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RAPID COMMUNICATION

Ab initio description of the first stages of laser-induced ultra-fast nonthermal melting of InSb

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Abstract Using first principles, all-electron calculations and dynamical simulations we study the behavior of solid InSb immediately after intense femtosecond excitation. First, we determine the laser-excited potential energy surfaces with high accuracy for different electronic temperatures (corresponding to different laser fluences). Then, we demonstrate that, although most phonon modes become only slightly softened even for high electron temperatures, the transverse acoustic modes at the boundary of the Brillouin zone undergo dramatic changes and become unstable. This is the origin of nonthermal melting. Based on these results, the dynamics during the first hundreds of femtoseconds after laser excitation can be unambiguously elucidated. Our results are in agreement with recent experiments and support the predictions made by Stampfli and Bennemann for silicon.

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1 Introduction

When an intense femtosecond laser pulse interacts with a semiconductor in such a way that a considerable fraction of the valence electrons is excited, the interatomic potential, or potential energy surface (PES), can change dramatically, and the solid can undergo ultra-fast structural transitions. The ultra-short laser pulse creates an extreme nonequilibrium situation in which the electrons acquire very high temperatures (10^3–10^4 K), while the lattice structure remains at room temperature and accelerates following the gradients of the new PES. Thus, laser-induced ultra-fast phase transitions have a clear nonthermal character. The possibility of using femtosecond-laser pulses to induce nonthermal melting of different materials has been investigated theoretically and experimentally for more than two decades [1–11]. The most direct experimental method to detect, in a time-resolved way, the disappearance of the long-range order and the emergence of the nonequilibrium liquid phase is the measurement of transient rocking curves using ultra-short X-ray probe pulses [8, 9]. In this method, the intensity of a particular Bragg peak is measured as a function of the delay time between the excitation by a pump laser pulse and the diffraction measurement using a probe X-ray pulse. When the lattice starts to accelerate the Bragg condition is no longer strictly fulfilled. This leads to a loss of coherence among the scattered X-rays, which results in a decrease of the Bragg-peak height.

Recently, Lindenberg et al. [9] have measured the time evolution of the (111) and (220) Bragg-peak heights of InSb after intense laser excitation. They found that the intensity of the diffraction peaks follows a Gaussian decay with an ultra-short time constant (400 fs for the (111) peak). Assuming that the Debye–Waller theory is valid for time-dependent phenomena, one can then describe the decay of the Bragg-peak intensity $I(\mathbf{Q}, t)$ by [9]

$$I(\mathbf{Q}, t) = \mathrm{e}^{-Q^2\langle x^2(t)\rangle/3}, \tag{1}$$

where $\mathbf{Q}$ is the reciprocal lattice vector corresponding to the Bragg peak considered and $\langle x^2(t)\rangle$ refers to the mean-square displacements of the ions. Since $I(\mathbf{Q}, t)$ has a Gaussian time

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behavior, inversion of (1) leads to a quadratic behavior of $\langle x^2(t)\rangle$, meaning that the root-mean-square (rms) displacements exhibit, within the experimental error bars, a linear dependence on time during the first 400 fs after the excitation by the pump pulse. The other remarkable feature of the mentioned experimental results is that within these 400 fs the ions cover on average a distance of about 1 Å, which is extremely large compared to the constrained motion of ions in a solid. Moreover, the almost constant slope of the rms displacements, which the authors interpret as a velocity, roughly corresponds to the thermal velocity of atoms at 300 K (i.e. at the temperature before excitation), which is $\langle v\rangle_{300} = 2.5$ Å/ps.

Based on these remarkable results, Lindenberg et al. concluded that the action of the laser pulse must lead to a complete flattening of the PES, in such a way that after excitation the ions move with their initial velocities in a planar potential. In a further work [11], they applied this idea in the framework of the Debye model for the atomic vibrations, which assumes a linear and equal dispersion relation for the three acoustic phonon branches, approximates the Brillouin zone by a sphere and represents the optical phonon branches by doubling the volume of the sphere. The laser excitation has been assumed to produce a uniform softening of all phonon frequencies [11]. Using this model, Hillyard et al. [11] concluded that all phonon frequencies become zero upon laser excitation. This result is in clear contrast with theoretical predictions for Si, C and Ge made by Stampfli and Bennemann [2, 3].

In this Rapid Communication we provide a qualitative and quantitative explanation of the experimental results of [9], and show unambiguously that the model of laser-induced homogeneous phonon softening and flat potential surfaces for InSb is wrong. By performing accurate, all-electron density functional theory (DFT) calculations of the laser-excited PES we demonstrate that most phonon modes only suffer a slight softening upon laser excitation, even for considerably high laser intensities. Moreover, we show that only particular phonon modes at the boundary of the Brillouin zone are dramatically affected by the laser excitation. This means that during the first stages of lattice destabilization, some particular vibrational degrees of freedom become active, i.e. the lattice motion is strongly nonthermal, in contrast to the initial interpretation of the time-resolved diffraction experiment.

2 Method

We calculated phonon frequencies in InSb, which is a semiconductor with a zinc-blende crystalline structure, using the frozen phonon method with the WIEN2k code [12], which has been designed to make accurate DFT predictions without relying on any approximation other than the local density approximation. The action of the laser pulse was simulated by heating the electrons and holes to a very high common temperature and a common chemical potential. Note that for high excited-carrier densities the thermalization has been shown to be very fast [13]. The PES was then calculated as

$$U\left(\{\mathbf{R}_i\}, T_{el}\right) = E_{tot}\left(\{\mathbf{R}_i\}, T_{el}\right) - T_{el}S_{el}, \tag{2}$$

where T_{el} is the electronic temperature reached after laser excitation, $\mathbf{R}_i$ refers to the ionic coordinates, E_{tot} is the total energy obtained from the all-electron DFT calculation and S_{el} is the entropy of the electrons in the laser-excited state. For a particular ionic configuration, $U(\{\mathbf{R}_i\}, T_{el})$ is the Mermin free energy of the solid. The phonon frequencies were then obtained from second derivatives of the PES. We performed calculations on several optical and acoustic modes at the Γ point and at high-symmetry points (L and X) on the zone boundary. Both longitudinal and transverse types of phonon modes were considered.

3 Results

We show first the results that demonstrate that the model of laser-induced planar potential surfaces, suggested in [9] and [11], is incorrect. In Fig. 1, we plot the *ab initio* PES for atomic motion along the longitudinal optical phonon at

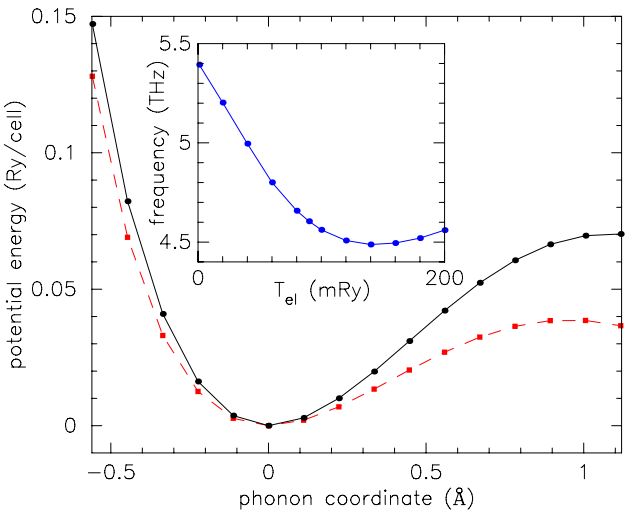

Fig. 1 Difference of the interatomic potential with respect to the equilibrium value as a function of the interatomic distance along the longitudinal optical (LO) phonon coordinate of InSb at the Γ point. The *solid black curve* corresponds to an electronic temperature of 1 mRy, whereas the *dashed red line* was calculated for an electronic temperature of 100 mRy (16000 K). *Inset*: frequency of the LO phonon for increasing electronic temperatures, simulating increasing laser fluences

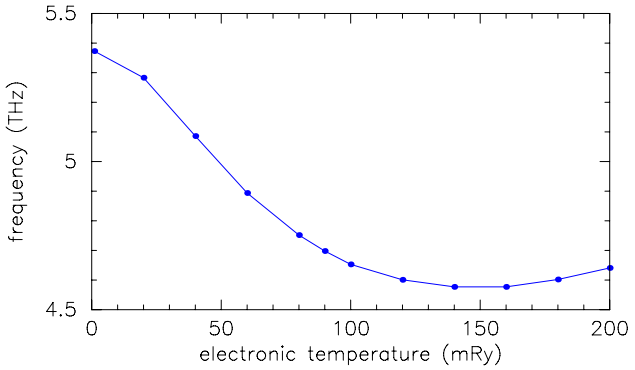

Fig. 2 Frequency of a transverse optical phonon of InSb at the Γ point as a function of the electronic temperature induced by a femtosecond-laser pulse

the Γ point for two dramatically different values of T_{el}, namely $T_{\mathrm{el}}^0 = 1$ mRy and $T_{\mathrm{el}}^1 = 100$ mRy, which correspond to 160 K and 16000 K, respectively. Note that for achieving $T_{\mathrm{el}} = 16000$ K an intense laser pulse has to be applied, which excites almost 10% of the valence electrons. As can be clearly seen in Fig. 1, no flattening of the potential surface takes place. The effect of an intense laser pulse consists of a small decrease of the potential at large interatomic distances, which leads to a slight softening of the mode. The inset of Fig. 1 shows that the decrease of the phonon frequency for increasing electronic temperature is always less than 20%.

We find a similar behavior for the transverse optical phonon modes at the Γ point, as is shown in Fig. 2. Again, the laser-induced softening is less than 20% even for very high electronic temperatures. Moreover, we also investigated the behavior of the phonon frequencies for the longitudinal modes at the X and L points of the Brillouin zone of InSb, and did not find considerable softening either. The results shown in Figs. 1 and 2 clearly demonstrate that the interatomic potential as a whole does not become flat. However, they cannot explain the experimental results. As mentioned in the Introduction, the rms displacements of the atoms after excitation increase almost linearly with a slope of about 2 Å/ps and achieve values of 1 Å for a pump–probe delay of 400 fs.

In order to elucidate the physics occurring during the first stages of nonthermal melting of InSb, we investigated the behavior of the transverse acoustic (TA) modes at the X and L points, situated at the zone boundary. Note that those modes are strongly related to the shear modulus of the crystal [2, 3]. Since the more striking difference between the solid and the liquid phase is given by their shear moduli (positive in the solid, zero in the liquid), the behavior of the potential surface along the TA modes at the zone boundary might be useful to shed light onto the problem.

In Fig. 3a, we plot the interatomic potential $U(\{\mathbf{R}_i\}, T_{\mathrm{el}})$ in the TA mode of InSb at the X point of the Brillouin

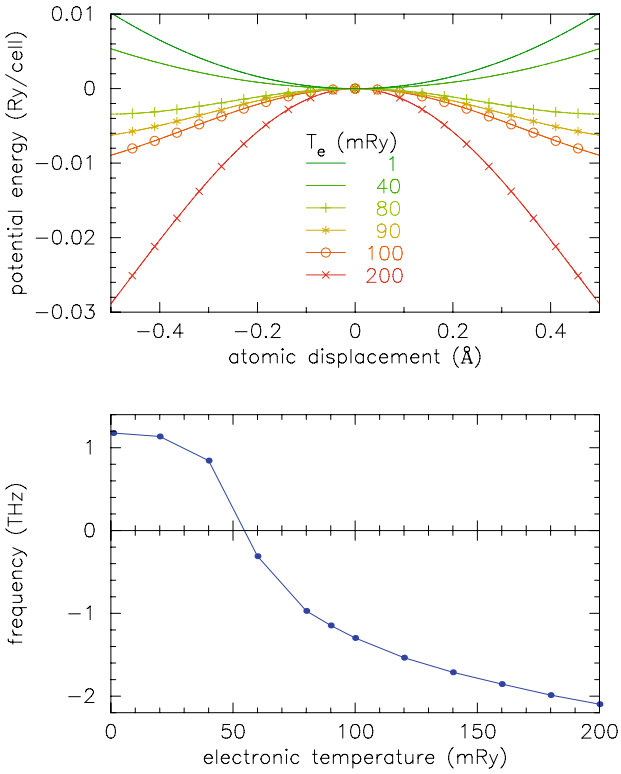

Fig. 3 **a** Difference of the electronic free energy (interatomic potential) with respect to the equilibrium value as a function of the atomic displacements along the transverse acoustic (TA) phonon coordinate of InSb at the X point for different electronic temperatures. Note the dramatic changes in this mode that can be produced by femtosecond-laser excitation. **b** Frequency of the TA phonon of InSb at the X point as a function of the electronic temperature. The negative y axis represents imaginary frequencies

zone for several values of T_{el}. We recall that increasing electronic temperature means increasing pump-laser-pulse fluence. Remarkably, a dramatic change of the PES in the zone-boundary TA modes occurs upon increasing T_{el}. As can be seen in Fig. 3a, laser excitation at a relatively low fluence leads to a strong softening of the mode. Further increase of the fluence can produce a complete softening and even a change to a repulsive PES, i.e. to an imaginary phonon frequency. This means that for sufficiently high laser fluences the TA phonons at the studied zone-boundary points become unstable, which reveals the emergence of the nonthermal liquid state. In Fig. 3b we show the behavior of the frequency of the TA mode as a function of T_{el}. From this figure the threshold temperature can be extracted, for which the phonon mode becomes unstable. It is important to mention that the effect shown in Fig. 3 was predicted to occur in silicon by Stampfli and Bennemann [2] in the framework of a tight-binding model.

From the comparison of Figs. 1 and 3, we conclude that the model of homogeneous laser induced softening, proposed in [11], is not valid. Moreover, the comparison

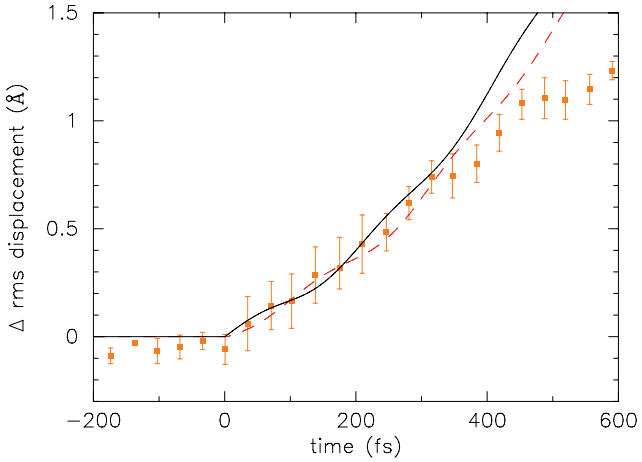

Fig. 4 Time evolution of the root-mean-square displacements of the atoms in InSb after femtosecond-laser excitation leading to an electronic temperature of 80 mRy, which corresponds to the excitation of about 7% of the valence electrons. The *solid curve* refers to the motion of the In atoms, whereas the *red dashed curve* describes the displacements of the Sb atoms. The experimental points and error bars (*orange*), obtained from Fig. 3 of [9], are also shown for comparison

demonstrates clearly why the concept of nonthermal melting applies to this type of problem. When the femtosecond-laser pulse excites the solid, it couples primarily to the electrons, which absorb the energy of the photons and thermalize rapidly. Part of the energy is then transferred to the lattice via the deformation of the PES. As we have seen, this deformation is produced in particular modes, which leads to the destabilization of the crystal structure. This means that the additional energy is not distributed among the phonon modes according to the equipartition theorem, but only a fraction of the modes becomes active.

In order to compare our results with the experiments of [9], we have simulated the motion of the atoms on the basis of the calculated PES by solving Newton's equations and averaging over an ensemble of initial conditions (previous to laser excitation). Then, we have calculated the rms displacements of the atoms as a function of time for different laser-induced electronic temperatures. Details of our method are as follows. The computed phonon frequencies for the Γ, X and L points were used to describe the dynamics of a 16-atom unit cell in the harmonic approximation before laser excitation. For each phonon mode, we averaged over initial energies E_i with weights $\exp(-E_i/k_B T)$ and over initial phases φ_i (see [2]). After the laser pulse, the time evolution of each configuration was computed using the phonon degrees of freedom including the full anharmonicity of the potential for each phonon mode and neglecting the coupling between different phonon coordinates. We expect that this approximation is valid for $t \lesssim 400$ fs. In Fig. 4, we show the results for $T_{el} = 80$ mRy, which corresponds to an excitation of about 7% of the valence electrons of InSb, which is roughly the value estimated by Lindenberg et al. [9, 11] for this measurement. A very good agreement with experiment is obtained, both qualitatively and quantitatively. In our case we are able to distinguish the displacements of the Sb and In ions. As can be observed, the rms displacements do not show a strict linear behavior. It has to be mentioned that the experimental points of [9] were not accurate enough to resolve the exact curve shape. The results presented in Fig. 4 should motivate further experiments with higher accuracy. The average slope of the curve in Fig. 4 is about 2.5 Å/ps, which is coincidentally similar to the thermal velocity at 300 K. This fact might have led the authors of [9] to make a wrong interpretation of the experimental results in terms of a planar PES. Figures 3 and 4 clearly explain the experimental results.

It is interesting to compare our results for InSb to what happens in other materials upon intense laser excitation. Here, we focus on bismuth, a much-studied model system for investigating the effects of femtosecond lasers. The structure of Bi is very close to the simple cubic one [14], but it is stabilized by a Peierls distortion, which leads to a unit-cell doubling. Therefore, the optical Γ point phonons in Bi play a similar role as the zone-boundary acoustic phonons in InSb. Comparable to the results described in the present work, DFT calculations have confirmed that the optical Γ point phonons in Bi soften significantly upon fs-laser excitation [14].

4 Conclusions

Based on the *ab initio* calculations presented in this paper we can now discuss the correct physical picture of nonthermal melting. The femtosecond-laser pulse creates a high density of electron–hole pairs, which thermalize on a very short time and find a common chemical potential. As a consequence, a very high electronic temperature is achieved, which reflects the large amount of energy absorbed from the laser pulse. This high T_{el} leads to dramatic changes in the total energy and in the entropy of the electronic system, which produce a dramatic change of the potential landscape for the lattice motion. However, this change affects only a fraction of the lattice degrees of freedom, and in particular the TA modes at the boundary of the Brillouin zone, while most of the other lattice modes are only slightly softened. Remarkably, in the few modes affected, the PES is so strongly changed into a repulsive potential that the ions experience large forces which make them cover average distances as large as 1 Å within the first 400 fs after excitation. No homogeneous softening of phonons occurs. Our results confirm the original physical picture proposed by Stampfli and Bennemann [2, 3].

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