Effect of Intense Laser Irradiation on the Lattice Stability of Semiconductors and Metals

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The effect of intense ultrashort irradiation on interatomic forces, crystal stability, and possible melting transition of the underlying lattice is not completely elucidated. By using *ab initio* linear response to compute the phonon spectrum of gold, silicon, and aluminum, we found that silicon and gold behave in opposite ways when increasing radiation intensity: whereas a weakening of the silicon bond induces a lattice instability, gold undergoes a sharp increase of its melting temperature, while a significantly smaller effect is observed for aluminum for electronic temperatures up to 6 eV.

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Improving our understanding of the response of materials submitted to intense laser irradiation is critical for various applications ranging from laser micromachining to surface treatment or even surgery [1]. The recent advance and use of ultrashort laser pulses (100 fs) has also brought a new set of fundamental questions regarding the nature of the structural evolution of various metallic and semiconducting materials as well as the time scales involved in these nonequilibrium transitions [2–4].

In semiconductors, a solid to liquid melting transition occurring in hundreds of femtoseconds after laser irradiation has been observed by many groups on various systems such as indium antimonide [5], gallium arsenide [6], and silicon [7]. Latest experiments [3] using *in situ* x-ray diffraction further provided a direct visualization of the atomic motion on indium antimonide and clearly demonstrated the athermal nature of the transition. This experiment also provided bounds for the curvature of the potential energy surface modified by the thermal excitation. *Ab initio* molecular dynamics simulations performed on silicon [8,9] also shows a destabilization of the lattice. For semiconductors, melting under intense laser irradiation is now generally accepted as an *athermal* transition mostly induced by a softening of the interatomic bonds, which takes place long before the more conventional *thermal* transition due to the energy transfer from the electrons to the ionic lattice.

For metals, it is generally accepted that the laser directly excites the electrons which thermalize and reach their electronic temperature T_e in a few tens of femtoseconds (mostly as a result of electron-electron and electron-hole collisions). Because of the electron-phonon coupling, the energy is subsequently transferred from the electrons to the ions within a few tens of picoseconds leading to the thermal melting of the lattice [10,11]. However, several questions remain regarding the time and structural evolution of the lattice structure during the first tens of picoseconds after laser illumination. For gold, the assumption that the ions retain their initial lattice structure for times longer than anticipated by the electron-phonon coupling alone yields excellent agreement between the calculated and recently measured optical conductivity [12,13]. For gallium, recent experimental measurements indicate the existence of a transient phase lasting tens of ps after laser illumination [4].

These two experiments suggest that, as for semiconductors, the short pulse interaction may lead to a significant modification of the ion-ion interaction for some metallic systems. This, in turn, may significantly affect their structural and time evolution after the initial laser illumination. To rigorously quantify the effect of the electronic excitation on the potential energy surface, we use density functional perturbation theory (DFPT), where the effects of electronic excitation are incorporated using the Fermi-Dirac distribution [14,15]. We compute the evolution of the phonon spectrum as a function of the electronic temperature for three representative systems, a semiconductor, Si, a free-electron-like metal, Al, and a noble metal Au. These calculations provide a comprehensive study of the effect of the laser illumination on the structural stability of the underlying lattice immediately after the electrons have reached their equilibrium temperature T_e. This corresponds to a few femtoseconds after the laser illumination, when the ions have not yet responded to the elevation of the electron temperature and are still within their equilibrium positions and the density of the system staying unchanged. For Si, this study shows that the athermal melting observed experimentally and using molecular dynamics methods results from the transverse acoustic mode becoming unstable as the electron temperature is elevated. For Al the ion-ion interaction stays mostly unaffected by the elevation of temperature, whereas for Au, the latter leads to a significant hardening of the phonon modes. While counterintuitive, this result indicates that for gold, the elevation of the electron temperature and the resulting modification of the ion-ion interaction lead to a stabilization of the lattice and an increase in the melting temperature which in turn may result in a significant time delay for the lattice to melt.

We performed all the calculations using the ABINIT code [16]. The calculations are based on the local density approximation (LDA) [17] combined with the norm-conserving pseudopotential technique [18]. The $5d$, $6s$, the $3s$, $3p$, and $3d$, and the $3s$, $3p$ are retained as valence for, respectively, Au, Si, and Al. The valence pseudowave functions are expanded in plane waves up to a cutoff of 1090 eV, 544 eV, and 165 eV for, respectively, Au, Si, and Al. A $6 \times 6 \times 6$ Monkhorst-Pack $\boldsymbol{k}$-points mesh is used. The calculated equilibrium lattice parameter is 7.718 bohr for gold ($a_{\rm exp} = 7.709$ bohr). For silicon, the value obtained is 10.180 bohr ($a_{\rm exp} = 10.258$ bohr) and 7.655 bohr for aluminum ($a_{\rm exp} = 7.655$ bohr). The phonon dispersion curves were calculated along the [100], [110], and [111] symmetry directions for different electronic temperatures. The ions are kept in their perfect crystal positions (fcc for gold and aluminum and diamond-type for silicon). Dynamical matrices are computed at 6 $\boldsymbol{q}$ vectors in the irreducible Brillouin zone of the calculated equilibrium cell size and are used for interpolation to obtain the phonon dispersion curves.

In Fig. 1, we display our computed Si phonon dispersion curve at two different electronic temperatures T_e compared with the experimental results obtained at 300 K. First, we see that the *ab initio* calculations for $Te = 0$ eV are in a very good agreement with the experiment. We further see a change in the phonon spectrum when the electronic temperature is increased. The frequencies of the two lower branches which correspond to the transverse acoustic (TA) modes become imaginary (and are displayed as negative on Fig. 1 for clarity). Beyond a temperature of 1.5 eV, the frequency of the transverse acoustic mode at L goes through zero, and the complete branch becomes gradually unstable. We interpret this as the clear signature of the lattice instability induced by the thermal excitation of the electrons.

These *ab initio* calculations are in good agreement with the pioneering work of Biswas and Ambegaokar [19]. In an attempt to quantify the Si lattice stability, they used an empirical approach based on a combination of a linear screened potential and a bond charge model to compute the phonon spectrum. The softening of the L mode with temperature was attributed to a diminution of the bond charge due to the increase in the dielectric constant which acquires a partially metallic character. In another work, Silvestrelli *et al.* [8,9], performed *ab initio* molecular dynamics simulations of laser irradiated Si samples. They found a rapid transition to a liquid state at an electronic temperature $T_e = 25\,000$ K $\simeq 2.15$ eV. The resulting liquid exhibits a pair correlation function somewhat different from the normal liquid one and presenting a pronounced shoulder. The result shown here goes a step further than the molecular dynamics simulations and attributes the observed melting to the transverse acoustic modes becoming unstable as the electron temperature is increased beyond 1.5 eV. This result also casts within an *ab initio* framework the earlier work of Biswas *et al.* discussed above.

A similar calculation for gold yields very different results. At room temperature, the gold vibration spectrum is typical of a simple fcc solid and very similar to the aluminum spectrum. Our calculations for two different electronic temperatures are displayed in Fig. 2. We note again the very good agreement with the experimental data at room temperature. In contrast to Si, we now observe a very strong *increase* in the amplitude. The frequency of the L mode now changes from 1.76 THz to 2. 63 THz as the T_e is elevated to $Te = 6$ eV. As the electronic temperature is increased, the pressure increases dramatically up to 200 Gpa for an electronic temperature of 6 eV at constant volume. We also note that the free energy does not present a minimum as a function of volume beyond 6 eV.

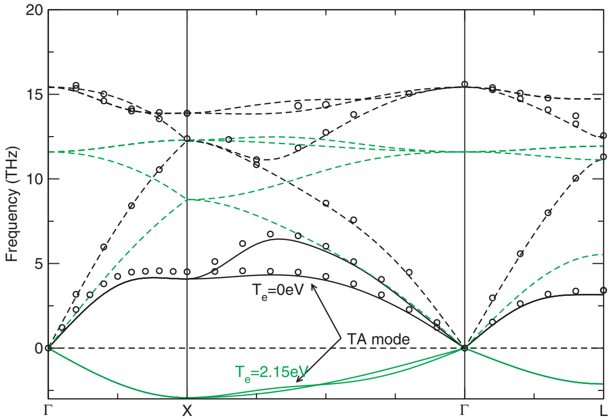

FIG. 1 (color online). Phonon spectrum of Si at different electronic temperature. The black curve is the spectrum for $Te = 0$ eV. The green curves are for $Te = 2.15$ eV. Open circles are experimental results from [26].

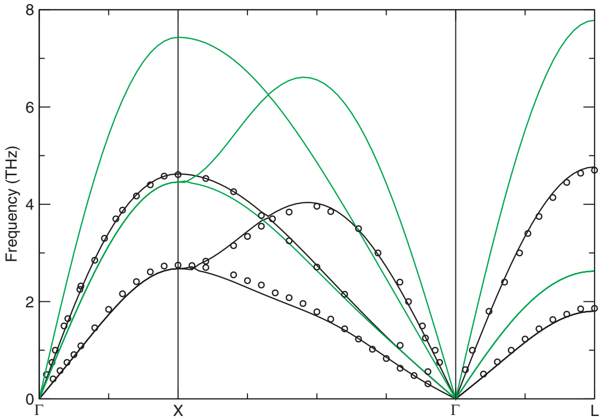

FIG. 2 (color online). Phonon spectrum of Au at different electronic temperatures. The black curves are the spectrum for room temperature. The green curves are for $Te = 6$ eV. Open circles are experimental results from [27].

A quantitative assessment can be drawn from the variation of the ionic specific heat at constant volume as a function of the ionic temperature T_i. Within the harmonic approximation [20]:

$$C_V(T_i) = 3nNk_B \int_0^{\omega_L} \left(\frac{\hbar\omega}{2k_BT_i}\right) 2\mathrm{csch}^2\left(\frac{\hbar\omega}{2k_BT_i}\right) g(\omega)d\omega, \tag{1}$$

where $g(\omega)$ is the normalized phonon density of state (DOS) as a function of the electronic temperature, k_B is the Boltzmann constant, n is the number of atoms per unit cell, N is the number of unit cell, and ω_L the largest phonon frequency. When the electronic temperature is close to room temperature, the heat capacity can be fitted to a Debye function. We find a Debye temperature $\Theta_D = 186$ K, in very good agreement with the value obtained from the experimental heat capacity. When the electronic temperature increases, the ionic heat capacity diminishes or, equivalently, the Debye temperature increases. As a result, when the electronic temperature increases from normal conditions to 6 eV, we found that Θ_D roughly doubles (see Fig. 3). Within the framework of the Debye-Lindemann's theory, the variation of Θ_D yields a quantitative indication of the variation of the melting temperature ($T_m = A\Theta_D^2$, where A depends only upon the density and the atom mass). It is then reasonable to assume that the melting temperature evolves like the squares of the Θ_D. In other words, the melting ionic temperature corresponding to an electronic temperature of $T_e = 6$ eV, $T_m(T_e = 6 \text{ eV})$ is obtained from the relation: $T_m(T_e = 6 \text{ eV})/T_m = (\Theta_D(T_e = 6 \text{ eV})/\Theta_D)^2$ (T_m and Θ_D are the corresponding values at normal temperature). This implies a change in the melting temperature by nearly a factor of 3 from 1337 K to 3604 K. Elastic constants display a similar pattern. As an example, we consider the shear stress, C_{44}, which is related to the sound speed by $\rho c_t^2 = B_{44} = C_{44} - P$. We adopt here the notations of Wallace [21] to describe the elastic constants under an initial stress. We find that under normal conditions, $B_{44} = C_{44} = 40$ GPa, whereas when $T_e = 6$ eV, we obtain $B_{44} = C_{44} - P = 155$ GPa, while $P = 200$ GPa. These numbers were confirmed by a direct calculation involving a shear strain, and by the application of the recently developed linear response to the strain formula [22], both yielding the same values within a few percent.

We have confirmed the results obtained for the Au lattice stabilization due to the increase in electronic temperature obtained above by using classical molecular dynamics. An embedded atom model potential has been built for gold for an electronic temperature of 6.5 eV. The embedding part is based on the formalism proposed by Baskes in [23], subsequently modified in [24] while its pair interaction is a simple screened Coulombic potential. To construct a potential of high quality, we imposed that it reproduces the theoretical equation of state for the three phases: fcc, cc, and sc. The phonon spectrum obtained is in reasonable agreement with the *ab initio* results shown above. Using the two phases method [25], we confirm the trend deduced from the previous analysis and find a melting temperature around 4600 K.

Finally, we now consider aluminum which is the prototype of a simple free-electron-like metal. The Al phonon spectrum of aluminum at different electronic temperatures shows a much smaller change in amplitude. (The TA frequency at L changes from 4.04 THz to 4.22 THz at $Te = 6$ eV.) Using the same procedure as for gold, we obtain a melting temperature which increases from 933 K to 1430 K.

This difference in the Al and Au behavior can be traced to the change in density of states as the electronic temperature increases. This comparison (Fig. 4) reveals that the

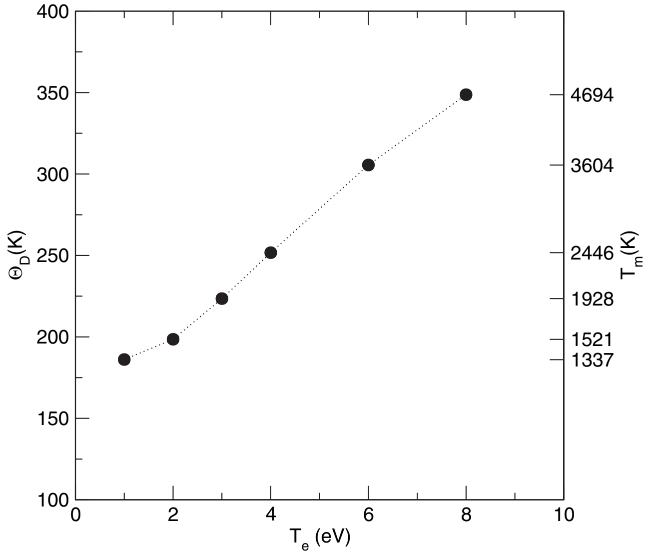

FIG. 3. Debye temperature variation as a function of electronic temperature for gold. On the right-hand side is the corresponding melting temperature.

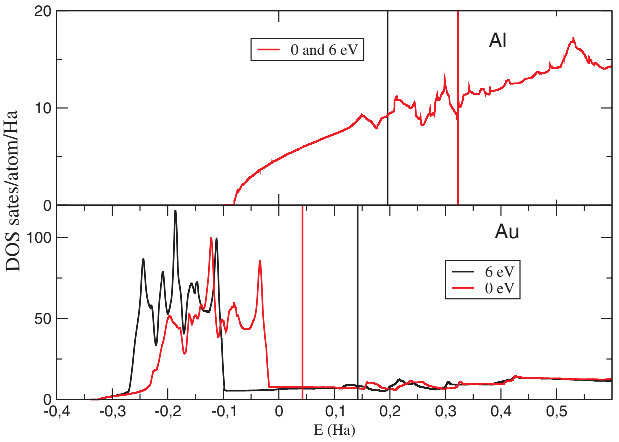

FIG. 4 (color online). Density of state of aluminum and gold at 0 K and 6 eV. Whereas the DOS of aluminum is practically unaffected, the DOS of gold is shifted and shrunk.

aluminum DOS remains free-electron-like and does not change with T_e (only the Fermi level is shifted). For Au, the DOS changes considerably. The *d* band is shifted toward lower energies, while its width becomes significantly smaller. In Au, the excitation of 5*d* electrons reduces the screening and makes the effective electron-ion potential more attractive. The 5*d* states are now more localized around the nucleus, more atomiclike, and the width of the DOS becomes smaller. This results in an increase of the effective ion-ion potential. In a simple metal like Al, which can be described by the standard linear screening approach, the very weak dependence upon the temperature of the electron gas dielectric constant in this density and temperature range yields a quasiconstant interatomic potential. We also note that, since the Al DOS does not change and preserves its positive slope, the Fermi level will move towards lower energy in order to keep the number of electrons constant. For Au, the smaller width of the *d* DOS will impose a motion towards higher energies.

In conclusion, we studied the effect of intense electronic excitations on the interatomic potential energy for electronic temperatures attained under intense laser irradiation. Whereas for silicon the lattice becomes instable through a transverse acoustic phonon instability, we find that metals tend to become more stable, with an increasing Debye temperature, elastic constants, and a higher melting temperature. This effect is small for free-electron-like metals such as aluminum, but appears to become large for a noble metal like gold. We believe that such a large effect on the lattice stability of solids will be found for any metal where localized electrons participate in the bonding (*d* or *f* orbitals).

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