Lattice dynamics for isochorically heated metals: A model study

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The electron-excitation induced bond strength variations in metals have been predicted from density-functional theory calculations and observed experimentally, while the microscopic mechanism has yet to be elucidated. Here, we present a minimal model that reproduces the phonon hardening and softening for fcc- and bcc-structured metals as a result of the electron thermal excitation. We explain why the phonon mode softens at the N point for bcc-structured metals.

I. INTRODUCTION

The effect of strong nonequilibrium condition between electrons and phonons on solid state properties has been investigated both experimentally and theoretically. It influences not only thermodynamic properties, such as the electron specific heat and density-of-states [1], but also the lattice dynamics spectra (i.e., phonon dispersion relations). Since the values of the force constants for ions are determined by the adiabatic potential that is a sum of the ion-ion repulsive and the ion-electron-ion interaction potential energies, it is possible to manipulate the lattice dynamics spectra by tuning the electron-mediated interaction potential. Based on density-functional theory (DFT) calculations, Recoules et al. have predicted that the phonon frequencies of Au increase over the entire Brillouin zone (BZ) when the electron temperature $T_e$ is increased up to several eV [2]. This is understood as a decrease in the electron-ion screening as a result of the thermal excitation of 5d-electrons located below the Fermi level by a few eV. The femtosecond pump-probe technique has confirmed the bond hardening as an increase in the melting temperature of Au [3], which paves the way for understanding the fundamental properties of warm-dense aluminum [4], copper [5], molybdenum [6], and electron gas [7].

By this argument recent studies based on DFT calculations in Ref. [8–11] is interesting; Even if $d$-electrons are absent in a system, a noticeable change in the phonon dispersion relations has been predicted when $T_e$ increases. For example, fcc-structured metals such as Al show a phonon hardening over the entire BZ, while bcc-structured metals such as Na show a phonon softening at the point N within the BZ [8]. A similar conclusion has been reached in a recent study [10], where the neutral pseudoatom model developed from DFT and molecular dynamics simulations has been used. Interestingly, Botvin et al. have shown that for both Al and Au crystals the monovacancy formation enthalpy increases with $T_e$ (i.e., the bond hardening), while its origin is different: The largest contribution to the stress is from the kinetic energy part for Al and the pseudopotential (ion-electron potential) energy part for Au [11]. Since Al and Na are a typical free-electron metal in the ground state, as well as the supporting evidence for high $T_e$ [11], it must be possible to develop a simple model to understand such a crystal structure dependence of the phonon property.

In this paper, we construct a minimal model for phonons in isochorically heated nearly free-electron metals and calculate the $T_e$-dependence of the phonon dispersion relations. The phonon hardening and softening occur in fcc- and bcc-structured metals, respectively, which are consistent with DFT based calculations [2][10]. The phonon hardening originates from a significant increase in the force constant for the first nearest neighbor (NN) sites, while the phonon softening at the N point in bcc-structured metals originates from a delicate balance between force constants for the first and second NN sites.

II. FORMULATION

To compute the phonon dispersion relations in metals, we extend the theory of the lattice dynamics for simple metals at $T_e = 0$ K [12] to the case at $T_e \neq 0$ K. We consider a simple metal that consists of ions and conducting electrons. Each ion and electron have charges $Ze$ and $-e$, respectively, where $Z$ is the valence of the ion. With a charge neutrality condition, the number of electrons is uniquely determined when that of ions is given. We assume that the total potential energy between ions separated by a distance $R$ is

$$V_{\text{tot}}(R) = v_d(R) + v_{\text{ind}}(R),$$

where $v_d$ is the direct interaction potential between ions and given by

$$v_d(R) = \frac{Z^2e^2}{4\pi\epsilon_0 R}$$

with the dielectric constant of vacuum $\epsilon_0$. $v_{\text{ind}}$ in Eq. (1) is the indirect interaction potential that is derived from the electron-mediated ion-ion interaction. This is written as (see Appendix A for the derivation)

$$v_{\text{ind}}(R) = \int_0^\infty dq C(q)\frac{\sin(qR)}{qR}$$

with the wavenumber $q$. The kernel $C(q)$ in Eq. (3) is

$$C(q) = -\left(\frac{\epsilon_0q^4}{2\pi^2e^2}\right)v_{\text{ps}}^2(q)\frac{\chi(q,T_e)}{1 + [1 - G(q)]\chi(q,T_e)}.$$
where $v_{ps}(q)$ is the Fourier component of the model pseudopotential. $\chi(q, T_e)$ is the $T_e$-dependent response function and explicitly written as

$$\chi(q, T_e) = \frac{4}{\pi k_F a_B y^2} \int_0^\infty dx \frac{x}{y} f(x, T_e) \ln \left| \frac{2 + y/x}{2 - y/x} \right|$$

(5)

with the Fermi wavenumber $k_F$, the Bohr radius $a_B$, $x = k/k_F$, $y = q/k_F$, and the Fermi-Dirac distribution function

$$f(x, T_e) = \left[ e^{(e_F x^2 - \mu)/(k_B T_e)} \right]^{-1}$$

(6)

with the Fermi energy $e_F$ at $T_e = 0$ K, the chemical potential $\mu$, and the Boltzmann constant $k_B$. When $T_e = 0$ K, Eq. (5) can be reduced to the Hartree formula [12]

$$\chi(q, 0) = \frac{4}{\pi k_F a_B y^2} \left( \frac{1}{2} + \frac{4 - y^2}{8 y} \ln \left| \frac{2 + y}{2 - y} \right| \right).$$

(7)

In our model, the effect of $T_e$ (i.e., electron occupation) on the phonon dispersion relations is entered into $\chi(q, T_e)$. Finally, $G(q)$ in Eq. (8) accounts for the effects of exchange and correlation. The model functions $v_{ps}(q)$ and $G(q)$ with material parameters will be given later.

The phonon dispersion relations for the central potential of Eq. (1) are calculated by a diagonalization of the dynamical matrix [13]

$$\mathcal{D}(q) = \sum_{l} \sin^2 \left( \frac{q \cdot R_l}{2} \right) \left[ A1 + B \hat{R}_l \hat{R}_l \right],$$

(8)

where $q$ is the wavevector of phonons, $R_l = (R_{lx}, R_{ly}, R_{lz})$ is the $l$th ion position, $1$ is the $3 \times 3$ unit matrix, and $\hat{R}_l \hat{R}_l$ is the dyadic formed from the unit vectors $\hat{R}_l = R_l/|R_l|$. $A$ and $B$ are the force constants defined as

$$A = 2 \left[ \frac{dV_{tot}(R)}{dR} \right]_{R=R_l},$$

(9)

$$B = 2 \left[ \frac{d^2V_{tot}(R)}{dR^2} \right]_{R=R_l} - \left[ \frac{1}{R_l} \frac{dV_{tot}(R)}{dR} \right]_{R=R_l},$$

(10)

where the derivatives of $V_{tot}$ are evaluated at $R_l = |R_l|$. For later use, we define $A_p$ and $B_p$ as the force constant of Eqs. (9) and (10) for the $p$th NN ions. The phonon frequencies are given by $\omega = \sqrt{\lambda/M_{ion}}$ with the ion mass $M_{ion}$ and three eigenvalues $\lambda$ of Eq. (5).

### III. RESULTS AND DISCUSSION

We study the phonon properties of Al ($Z = 3$) and Na ($Z = 1$) that show a fcc and bcc structure in the ground state, respectively. The lattice constant is $a_{lat} = 4.049$ Å for Al and 4.225 Å for Na. The Wigner-Seitz radius is $r_s = 2.07$ for Al and 3.93 for Na (in units of Bohr radius $a_B$). The Fermi energy is then calculated to be 11.65 eV for Al and 3.24 eV for Na. For the model potential, we use the Ashcroft pseudopotential

$$v_{ps}(q) = -\frac{Ze^2}{\alpha q^2} \cos(q r_c),$$

(11)

where $r_c$ is the cutoff radius, which is set to be 0.5911 Å for Al and 0.8784 Å for Na [14]. For the correction $G(q)$ for exchange and correlation energies, we use the Hubbard-type function

$$G(q) = \frac{aq^2}{q^2 + b},$$

(12)

where the parameters of $a$ and $b$ are determined from an analytical formula given in Ref. [15]. We have confirmed that the same conclusion (phonon hardening and softening with $T_e$) holds when $G(q)$ is set to be zero. We have also performed other bcc-structured crystals (Li, K, Rb, and Cs) and confirmed that the trend of their results is similar to that of Na shown below.

#### A. fcc-structured Al

Figure 1(a) shows the phonon dispersion relations of Al for $k_B T_e = 0.025, 2.0,$ and $4.0$ eV. A significant increase in the phonon energies is observed at $k_B T_e = 4.0$ eV, which is consistent with the DFT results in Ref. [9, 10]. To understand the phonon hardening driven by an electronic excitation, we show $T_e$-dependence of $A_p$ and $B_p$ ($p = 1, 2, 3,$ and 4) in Fig. 1(b) and (c), respectively. The magnitude of $B_1$ starts to increase from $T_e \approx 2 eV$, while that of $B_p$ for $p \geq 2$ converges to zero, and $A_1$ decreases negatively. These changes are caused by the $T_e$-dependence of $V_{tot}(R)$ in Eq. (1), shown in Fig. 1(d). When $k_B T_e = 0.025$ eV, $V_{tot}(R)$ shows a Friedel oscillation that originates from the presence of the Fermi surface. As $T_e$ increases, the oscillating amplitude becomes weak and thus the value of $V_{tot}$ for $R/a_{lat} > 1$ becomes negligibly small, which lead to a significant decrease in $B_p$ for $p \geq 2$. In addition, $V_{tot}$ becomes more repulsive at $p = 1$ sites since $v_d > |v_{ind}|$. This also leads to an increase in $|A_1|$ and $B_1$ that are defined as Eqs. (11) and (10), respectively.

As is clear from Figs. 1(b) and 1(c), the lattice dynamics up to $k_B T_e = 4.0$ eV is almost regulated by $B_1$ only because $B_1 \gg |B_p| (p = 2, 3, $ and 4) and $B_1 \gg |A_p|$. A simple analysis, where the contribution from $A_p$ and $B_p$ with $p \geq 2$ is ignored, enables us to understand the phonon hardening phenomena observed above. For example, we focus on the phonon frequency at the X point, at which the phonon frequencies are given by

$$\omega_{1,2} = \sqrt{\frac{8A_1 + 2B_1}{M_{ion}}}, \quad \omega_3 = \sqrt{\frac{8A_1 + 4B_1}{M_{ion}}},$$

(13)

where $\omega_1$ and $\omega_2$ are the doubly degenerate TA phonon frequencies and $\omega_3$ is the LA phonon frequency. From
negligible. This is because the profile of frequency at the N point decreases with higher frequency region, while the lowest phonon frequency is indicated up to $p=1$.

From Eq. (8), the frequencies at the N point are written as

$$\omega_1 = \sqrt{4(A_1 + A_2) + 2B_2},$$

$$\omega_2 = \sqrt{4(A_1 + A_2) + \frac{8}{3}B_1},$$

$$\omega_3 = \sqrt{4(A_1 + A_2) + \frac{8}{3}B_1 + 2B_2},$$

where $A_p$ and $B_p$ up to $p=2$ are considered because the use of two parameters $A_1(<0)$ and $B_1$ only is not enough to obtain a dynamically stable structure at $T_c = 0$ K. We emphasize that the expression for the lowest frequency $\omega_1$ in Eq. (14) does not include the largest force constant $B_1$.

**FIG. 1:** (a) The phonon dispersion relations of fcc-structured Al along symmetry lines for $k_B T_c =$0.025 (black), 2.0 (blue), and 4.0 (red) eV. $T_c$-dependence of the force constants (b) $A_p$ and (c) $B_p$ in units of eV/$\text{Å}^2$. (d) The total potential $V_{\text{tot}}$ defined as Eq. (4). The vertical dotted lines indicate the interatomic distance up to $p = 4$.

**FIG. 2:** Same as Fig. 1 but for Na. The phonon dispersion relations and $V_{\text{tot}}$ are calculated for $k_B T_c =$0.025, 1.0, and 2.0 eV. The lower frequency phonon at the N point decreases with $T_c$ enclosed by a rounded rectangle. The interatomic distance is indicated up to $p = 3$.

Eq. (13), it is obvious that the increase in the phonon energy in Fig. 1(a) is directly related to the increase in $B_1$.

**B. bcc-structured Na**

We next investigate the phonon properties of Na. Figures 2(a), 2(b) and 2(c), and 2(d) show the phonon dispersion relations (for $k_B T_c =$0.025, 1.0, and 2.0 eV), $A_p$ and $B_p$ ($p = 1, 2, 3$), and $V_{\text{tot}}(R)$, respectively. As shown in Fig. 2(a), the phonon energy increases slightly for higher frequency region, while the lowest phonon frequency at the N point decreases with $T_c$. Similar softening behavior and an imaginary frequency at the N point have been reported in Ref. [9, 10]. For lower $T_c$, the lattice dynamics is almost regulated by $B_1$ again. However, the changes in $A_1$, $A_2$, and $B_2$ in response to $T_c$ cannot be negligible. This is because the profile of $V_{\text{tot}}$ is different from that in Al (Fig. 1(d)): The Friedel oscillation is not clearly observed, since the value of $k_F$ of Na is smaller than that of Al.

To understand the phonon softening at the N point, we derive analytical expressions for the phonon frequency. From Eq. (8), the frequencies at the N point are written as

$$\omega_1 = \sqrt{4(A_1 + A_2) + 2B_2},$$

$$\omega_2 = \sqrt{4(A_1 + A_2) + \frac{8}{3}B_1},$$

$$\omega_3 = \sqrt{4(A_1 + A_2) + \frac{8}{3}B_1 + 2B_2},$$
The magnitude of $\omega_1$ is determined by a delicate balance between $A_1$, $A_2$, and $B_2$. Although $B_2$ increases with $T_e$, the amount of the increase is completely cancelled out by the decrease in $A_1$ and $A_2$. The latter contributions are large enough to cause $\omega_1$ to decrease with $T_e$.

The polarization vectors $e_1$, $e_2$, and $e_3$ corresponding to $\omega_1$, $\omega_2$, and $\omega_3$ in Eqs. (13)-(16), respectively, are written as

$$e_1 = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 \\ 1 \\ -1 \end{pmatrix}, \quad e_2 = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \quad e_3 = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 \\ 1 \\ 1 \end{pmatrix}.$$ (17)

The vectors $e_i$ ($i = 1$ and 2) and $e_3$ are perpendicular to and parallel to the N point wavevector $q = (0, 1/2, 1/2)$ in units of $2\pi/a_{\text{lat}}$, respectively, which will be helpful to identify the soft mode experimentally.

It should be noted that also for simple cubic structured lattices $B_1$ is not entered into the expression of the phonon frequencies at points X and M, implying an appearance of the phonon softening with $T_e$. We thus speculate that the larger the NN coordination number $Z_C$, the stronger the bond strength against the electron excitation. In fact, it has been shown that an electronic excitation can lead to a phonon softening in Bi with $Z_C = 6$ [14, 16] and Si with $Z_C = 4$ [2, 9], while it leads to a phonon hardening in hexagonal closed-packed structure of Mg with $Z_C = 12$ [9].

IV. SUMMARY

We have studied the effect of the electron temperature on the phonon dispersion relations for fcc- and bcc-structured metals within a model pseudopotential approach. The phonon hardening and softening in simple metals are discussed in terms of the force constants and the adiabatic potential as a function of the electron temperature. The phonon hardening originates from a significant increase in the force constant for the first NN sites, while the phonon softening at the N point in bcc-structured metals originates from a delicate balance between force constants for the first and second NN sites.

The formulation of the present work can be extended to metals with $d$-electrons in a sense of the valence $Z$ change as discussed in the study of warm-dense gold [17], while parametrizing the relationship between $Z$ and $T_e$ is necessary.

Appendix A: Effective ion-ion interaction

We outline the derivation of the ion-electron-ion interaction potential [12, 18] for the case of finite $T_e$ by considering the effect of the electron-ion interaction to the total electron energy of the free-electron system.

The Schrödinger equation for the free-electron in a volume $\Omega$ is given by

$$H_0 |k\rangle = \varepsilon(k) |k\rangle,$$ (A1)

where $\varepsilon(k) = h^2 k^2/(2m)$ is the free-electron energy and $|k\rangle = e^{ik \cdot r}/\sqrt{\Omega} |k\rangle$ is the electron eigenstate. $h$ is the Planck constant, $m$ is the bare electron mass $m$, and $k$ is the wavevector. The Schrödinger equation for the electron in a crystal with the number of the unit cell $N_c$ is given as

$$(H_0 + W) |\Psi\rangle = E |\Psi\rangle,$$ (A2)

where $W$ is a weak periodic potential, to which the electron-electron (e-e) interaction is also included, and written as

$$W(r) = \sum_j w(r - R_j)$$ (A3)

with $w(r - R_j)$ being the potential energy of the lattice sites $R_j$. Within the perturbation theory, the electron wavefunction is written as

$$|\Psi\rangle = |k\rangle + \sum_{q \neq 0} \frac{(k + q) W(k)}{\varepsilon(k) - \varepsilon(k + q)} |k + q\rangle,$$ (A4)

while the electron eigenenergy is written as

$$E(k) = \varepsilon(k) + \langle k | W(k) | k \rangle + \sum_{q \neq 0} \frac{(k + q) W(k) \langle k | W(k + q) | k \rangle}{\varepsilon(k) - \varepsilon(k + q)}.$$ (A5)

The total energy per a unit cell is then given as

$$E_{\text{tot}} = \frac{2}{N_c} \sum_k f(k; T_e) E(k) + E_{\text{dc}},$$ (A6)

where $f(k; T_e)$ is the Fermi-Dirac distribution function for the energy $E(k)$ and the temperature $T_e$, which is introduced in this work to account for the electron excitation. The prefactor 2 in the first term in Eq. (A6) comes from spin degeneracy. The second term $E_{\text{dc}}$ accounts for the double-counting of the e-e interaction energy. As usual, we decompose $E_{\text{tot}}$ into

$$E_{\text{tot}} = E_{\text{free}} + E_{\text{bs}},$$ (A7)

where $E_{\text{free}}$ is the free-electron energy that is independent of the ion position, while $E_{\text{bs}}$ is the bandstructure energy that depends on the geometrical configuration of the ions. $E_{\text{bs}}$ comes from both the last term of Eq. (A6) and $E_{\text{dc}}$, and can be expressed as

$$E_{\text{bs}} = \sum_{q \neq 0} S^*(q) S(q) F(q)$$ (A8)

with the structure factor

$$S(q) = \frac{1}{N_c} \sum_j e^{-ik \cdot R_j}.$$ (A9)
and the energy-wavenumber characteristic $F(q)$. By using Eq. (A9), one obtains

$$E_{bs} = \frac{1}{N_c^2} \sum_{q \neq 0} \sum_{i} \sum_{j} e^{i q \cdot (R_i - R_j)} F(q)$$

$$= \frac{1}{2N_c} \sum_{i \neq j} v_{ind}(|R_i - R_j|) + \frac{1}{N_c} \sum_{q \neq 0} F(q),$$

(A10)

where $v_{ind}(|R_i - R_j|)$ is the indirect interaction potential between ions at $R_i$ and $R_j$ and expressed as

$$v_{ind}(|R_i|) = \frac{2}{N_c} \sum_{q \neq 0} e^{i q \cdot R_i} F(q)$$

$$= \frac{\Omega}{\pi^2} \int_0^\infty dq q^2 \sin(qR) F(q)$$

(A11)

with $\Omega = \Omega/N_c$. We assumed that $F$ depends on the magnitude of $q$ only. When the contributions from the Hartree, exchange, and correlation interactions are included to $W$, $F(q)$ can be written as

$$F(q) = -\frac{\epsilon_0 q^2}{2e^2 \Omega a} \frac{\chi(q, T_e) v_{pa}(q)}{1 + [1 - G(q)] \chi(q, T_e)}.$$  

(A12)

By substituting Eq. (A12) into Eq. (A11), we obtain the expressions in Eqs. (9) and (10).

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