Photo-induced athermal phase transitions of HgX (X = S, Se, Te) by *ab initio* study*

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Ab initio calculations of lattice constants, lattice stabilities of HgX (X = S, Se, Te) at different electronic temperatures (T_e) have been performed within the density functional theory (DFT). We find that the lattice constants of HgX increase and the phonon frequencies reduce as T_e increases. Especially the transverse-acoustic (TA) phonon frequencies of HgX gradually become negative with the elevation of the electron temperature. That is to say ultrafast intense laser induces lattice instabilities of HgX and athermal melting appears for the increase of laser intensity. What is more, with the X atom number increasing, the critical electronic temperatures of HgX are decreased in sequence. This result would be helpful for understanding the athermal melting processes for femtosecond laser micromachining.

Keywords: *ab initio* calculation, mercury chalcogenides, lattice stability, athermal melting

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1. Introduction

The mercury chalcogenides HgX (X = S, Se, Te) are attracting increasing attention, because of their technological interest for electro–optical devices and spintronic applications.[1,2] As is known, HgS is a technologically important semiconductor for dichorism,[3] birefringence,[4] photoelectric,[5,6] and acousto–optic properties.[7] Recently, the structural, electronic, and thermal properties of HgX binary compounds have been investigated within the density functional theory (DFT).[8–14] Al Shafaay *et al.*[8] applied a first principle full potential-linearized augmented plane wave (FP-LAPW) method to study the structural, electronic, and thermal properties of HgX binary compounds as well as HgS_xSe_{1-x} and $HgSe_xTe_{1-x}$ ternary alloys. Svane *et al.*[9] have shown that HgS is a semiconductor with gap energy equal to 0.61 eV using hybrid quasi-particle selfconsistent GW (QSGW) approximations. Cardona *et al.*[10] also used the hybrid QSGW approach to investigate the electronic band structure and the phonon dispersion relations of the zinc blende type mercury chalcogenides, which showed that HgS is a semiconductor, and both HgSe and HgTe have inverted band structures with $\Gamma 6$ lying below $\Gamma 8$. Besides, Verma *et al.*[12] calculated the thermal properties of mercury chalcogenides. Secuk *et al.*[13] investigated the structural optimization, electronic band structure, density of electron states, optical, dynamic and thermodynamic properties of HgTe and HgSe within local density approximation (LDA). Wang *et al.*[14] reported that all II–VI semiconductors with a cubic zinc blende structure have negative thermal expansion (NTE) behavior at low temperatures within the framework of first-principles.

Material response under intense laser irradiation is of significant importance for various applications, such as laser micromachining, laser induced damage, surface treatment, and surgery.[15] Therefore, the interplay between ultrafast laser and material requires a comprehensive theoretical description. A large number of theoretical and experimental efforts have thus been stimulated to study the ultrafast laser–materials interactions.[16–22] Recent advances have revealed that semiconductors under intense laser irradiation firstly underwent an athermal transition induced by the softening inter-atomic bonds rather than conventional thermal transition.[16–20] Feng *et al.*[16] have investigated the photo-induced non-thermal phase transition of β-SiO_2 by *ab initio* calculation. To clarify the electronic-excitation effect under intense laser illumination, Recoules *et al.*[17] employed density functional perturbation theory (DFPT) to compute the evolution of the phonon spectrum at different electronic temperatures for Si, Al, and Au, which provides a comprehensive study of the lattice stability considering the effect of the laser illumination, meanwhile the electronic excitation in silicon can induce lattice instabilities as exhibited by transverse-acoustic (TA) phonon modes with imaginary frequencies. Shen *et al.*[18] studied the effect of intense laser irradiation on the lattice stability of β-SiC by *ab initio* calculation within the density functional perturbation theory (DFPT).

In the case of ultrashort laser irradiation, semiconductors produce a large number of strong inhomogeneous heating electrons. The heating electrons in the semiconductors

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rapidly exchange energy through electron–electron collisions and then instantaneously reach a high temperature (thousands of Kelvins, electronic temperatures) on the tens of femtosecond timescale.[23] Accurate knowledge of the rapidly evolving conditions is of importance.[24] At the same time, the inter-atomic potentials of semiconductors encounter dramatic changes and the lattices destabilize then the solids catch ultrafast structural transitions. A few groups have confirmed that the laser-semiconductor interaction occurs in an athermal transition.[16,17,22] Therefore, accurate evaluation of the electronic excitation is essential not only from a physical point of view but also for device engineering.

Even though there has been remarkable experimental and theoretical work on HgX, there are limited theoretical studies on the effect of ultrafast intense laser irradiation on HgX in the literature. It is very necessary to investigate the lattice stability of HgX considering the electronic excitation effect through *ab initio* calculations based on DFT. In this work, we aim to employ *ab initio* pseudopotential method to study the lattice constants, transverse-acoustic phonons of HgX at different electronic temperatures caused by different intensities of ultrafast intense laser irradiation. Finally, the lattice stabilities of HgX are further discussed at higher electronic temperatures.

2. Computational methods

The binary compounds HgX (X = S, Se, Te) crystallize in the zinc-blende structure and their space groups are F-43m, meanwhile the Hg atom is located at the origin and the X atom is located at (0.25, 0.25, 0.25).

We performed all calculations based on finite-temperature density functional theory (DFT) on the lattice parameters and dynamic properties of HgX with electronic temperatures (T_e) increasing from 0 eV to 4.0 eV. For the treatment of exchange and correlation, the generalized gradient approximation (GGA) parameterized by Perdew–Burk–Ernzerhof (PBE)[25–27] is used. The $3s^2$ $3p^2$, $4s^2$ $4p^2$, $5s^2$ $5p^2$, and $5d^{10}$ $6s^2$ are retained as valence electrons for S, Se, Te, and Hg, respectively. The projector-augmented wave (PAW)[28] method is employed to describe the electron–ion interactions as implemented in the Vienna *ab initio* simulation package (VASP).[29–31] The plane-wave kinetic energy cutoff is set to 370 eV for HgS, and 310 eV for HgSe and HgTe.[10] For the sampling of the Brillouin zone, we use $11 \times 11 \times 11$ k-point grids for geometry optimization at different electronic temperatures. All parameters have been tested for convergence. Lattice parameters and internal positions at various electronic temperatures in primitive cells are fully relaxed until residual Hellman–Feynmann (HF) forces are less than 1.0×10^{-4} eV/Å and the energy convergence threshold is set as 1.0×10^{-7} eV/atom. Moreover, a few hundred bands are chosen to make enough electrons occupy the conduction band at high electronic temperatures.

Phonon-dispersion calculations are performed by inter-atomic force constants in the real space[32,33] within density functional perturbation theory (DFPT).[34] In the calculation we use the supercell approach to achieve the real space force constants together with 16 atoms $2\times2\times2$ supercells, a Γ-centered $5 \times 5 \times 5$ k mesh. The phonon dispersion curves of HgX compounds in the considered structures are calculated by using the PHONOPY code[35] based on the frozen phonon method. Since HgX belongs to an ionic crystal, atomic displacement induces a dipole and inter-atomic force constants are remarkably influenced by dipole–dipole interaction which causes longitudinal optical–transverse optical (LO–TO) splitting at the wavelength vector of $\boldsymbol{q} = 0$.[36] The LO–TO splitting with a non-analytical term depends on the electronic dielectric constants and the Born effective charges.[37]

3. Results and discussion

3.1. Lattice parameters at different electronic temperatures

For the zinc-blende HgX, the calculated lattice constants a_0 at the ground state, compared with experimental and other theoretical results, are listed in Table 1. Our calculated values of 5.997 Å, 6.264 Å, and 6.648 Å for HgS, HgSe, and HgTe, are very close to the experimental values of 5.841 Å,[38] 6.085 Å,[39] and 6.453 Å.[40] Note that the GGA results for a_0 are usually longer than the experimental data. These results are in excellent agreement with other available calculations,[2,8,10] as shown in Table 1. Therefore, the optimized structure and calculated method are accurate and feasible enough to study other properties of HgX.

Table 1. Lattice constants of zinc-blende HgX are obtained by the ground-state calculation compared to other theoretical and experimental studies.

Compound	Present	Other calc.	Exp.
HgS	5.997	5.863[a], 5.999[b]	5.841[c]
HgSe	6.264	6.115[a], 6.255[b], 6.271[d]	6.085[e]
HgTe	6.648	6.521[a], 6.633[b], 6.664[d]	6.453[e,f]

[a]Ref. [8], [b]Ref. [10], [c]Ref. [38], [d]Ref. [2], [e]Ref. [39], [f]Ref. [40].

Figure 1 shows that the lattice parameters of HgX increase with the T_e elevating, which is similar to those theoretical results[17–20] and experimental findings.[21,22] These observations are consistent with the notion that a strong laser pulse will tend to destabilize the HgX structures and may induce a transition to another phase with higher atomic coordination, including the possibility of an athermal transition to the liquid state. The increasing slopes of lattice-parameters-electronic-temperature curves for HgX (X = S, Se, Te) are firstly small, then large, and finally small again from 0 eV to 4.0 eV. What

is more, the increasing trends of HgSe, HgTe catch the same, which are different from HgS for the reason that HgS is a semiconductor and both HgSe and HgTe are semimetals. This can be explained by the contribution of the inharmonic thermal vibration of HgX in the equilibrium position after ultrafast intense laser irradiation. With the increase of T_e, the more excited valence electrons are, the more repulsive the bonding force between atoms becomes. Hence, the equilibrium lattice constants of HgX expand at the electronic temperature ranges from 0 eV to 4.0 eV.

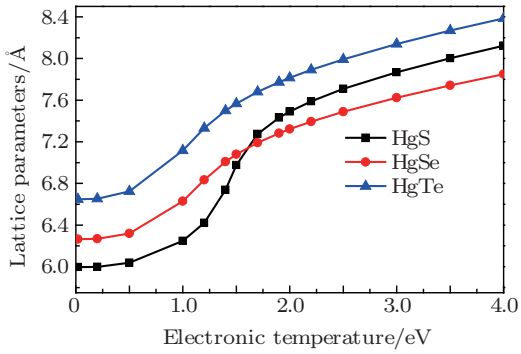


Fig. 1. (color online) The dependence of lattice parameters on electronic temperature T_e for HgX.

3.2. Lattice dynamics

To explore ultrafast intense laser inducing the lattice stabilities, the phonon-dispersion curves at four electronic temperatures are calculated, as shown in Fig. 2. In short, as the electronic temperature T_e increases, the crystal lattices of the zinc-blende HgX become destabilized due to the electronic excitation weakening the repulsive interactions between atoms.

Figure 2 presents the phonon spectra of HgX at different electronic temperatures. A few changes occur in the phonon spectra as the electronic temperature varies. Accordingly, all of the phonon frequencies for HgX decline with the elevation of the electronic temperature. The lattices of HgX become completely unstable when $T_e > 1.45$ eV for HgS, $T_e > 1.31$ eV for HgSe, $T_e > 1.20$ eV for HgTe, which is judged by the whole negative transverse acoustic (TA) phonon frequencies in Figs. 2(a)–2(c). As T_e increases to the critical electronic temperature, the acceleration of electronic thermal motions and the raises of the system energy induce the instability of the lattice of HgX and the possibility of athermal transitions to liquid states. Evidently, the critical electronic temperatures of HgX are decreased in sequence with the X atom number increasing. Note that the dispersion relations of the LO phonons become relatively flat while those of the TO phonons exhibit a slight bending at the Γ point at low electronic temperatures. However, at higher electronic temperatures, the curves of both the LO phonons and TO phonons turn into a platform. From Fig. 2, we can also see that the remarkable differences of phonon spectra of HgX are the transverse acoustic phonon branches at different electronic temperatures. The phonon dispersion relationships dramatically change from $T_e = 1.30$ eV to $T_e = 1.45$ eV for HgS, from $T_e = 1.20$ eV to $T_e = 1.31$ eV for HgSe, and from $T_e = 1.10$ eV to $T_e = 1.20$ eV for HgTe accompanied by the appearing athermal phase transitions. As the electronic temperature increases, the optic mode phonon frequencies can achieve certain limit values, meanwhile the TA phonon frequencies become more negative. Furthermore, other groups[17–20] have demonstrated the softening of the transverse-acoustic phonon modes for semiconductors under ultrafast intense laser irradiation.

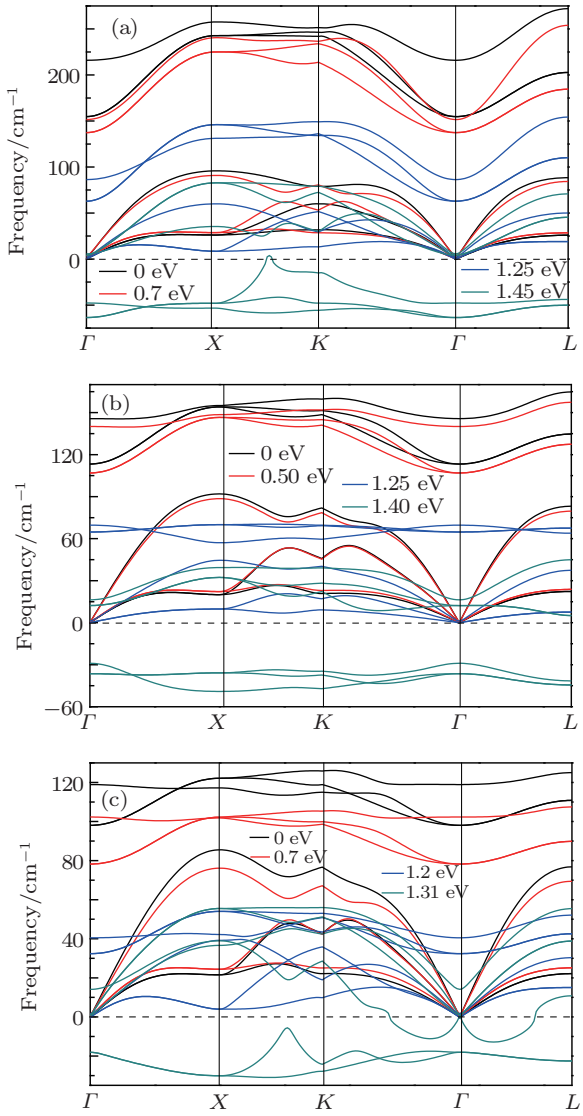


Fig. 2. (color online) Phonon spectra of (a) HgS, (b) HgSe, (c) HgTe at four different electronic temperatures.

In addition, we present TA phonon frequencies at high symmetry L point as a function of T_e in Fig. 3. Compared with a previous investigation,[41] similar conclusions can be made: the transverse acoustic phonons at the L point become soft upon intense laser excitation among all the calculated lattice vibrations. After comparing the variation tendency and values of TA phonon frequencies at the high symmetry L point

under electronic excitation, we ensure the validity of our research method. The frequencies of the two lower branches (corresponding to the transverse acoustic modes) gradually decreased as displayed in Fig. 3, which is induced by the thermal excitation of electrons. Beyond electronic temperatures of 1.35 eV for HgS, 1.20 eV for HgSe, and 1.10 eV for HgTe, the TA mode frequencies at the L point go through zero, and then the complete transverse acoustic branches gradually become more negative. Stampfli and Bennemann have demonstrated that the TA phonons of semiconductor Si become instable if more than 8% of the valence electrons are excited into the conduction band after laser irradiation.[42]

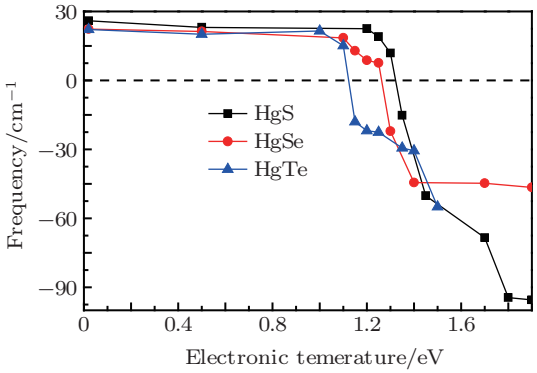


Fig. 3. (color online) The TA phonon modes of HgX at the L point as a function of the electronic temperature.

3.3. LO–TO splitting

For zinc-blende prototype II–VI semiconductors, the TO–LO phonon frequencies at the Γ point can be expressed by the following Lyddane–Sachs–Teller (LST) relation:[43] $\omega_{\rm LO}/\omega_{\rm TO} = [\varepsilon(0)/\varepsilon(\infty)]^{1/2}$, where $\varepsilon(0)$ and $\varepsilon(\infty)$ represent the static and high-frequency dielectric constants, respectively. As ionic crystals, the effective charge amount of positive and negative ions can affect the strength of the polarization electric field. The more effective charge amounts of ions attribute to the bigger divisions between $\omega_{\rm LO}$ and $\omega_{\rm TO}$.[43] Consequently, the dipoles induce the electric field and influence the LO–TO splitting degree ($\delta\omega$) which can assess the ionic strength of ionic crystals at the Γ point.[19] Seen from Table 2, our calculated values of the phonon frequencies of HgX at the high symmetry Γ point for $T_{\rm e} = 0$ eV accord well with the previous theoretical values[10,13,44] and experimental data.[10,45]

Table 2. Experimental and calculated phonon frequencies of HgX for the high symmetry point Γ in the Brillouin zone, in units of cm^{-1}.

Compounds		LO	TO
HgS	present	216	155
	calc.	230[a]	185[a]
	exp.	250[a]	175[a]
HgSe	present	146	113
	calc.	151[b]	132[b], 134[c]
	exp.	163[d]	136[d]
HgTe	present	119	98
	calc.	118[c], 128[b]	115[b]
	exp.	139[a]	116[a]

[a]Ref. [10], [b]Ref. [13], [c]Ref. [44], [d]Ref. [45].

The LO–TO splitting degrees ($\delta\omega$) of HgX (X = S, Se, Te) at the Γ point are a function of the $T_{\rm e}$ as shown in Fig. 4. At $T_{\rm e} = 0$ eV from S, Se to Te atoms, the effective charge amounts gradually decrease and thus make the LO–TO splitting degrees of HgX smaller one by one. It can be observed that the LO–TO splitting degree ($\delta\omega$) of HgS descends fast at first then slowly and finally goes to zero as $T_{\rm e}$ increases due to the electronic excitation weakening the ionic strength of HgS. As HgS has the most ionic strength, the LO–TO splitting degrees ($\delta\omega$) for semiconductor HgS are different from semimetal HgSe and HgTe. The LO–TO splitting degrees $\delta\omega$ of HgSe gradually decrease to zero while $\delta\omega$ of HgTe firstly increases then decreases and finally goes to zero due to the thermal electron excitation firstly enhancing the polarized electric field and then weakening the polarized electric field of HgTe for different charge transfers.

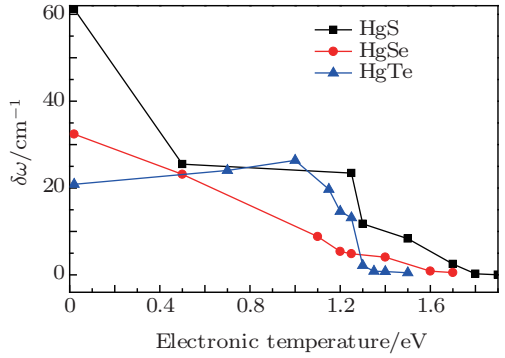


Fig. 4. (color online) The LO–TO splitting degree ($\delta\omega$) of HgX (X = S, Se, Te) at the Γ point as a function of the electronic temperature $T_{\rm e}$.

4. Conclusions

In conclusion, we have studied the electronic excitation effects of ultrafast intense laser exposure on the zinc-blende mercury chalcogenides HgX (X = S, Se, Te) at different electronic temperatures based on DFT. It is indicated that the lattice constants of HgX increase and all the phonon modes soften as the $T_{\rm e}$ is increased. The crystal lattices of HgX become more instable through the more negative TA phonon frequency due to the thermal electronic excitations. When the electronic temperature increases to 1.45 eV for HgS, 1.31 eV for HgSe, 1.20 eV for HgTe, the entire TA frequencies become negative, which gives signatures of athermal phase transitions. With the X atom number increasing, the critical electronic temperatures successively decrease. Moreover, as for semimetal HgSe and HgTe, the LO–TO splitting degrees ($\delta\omega$) are different from that of semiconductor HgS. This result can contribute to a good understanding for athermal melting processes of the femtosecond laser micromachining devices and materials.

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