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Electronic origin of bond softening and hardening in femtosecond-laser-excited magnesium

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Abstract
Many ultrafast structural phenomena in solids at high fluences are related to the hardening or softening of particular lattice vibrations at lower fluences. In this paper we relate femtosecond-laser-induced phonon frequency changes to changes in the electronic density of states, which need to be evaluated only in the electronic ground state, following phonon displacement patterns. We illustrate this relationship for a particular lattice vibration of magnesium, for which we—surprisingly—find that there is both softening and hardening as a function of the femtosecond-laser fluence. Using our theory, we explain these behaviours as arising from Van Hove singularities: We show that at low excitation densities Van Hove singularities near the Fermi level dominate the change of the phonon frequency while at higher excitations Van Hove singularities that are further away in energy also become important. We expect that our theory can as well shed light on the effects of laser excitation of other materials.

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1. Introduction

Femtosecond-laser pulses can transiently excite solids into a non-thermal state with electrons that are hot and ions that remain close to room temperature [1]. After an excitation, the electrons thermalize relatively slowly with the ions compared with the time needed for ultrafast structural changes. In general, the excited electrons modify the interatomic potentials [2], which may lead to a number of structural processes that would not take place under ordinary thermodynamic conditions, such as, ultrafast melting [3–7], solid-to-solid phase transitions on the subpicosecond time scale [8–13], the excitation of coherent phonons [14–17] and phonon squeezing [18]. At early times after the laser pulse, all of these phenomena can be described by the femtosecond-laser-induced changes to the phonon spectrum, which completely characterizes the harmonic part of the laser-excited potential energy surface, on which the ions move. Ultrafast melting, for example, has been related to the appearance of a lattice instability in the direction of transverse acoustic phonons at the Brillouin zone boundary of, e.g. Si [19, 20] and InSb [7, 21, 22]. In a similar way, the hardening of lattice vibrations in gold has been used to explain its delayed thermal melting upon intense femtosecond-laser excitation [23]. Another example is that the monoclinic-to-rutile laser-induced transition in VO_2 is proceeded by the excitation of a large-amplitude coherent phonon at fluences below the solid-to-solid transition threshold [24, 25]. Finally, the squeezing of phonons in opaque media has been demonstrated to be the direct consequence of a sudden laser-induced change of the phonon frequencies [26, 27].

In semiconductors and semimetals, the hot carriers typically induce bond softening [14, 28, 29] due to the excitation of electrons from bonding to antibonding states. In metals, phonons have been found to harden [29–32] upon femtosecond-laser excitation. In contrast, the phonon frequencies in Al and TiO_2 have been reported to change only little or not at all [29, 33]. Moreover, in Mg we have predicted that upon laser excitation the transverse acoustic parallel mode at the M point softens [31]. In this paper we report that the transverse optical parallel ($TO_{\parallel}$) phonon mode at the K point in the Brillouin zone even reveals both softening and hardening as a function of the absorbed laser energy. We present a general theory that relates changes in the phonon frequency as a function of the electronic temperature to changes in the ground state electronic density of states (DOS) as a function of atomic displacements using the so-called frozen-phonon approach. We show that this method explains the softening and hardening of the above-mentioned mode and point out how it could, for example, be used to clarify phonon softening in semiconductors and phonon hardening in noble metals.

2. Method

We computed laser-induced structural changes in Mg by instantaneously raising the electronic temperature in the framework of electronic-temperature-dependent density functional theory (DFT) [2] using the code WIEN2K [34], which is an all-electron implementation of the full-potential linearized augmented plane-wave (LAPW) method and is one of the most accurate DFT programmes available. No shape approximations for either the electronic charge density or potential are made and core and valence electrons are all explicitly taken into account meaning that the subtle effects of the core electrons are not simplified by, for example, pseudopotentials.

We determined phonon frequency changes as a function of the electronic temperature using the frozen-phonon method, which considers the propagation of a phonon with a fixed

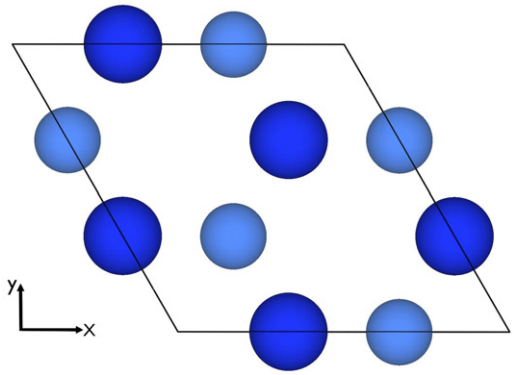

Figure 1. Top view of the Mg supercell in the (00−1) direction used for the frozen-phonon calculations of the $TO_{\|}$ mode at the K point. The light and dark blue atoms are in the $z = 1/4$ and $3/4$ planes, respectively, in their equilibrium positions.

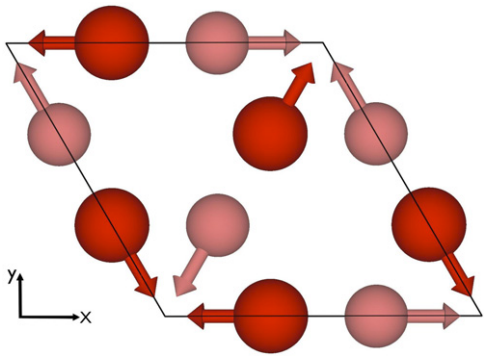

Figure 2. Top view of the Mg supercell in the (00−1) direction used for the frozen-phonon calculations of the $TO_{\|}$ mode at the K point. The light and dark red atoms are in the $z = 1/4$ and $3/4$ planes, respectively. The arrows indicate the directions of the atomic displacements.

wave vector $\mathbf{q}$, which involves atomic displacements $\{\mathbf{u_i}(\mathbf{q})\}$ leading to a new crystal structure consistent with the 'frozen' vibrational mode. In our calculations the atoms were displaced over sufficiently small distances u from their equilibrium positions. The phonon wave vectors must be commensurate with the solid, i.e. the displaced atoms must still form a supercell. Accordingly, for the $TO_{\|}$ phonon mode at the point K in the Brillouin zone, which we studied in the present work, we tripled the primitive unit cell. The supercell, which we used for our self-consistent frozen-phonon calculation is shown in figure 1, where the positions of atoms are at the 6g positions of space group $P6_3/mcm$ (no. 193), whose allowed displacements are indicated by arrows in figure 2.

We further chose the value $R_{\mathrm{MT}} = 2.42$ Bohr for the muffin-tin radii. The product of R_{MT} times the maximum value of the reciprocal lattice vector K_{max} of the LAPW basis set, which defines the dimensionless quantity RK_{max} [34], was set equal to $RK_{\mathrm{max}} = 7$. For the electrons, we used a $14 \times 14 \times 13$ $\mathbf{k}$ grid, excluding the Γ point [34].

2.1. Self-consistent approach

In DFT, a laser-excited material can be studied through the interatomic potential energy, which is determined by the Mermin free electronic energy [2]

$$F_{\mathrm{tot}}(\{R_{\mathrm{i}}\}) = F_{\mathrm{band}} + E_{\mathrm{xc}}[\rho(\mathbf{r})] - \int v_{\mathrm{xc}}(\mathbf{r})\rho(\mathbf{r})\,\mathrm{d}\mathbf{r} - \frac{1}{2}\int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}' + V_{\mathrm{II}}(\{R_{\mathrm{i}}\}), \tag{1}$$

where E_{xc} and v_{xc} are the exchange and correlation energy and potential, respectively, and $V_{\mathrm{II}}(\{R_{\mathrm{i}}\})$ is the ion–ion repulsive interaction. $\rho(\mathbf{r})$ is the electronic charge density:

$$\rho(\mathbf{r}) = \sum_m n(\varepsilon_m, t)\varphi_m^*(\mathbf{r})\varphi_m(\mathbf{r}). \tag{2}$$

Here, $\varphi_m(\mathbf{r})$ are the Kohn–Sham orbitals [35], with $m = \{\mathbf{k}, n\}$, where $\mathbf{k}$ is the electronic wave vector and n is the band index. In (1) the first term is the free band energy, which contains the band energy and the electronic temperature T_{el}:

$$F_{\mathrm{band}} = E_{\mathrm{band}}(t) - T_{\mathrm{el}}(t)S_{\mathrm{el}}(t). \tag{3}$$

S_{el} is the electronic entropy, which is given by

$$S_{\mathrm{el}} = -k_{\mathrm{B}}\sum_m [n(\varepsilon_m, t)\log(n(\varepsilon_m, t)) + (1 - n(\varepsilon_m, t))\log(1 - n(\varepsilon_m, t))] \tag{4}$$

and $E_{\mathrm{band}}(t)$ is the band energy, which can be obtained as

$$E_{\mathrm{band}}(t) = \sum_m n(\varepsilon_m, t)\varepsilon_m, \tag{5}$$

where $n(\varepsilon_m, t)$ are the occupation numbers of the electronic Kohn–Sham levels ε_m. The occupancies $n(\varepsilon_m, t)$ may depend on time.

It can be seen that the electronic free energy depends strongly on the occupation numbers, which appear only in the first term, and, to a lesser extent, also on the self-consistent electronic charge density. This means that if the electronic occupations undergo strong changes, then the potential energy will change significantly [36].

In order to quantify these changes and to determine the influence of the laser excitation on the phonon frequencies, we performed frozen-phonon self-consistent calculations and computed the total energies of laser-excited Mg with and without atomic displacements as a function of the electronic temperature. The phonon frequency in the harmonic approximation is in this case given by

$$\nu_{\mathrm{scf}}^2(T_{\mathrm{el}}) = \frac{F_{\mathrm{tot}}^{\mathrm{scf}}(u, T_{\mathrm{el}}) - F_{\mathrm{tot}}^{\mathrm{scf}}(u = 0, T_{\mathrm{el}})}{2\pi^2 m u^2}. \tag{6}$$

Here $u = \|\mathbf{u}_i(\mathbf{q})\|$ is the atomic displacement, $F_{\mathrm{tot}}^{\mathrm{scf}}(u, T_{\mathrm{el}})$ and $F_{\mathrm{tot}}^{\mathrm{scf}}(u = 0, T_{\mathrm{el}})$ are the total free energies with and without atomic displacements obtained self-consistently for a given temperature using (1), and m is the total weight of all displaced atoms in the supercell.

2.2. Non-self-consistent approximation

Following our ansatz from [14] we also performed non-self-consistent calculations, which provide a more intuitive picture of the behaviour of the phonon frequencies as a function of the electronic temperature. In this approximation total energies are calculated from

$$F_{\mathrm{tot}}^{\text{non-scf}}(T_{\mathrm{el}}) \approx F_{\mathrm{tot}}^{\mathrm{scf}}(T_{\mathrm{el}}=0) + \Delta F_{\mathrm{band}}^{\text{non-scf}}(T_{\mathrm{el}}), \tag{7}$$

where $F_{\mathrm{tot}}^{\mathrm{scf}}(T_{\mathrm{el}}=0)$ is the total self-consistent energy of the ground state and $\Delta F_{\mathrm{band}}^{\text{non-scf}}(T_{\mathrm{el}})$ is the difference of the band energies (5) at electronic temperature T_{el} and in the ground state. This approximation, which does not take into account self-consistent laser-induced changes to the electronic charge density $\rho(\mathbf{r})$, is based on the interpretation of the Kohn–Sham energies as single-electron excitation energies and has been shown to work well for Bi [37]. In a computationally convenient way such temperature-dependent non-self-consistent calculations provide a prediction of the behaviour of phonon frequencies, based on ground-state calculations only, via

$$\nu_{\text{non-scf}}^2(T_{\mathrm{el}}) \approx \frac{F_{\mathrm{tot}}^{\text{non-scf}}(u, T_{\mathrm{el}}) - F_{\mathrm{tot}}^{\text{non-scf}}(u=0, T_{\mathrm{el}})}{2\pi^2 m u^2}. \tag{8}$$

So, using the non-self-consistent approximation we can calculate properties at high electronic temperatures, far from the electronic ground state, relying on $T_{\mathrm{el}} = 0\,\mathrm{K}$ self-consistent calculations only. As we will show in the next section, (8) allows for a robust qualitative explanation of the non-trivial electronic-temperature-dependent structural response of magnesium to a femtosecond-laser pulse.

2.3. Sommerfeld expansion

For low induced electronic temperatures the laser excitation can also be described by the Sommerfeld expansion [38], which provides a systematic way of expanding the low temperature expression for the free energy in powers of T_{el}. For the band energy we used the Sommerfeld expansion up to second order:

$$F_{\mathrm{band}}(T_{\mathrm{el}}) \approx F_{\mathrm{band}}(T_{\mathrm{el}}=0) - \frac{\pi^2}{6}(k_{\mathrm{B}}T_{\mathrm{el}})^2 g(\varepsilon_{\mathrm{F}}), \tag{9}$$

where k_{B} is the Boltzmann constant and $g(\varepsilon_{\mathrm{F}})$ is the electronic DOS at the Fermi level. The first term of (10) is the band energy in the ground state, obtained from a self-consistent calculation, and the second term completes the band energy at higher electronic temperature and includes energetic and entropic contributions [39]. Using (10) we approximately obtained the change of phonon frequencies as a function of electronic temperature:

$$\nu_{\text{Sommerfeld}}^2(T_{\mathrm{el}}) \approx \nu_{\text{0scf}}^2(T_{\mathrm{el}}=0) - \frac{\pi^2}{6}(k_{\mathrm{B}}T_{\mathrm{el}})^2 \frac{\Delta g(\varepsilon_{\mathrm{F}})}{2\pi^2 m u^2}, \tag{10}$$

where ν_{0scf} is the phonon frequency at the ground state, $\Delta g(\varepsilon_{\mathrm{F}}) = g(u, \varepsilon_{\mathrm{F}}) - g(u=0, \varepsilon_{\mathrm{F}})$, and $g(u, \varepsilon_{\mathrm{F}})$ and $g(u=0, \varepsilon_{\mathrm{F}})$ are the DOSs at the Fermi level in the ground state with and without atomic displacements, respectively.

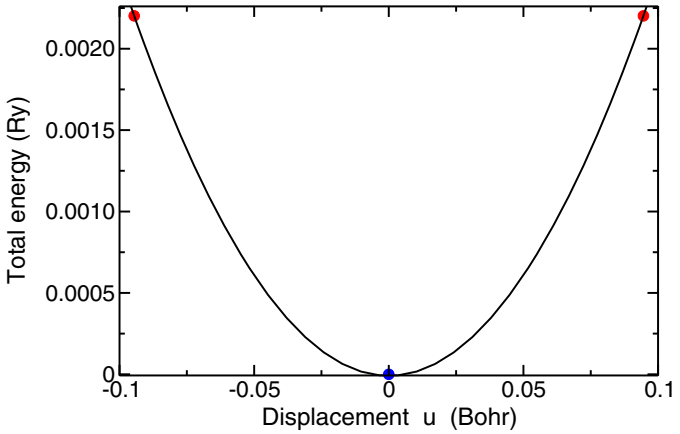

Figure 3. The total energy of Mg with (red point) and without (blue point) displaced atoms for the $TO_{\parallel}$ mode at the K point. The solid line shows the parabola connecting all data points.

3. Results

3.1. Self-consistent calculations

Our frozen-phonon calculation consisted of computing the total energy for the supercell shown in figures 1 and 2 with and without displaced atoms as illustrated in figure 3 for the electronic ground state. From the free total energies at different electronic temperatures we obtained the phonon frequency at different excitation densities. Our results are shown in figure 4. Surprisingly, at low temperatures (up to 9000 K), the $TO_{\parallel}$ (K) mode of Mg reveals *softening* and at higher electronic temperatures *hardening*. We would like to stress that although this result is significant, the self-consistent approach followed here does not offer a ready explanation. In contrast, our analysis below, which is based on the Sommerfeld expansion in the non-self-consistent approximation, explains this behaviour and shows how these opposite changes of the phonon frequency can subsequently occur in a single mode.

3.2. Non-self-consistent calculations

As a first step to analyse this behaviour, we computed the phonon frequency non-self-consistently as a function of the electronic temperature (8), which we also show in figure 4. As can be seen from a comparison with the self-consistent results in figure 4, at low temperatures the non-self-consistent approximation yields nearly identical results with self-consistent temperature-dependent DFT and at higher temperatures still reproduces the general trend, i.e. *hardening* or *softening* [37]. This shows that the laser-induced changes in the Mermin free electronic energy F_{tot} (1) are dominated by the changes in the band energy F_{band} (3) and that the contributions due to self-consistent changes of the density $\rho(\mathbf{r})$ (2) are comparatively small. Our comparison in figure 4 demonstrates that the non-self-consistently computed phonon frequencies can qualitatively explain the structural response of Mg to a femtosecond-laser pulse as a function of the induced electronic temperature. This is an important result, because it shows that we can interpret the laser-induced changes to the electronic subsystem in terms of a rigid electronic band structure, where only the occupation numbers change. Consequently, the

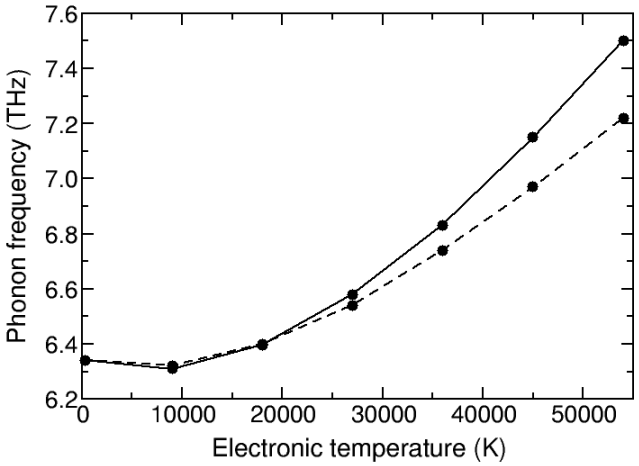

Figure 4. Phonon frequency variations as a function of electronic temperature for the $TO_{\parallel}$ mode at the K point in the Brillouin zone. Solid lines connect our results obtained from self-consistent DFT calculations. The dashed lines were computed non-self-consistently.

electronic band structure needs only to be computed self-consistently in the electronic ground state. This non-self-consistent approximation is also central to the Sommerfeld expansion discussed below.

3.3. Discussion

A physically appealing interpretation of the results of our non-self-consistent calculations, which are shown by a dashed line in figure 4, can be obtained using the Sommerfeld expansion, which approximates changes in the band energy using the electronic DOS evaluated at the Fermi energy (9). In figure 5 we compare the electronic DOS of Mg with the atoms in their equilibrium positions (solid blue line) with the electronic DOS of Mg, when the atoms are displaced from their equilibrium positions (dotted red line). It can be seen that after displacing the atoms, the Van Hove singularities [40] near the Fermi level, which are labelled B and C, become weaker and also that a new Van Hove singularity marked by A appears. In order to estimate the effect of the electronic temperature on the phonon frequency from the Sommerfeld expansion, in (10) we used the difference of the electronic DOS $\Delta g(\varepsilon)$, which is shown in figure 6 for different smearing levels. It is important to notice that $\Delta g(\varepsilon)$ is a highly irregular function of energy, which has cusps due to the Van Hove singularities. Due to these singular points one can not describe electronic excitations beyond the nearest Van Hove singularity using the standard Sommerfeld expansion, because all orders in this expansion involve only $\Delta g(\varepsilon)$ and its nth order energy derivatives evaluated at the Fermi level. Instead, we found it helpful to smear the electronic DOS by convoluting it with Gaussians with different widths. The result for the smearing levels of 1 and 2.5 eV are shown in figures 6(b) and (c), respectively. The higher values of smearing effectively describe the behaviour of phonons at higher electronic temperatures: whereas at low electronic temperature the fine features in the DOS near the Fermi level dominate the changes in vibrational frequencies, at higher electronic temperature the average change arises from the broadening of the relevant energy interval. The peaks in figure 6 appear from Van Hove singularities in both DOSs of Mg, i.e. those with and without

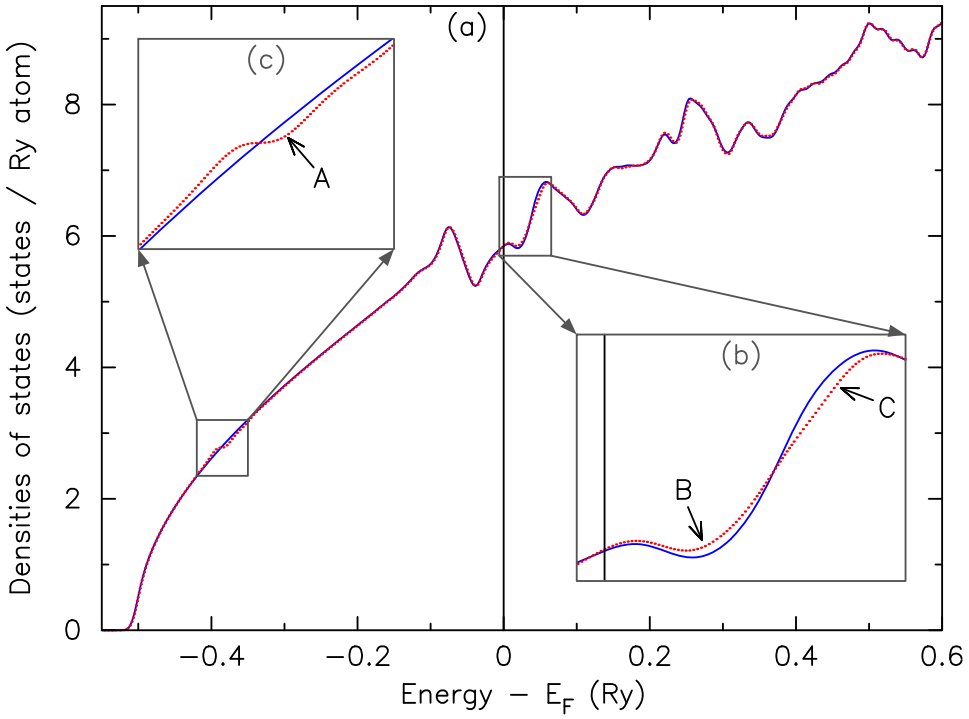

Figure 5. (a) Electronic DOS of Mg. Panels (b) and (c) are enlarged parts of the DOS. The solid blue line shows the DOS of Mg without atomic displacements and the dotted red line is the DOS of Mg with atoms displaced in the direction of the $TO_{\parallel}$ phonon mode at the K point of the Brillouin zone. A, B and C label the Van Hove singularities that are relevant for the phonon frequency changes after femtosecond-laser excitation (see text).

displaced atoms. The peaks of the relevant Van Hove singularities are marked by A, B and C in figures 5 and 6 at the same energies. The Van Hove singularity peak labelled A appears in the DOS only after displacing the atoms, B and C are from the existence of Van Hove singularities at the M and K points in the Brillouin zone of Mg, respectively. In figure 6 we see that the difference of the DOS evaluated at the Fermi energy has a positive value for low smearing levels and that by increasing the smearing its value decreases. Even from some point it decreases below zero and becomes negative, which originates from the combination of the contributions from Van Hove singularities A and C. The electronic temperature dependent sign change of $\Delta g(\varepsilon_F)$ explains why the $TO_{\parallel}$ phonon mode at the K point of Mg shows *softening* for low and *hardening* for high excitation densities. This is elaborated in figure 7, where we show the phonon frequencies resulting from the Sommerfeld expansion. By comparing with the results from self- and non-self-consistent calculations (figure 4) we can see the same behaviour of the phonon frequency as a function of electronic temperature. Depending on the smearing level we see that the Sommerfeld expansion (10) qualitatively explains the phonon softening up to ∼2300 K (0.2 eV) and ∼12 000 K (1 eV) as well as the phonon hardening around ∼29 000 K (2.5 eV). From the fact that the phonon softening at low electronic temperature and the hardening at higher temperatures are well reproduced using different smearing levels for the DOS and from our above analysis of the DOS changes (figure 6) we conclude that Van Hove singularities in figure 5 are responsible for the non-trivial behaviour of the phonon frequency as a function of laser fluence.

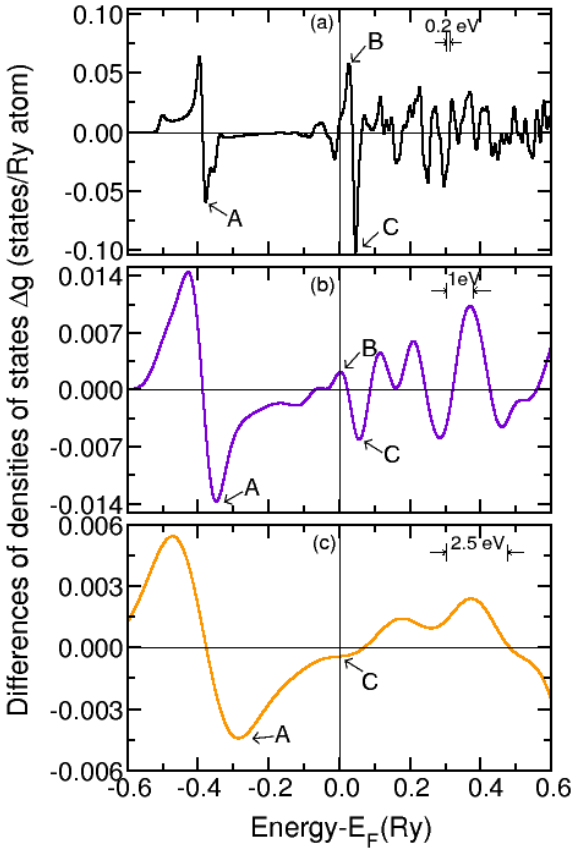

Figure 6. The differences of the DOSs of Mg with and without displacements for the $TO_{\parallel}$ mode at the K point with smearing levels (a) 0.2 eV, (b) 1 eV and (c) 2.5 eV.

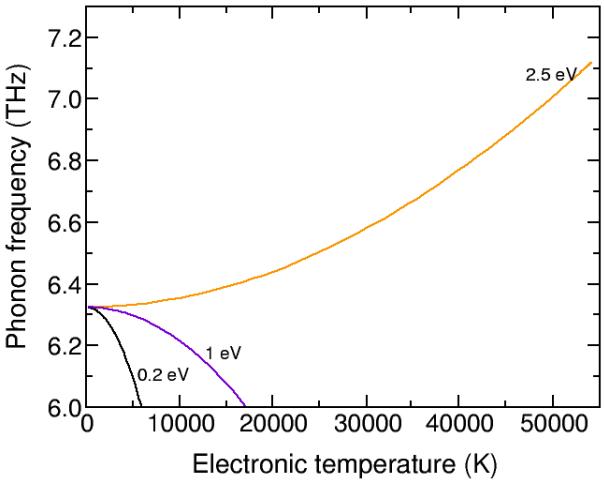

Figure 7. Phonon frequency change as a function of electronic temperature for the $TO_{\parallel}$ mode at the K point. The solid lines are showing the results from the Sommerfeld expansion (10) using different smearing levels, which are indicated.

4. Conclusion

In this paper we have computed the behaviour of the $TO_{\parallel}$ mode at the K point of ultrafast laser-excited Mg for different electronic temperatures corresponding to different laser fluences using the full-potential LAPW method. We found both softening and hardening as a function of the excitation density. In order to analyse our results we have computed the temperature dependence of the phonon frequency via Sommerfeld expansions. We related the phonon frequency changes upon laser excitation to changes in the Van Hove singularities upon displacing the atoms in the direction of the $TO_{\parallel}$ phonon mode at the K point. To the best of our knowledge, Mg is the first material in which a single mode shows both significant laser-induced bond softening and hardening. Because the lattice dynamics of solids is an electronically determined property we further expect that our method can help to clarify why most semiconductors, e.g. Si show femtosecond-laser-induced phonon softening while many metals, e.g. Au show hardening. We wish to stress that the explanations for these crystals may be different from the origin of phonon hardening and softening in Mg, i.e. they may or may not involve Van Hove singularities, but our approach used here based on a detailed analysis of the differences in the electronic DOSs within the frozen-phonon method is in principle also applicable to these and other materials.

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