2, respectively. The first value is in reasonable agreement with the experimental fluence of 50 mJ/cm^2. (iv) The absorbed laser energy is 1.6 times larger in Fig. 3(b) than in Fig. 3(a). In [11] the variation of the fluence by a factor of 2.6 led to a considerably smaller change of slope than in Fig. 3. This shows that the absorbed energy does not vary linearly with the fluence, a clear indication that the laser pulse modifies the optical properties of InSb at high fluences [23]. (v) At times greater than ~400 fs, the curves in Fig. 3 flatten off. Here, we expect that interactions that we have not taken into account become important, such as the coupling to longitudinal optical phonons [16].

In conclusion, we have performed a density functional theory study of the ultrafast melting of InSb. In agreement with a previous theoretical description of laser-induced melting of materials that crystallize in the diamond and zinc blende structures [14], we have seen that ultrafast melting occurs due to a softening of the transverse acoustic phonons and that at high excitation densities the anharmonicity of the potential energy surface becomes significant after ~100 fs. Including anharmonic effects our results have been shown to be in good agreement with recent time-resolved x-ray diffraction experiments [10–12]. On the basis of our calculations we rule out the validity of an alternative model of ultrafast melting proposed in [10].

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