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Ab initio calculation of phonon frequencies of Al

Pui K. Lam and Marvin L. Cohen
Department of Physics, University of California, Berkeley, California 94720
and Materials and Molecular Research Division, Lawrence Berkeley Laboratory,
Berkeley, California 94720
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We report a first-principles calculation of the phonon frequencies and mode-Grüneisen parameters of Al with the use of the atomic number and the atomic mass as the only inputs. The phonon frequencies are determined by calculating the total energy of the perfect crystal and that of the crystal distorted by a frozen-phonon mode. Calculated results agree very well with experimental values. The contributions to the restoring force for various phonon modes are analyzed and discussed.

I. INTRODUCTION

One approach to calculating phonon spectra is based on the Born—von Kármán[1] force-constant model. In this semiempirical approach, the force constants are determined by fitting to some measured values of the phonon frequencies. Because of the long-range forces in metals, an adequate description of the phonon frequencies using force constants requires interactions involving at least eight or nine neighbors.[2] It is often difficult to extract meaningful physical trends from such a large parameter space.

Another possible approach is the frozen-phonon method,[3] where one calculates the energy caused by a phonon distortion. Within the harmonic approximation the phonon frequency is linearly proportional to the square root of the distortion energy. Applications of this approach to metals have been mostly based on a nearly-free-electron model (NFM).[3] The electron-ion (*e*-*i*) interaction is represented by a weak pseudopotential, the electron wave functions are calculated using perturbation theory to second order in the *e*-*i* interaction, and the effect of electron screening is represented by some model dielectric functions.[3,4] While the NFM method has been quite successful, the calculated phonon frequencies are often dependent on the model pseudopotential and the dielectric function used.[4]

In this paper we report a successful calculation of the phonon frequencies and mode-Grüneisen parameters of Al using the frozen-phonon approach but without involving perturbation or linear screening. The electron wave functions are calculated self-consistently within the density-functional (DF) formalism,[5] and *ab initio* pseudopotentials are used to represent the *e*-*i* interactions. This approach has been applied recently by Yin and Cohen[6] to study the phonon spectrum of Si, and excellent agreement with experimental measurements was obtained.

In the NFM the various contributions to the phonon frequency are grouped together into a single term, the band-structure term.[3] In the present calculations the various contributions are calculated explicitly; hence an analysis of the microscopic restoring forces for the phonon modes is possible in principle.

This paper is organized as follows: In Sec. II the frozen-phonon formalism is presented, in Sec. III the calculational procedure is described, in Sec. IV the results are discussed and compared with the experimental values, and in Sec. V the microscopic contributions to the phonon frequencies are analyzed.

II. GENERAL FORMALISM

For simplicity consider a crystal with only one atom per lattice site; the atomic positions of a phonon mode are given in the harmonic approximation by

$$\vec{R}_i = \vec{R}_i^0 + \vec{u}^0 \cos(\vec{q}\cdot\vec{R}_i^0)\cos\omega_q t \ , \tag{1}$$

where $\{R_i^0\}$ are the equilibrium atomic positions. The kinetic energy per atom T and the potential energy per atom V for this phonon mode are given by

$$T=\frac{1}{N}\sum_i \tfrac{1}{2}M\left|\frac{d\vec{R}_i}{dt}\right|^2 \tag{2}$$

$$=\tfrac{1}{2}M\omega_q^2\left[\frac{1}{N}\,|\vec{u}^0|^2\sum_i \cos^2(\vec{q}\cdot\vec{R}_i^0)\right]\sin^2\omega_q t \tag{3}$$

and

$$V=\frac{1}{N}\sum_i \tfrac{1}{2}M\omega_q^2\,|\vec{R}_i-\vec{R}_i^0|^2 \tag{4}$$

$$=\tfrac{1}{2}M\omega_q^2\left[\frac{1}{N}\,|\vec{u}^0|^2\sum_i \cos^2(\vec{q}\cdot\vec{R}_i^0)\right]\cos^2\omega_q t\ , \tag{5}$$

where M is the ion mass and N is the total number of atoms. The phonon energy per atom E_{ph} is the sum of T and V and it is time independent. In particular, $E_{\text{ph}}=V(t=0)$,

$$E_{\text{ph}}=\tfrac{1}{2}M\omega_q^2\left[\frac{1}{N}\,|\vec{u}^0|^2\sum_i \cos^2(\vec{q}\cdot\vec{R}_i^0)\right] \tag{6}$$

$$=\tfrac{1}{2}M\omega_q^2\langle u^2\rangle\ , \tag{7}$$

where the mean-square distortion u^2 is defined as

$$\langle u^2\rangle=\frac{1}{N}\,|\vec{u}^0|^2\sum_i \cos^2(\vec{q}\cdot\vec{R}_i^0)\ . \tag{8}$$

For a $\vec{q}$ at the zone boundary, that is, $\vec{q}=\vec{G}/2$,

$$\langle\vec{u}^2\rangle=|\vec{u}^0|^2\ , \tag{9}$$

and for an arbitrary q,

$$\langle\vec{u}^2\rangle=|\vec{u}^0|^2\ . \tag{10}$$

Equation (7) is the starting point for the frozen-phonon approach. If E_{ph} is determined by calculating the total energy of a perfect crystal and a crystal distorted by a frozen-lattice wave,

$$\vec{R}_i=\vec{R}_i^0+\vec{u}^0\cos(\vec{q}\cdot\vec{R}_i^0)\ , \tag{11}$$

then Eq. (7) is used to obtain the phonon frequency.

Implicitly assumed in this approach is the Born-Oppenheimer (adiabatic) approximation which states that the electron wave functions adjust quickly to any lattice distortion. A successful calculation of the phonon frequencies using this approach is, therefore, also a confirmation of the validity of the Born-Oppenheimer approximation.

III. CALCULATIONAL PROCEDURES

The calculation of the electronic wave functions of a perfect crystal is facilitated by the periodic properties of the crystal. For an arbitrary phonon mode, such periodicity is destroyed. However, for phonon wave vector $\vec{q}$, which is commensurate with the undistorted lattice, that is, $n\vec{q}=\vec{G}$, where n is an integer and $\vec{G}$ is a reciprocal-lattice vector of the undistorted crystal, the distorted crystal is again periodic but with a larger real-space unit cell. For these commensurate $\vec{q}$'s, the calculation proceeds in analogy with that of a perfect-crystal calculation. In this paper we use this approach to examine the phonon mode at $q=(1,0,0)2\pi/a$, $(\frac{1}{2},\frac{1}{2},\frac{1}{2})2\pi/a$, and $(\frac{1}{2},0,0)2\pi/a$.

The total energy per atom is represented by the DF expression[5] with the Wigner interpolation formula for the correlation energy[7] and is calculated in the momentum-space representation.[8] The nonlocal pseudopotentials for Al are determined using the method developed by Hamann, Schlüter, and Chiang.[9] The same potentials were used recently by the authors to calculate the static structural properties of Al,[10] and excellent agreement with experiment was obtained.

The crystal wave functions are expanded in plane waves with energies up to $E_{\text{PW}}=10$ Ry. An even grid of k points is sampled,

$$\vec{k}=\frac{n_i+0.5}{N_i}\vec{G}_1+\frac{n_2+0.5}{N_2}\vec{G}_2+\frac{n_3+0.5}{N_3}\vec{G}_3\ , \tag{12}$$

where $\vec{G}_1$, $\vec{G}_2$, and $\vec{G}_3$ are the three primitive reciprocal-lattice vectors; N_1, N_2, and N_3 are the numbers of divisions along $\vec{G}_1$, $\vec{G}_2$, and $\vec{G}_3$, respectively, and the ranges of n_1, n_2, and n_3 are

$$0\le n_1\le N_1-1\ , \tag{13a}$$

$$0\le n_2\le N_2-1\ , \tag{13b}$$

$$0\le n_3\le N_3-1\ . \tag{13c}$$

The even grid is centered at $[0.5/N_1, 0.5/N_2, 0.5/N_3]$ instead of the origin to avoid sampling of high-symmetry k point; [ ] denotes vectors in the basis of $\vec{G}_1$, $\vec{G}_2$, and $\vec{G}_3$. An even grid is chosen because it gives an unprejudiced representation of the Fermi surface.

The calculations are iterated until the total energy is self-consistent to better than 10^{-6} Ry. The iteration procedure is described elsewhere.[11] For

TABLE I. Convergence test. The phonon amplitudes u are in units of the lattice constant and the phonon frequencies in 10^{13} rad/sec. The k-point sampling is denoted by $N_1 \times N_2 \times N_3$.

	$E_{\mathrm{PW}}=10$ Ry				$E_{\mathrm{PW}}=12$ Ry			
	E_T $u=0$	E_T $u=0.01$	E_{ph} (Ry)	ω_{ph} $(\times 10^{13})$	E_T $u=0$	T_T $u=0.01$	E_{ph} (Ry)	ω_{ph} $(\times 10^{13})$
$L(100)$								
k points								
$6\times6\times6$	−4.197092	−4.196441	+0.000651	6.27	−4.200560	−4.199937	+0.000623	6.13
$8\times6\times6$	−4.198212	−4.197569	+0.000643	6.23	−4.201595	−4.200977	+0.000618	6.11
$T(100)$								
k points								
$6\times4\times4$	−4.205422	−4.205203	+0.000219	3.63	−4.209015	−4.208808	+0.000207	3.54
$6\times6\times6$	−4.197092	−4.196853	+0.000239	3.79	−4.200561	−4.200332	+0.000229	3.72

each phonon mode the total energies of the undistorted and distorted crystal are calculated with the same E_{PW} and k points to insure good convergence. The convergence of calculated quantities with respect to E_{PW} and k points will be discussed in the next section. For the mode-Grüneisen parameter γ_G, the volume is change by $\pm 3\%$ and γ_G is given by $-d\ln\omega/d\ln V$. The equilibrium lattice constant a_0 is taken to be 7.586015 a.u. or 4.013 Å, and the ion mass which enters into Eq. (7) is taken to be 26.985 atomic mass units or 4.4796×10^{-23} g.

IV. RESULTS

In this section, we will consider the following aspects of the calculation:

(1) convergence of the calculated quantities,
(2) validity of the harmonic approximation, and
(3) comparison with experimental values.

The convergence of the calculations is tested by increasing E_{PW} and the number of k points sampled. The convergence test for the longitudinal and transverse modes at $q=(100)2\pi/a$, $L(100)$, and $T(100)$ are illustrated in Table I. The phonon amplitude u is given in units of the lattice constant. E_{PW} is increased across the table and the number of k points increases going down the table. The k-point sampling is denoted by $N_1\times N_2\times N_3$ [Eq. (12)]. Note that although the individual total energies are converged only to 10^{-3} Ry, the energy difference E_{ph} is converged to $\sim10^{-5}$ Ry. We estimate that the phonon frequencies are converged to within a few percent.

The phonon frequencies are also calculated for several phonon amplitudes to examine the degree of anharmonicity (see Table II). It appears that the harmonic approximation is quite good since the variation in ω_{ph} is $\sim1\%$ for the different assumed amplitudes.

The calculated phonon frequencies and mode-Grüneisen parameters are shown in Table III along with the experimental phonon frequencies.[12] The authors are not aware of any experimental values for the mode-Grüieisen parameters; however, an average $\gamma_G=2.2$ is obtained from thermal expansion data.[13]

V. ANALYSIS

The contributions from various energy components to the phonon frequencies and their

TABLE II. Contribution of anharmonicity to the phonon frequency calculations. The units are same as in Table I. $\langle\omega\rangle$ is the average value of ω for the three phonon amplitudes.

	$u=0.005$	$u=0.01$	$u=0.02$	
$L(100)$	$\omega=6.26$	6.27	6.34	$\langle\omega\rangle=6.29\pm1\%$
$T(100)$	$\omega=3.61$	3.63	3.66	$\langle\omega\rangle=3.63\pm1\%$

TABLE III. Comparison between calculational and experimental results for phonon frequencies (10^{13} rad/sec) and mode-Grüneisen parameters.

	$L(100)$	$T(100)$	$L(\frac{1}{2}\frac{1}{2}\frac{1}{2})$	$T(\frac{1}{2}\frac{1}{2}\frac{1}{2})$	$L(\frac{1}{2}00)$	$T(\frac{1}{2}00)$
ω (10^{13} rad/sec)						
theory	6.11	3.63	6.21	2.74	4.56	2.86
experiment[a]	6.08	3.65	6.06	2.63	4.45	2.60
difference	1%	1%	2.5%	4%	2%	10%
γ_G mode-Grüneisen parameter						
theory	1.71	2.83	2.10	2.37	1.65	1.70
experiment[b]	$\langle\gamma\rangle=2.2$					

[a] Reference 12.

[b] Reference 13.

volume dependence are examined in this section. Since the energy components depend on the magnitude of the phonon amplitude, it is best to analyze ω^2, which is a normalized quantity,

$$\omega^2=\frac{E_{\mathrm{ph}}}{\frac{1}{2}M\langle u^2\rangle}\ . \tag{14}$$

The quantity ω^2 can be broken down into the following contributions:

$$\omega^2=\omega_{\mathrm{kin}}^2+\omega_{e\text{-}i}^2+\omega_{e\text{-}e}^2+\omega_{\mathrm{xc}}^2+\omega_{i\text{-}i}^2\ . \tag{15}$$

These quantities represent the electron kinetic energy, *e-i* interaction, *e-e* Coulomb repulsion, electron exchange correlation, and ion-ion Coulomb interaction. The divergences in the *e-i*, *e-e*, and the *i-i* terms are properly taken out.[8] It is also customary to separate ω^2 into

$$\omega^2=\omega_e^2+\omega_{i\text{-}i}^2\ , \tag{16}$$

where ω_e^2 can be thought of as the electronic screening to the ion distortion. One can also separate ω^2 into a kinetic and a potential contribution,

$$\omega^2=\omega_{\mathrm{kin}}^2+\omega_{\mathrm{pot}}^2\ . \tag{17}$$

The contributions from all these terms are shown in Tables IV and V for two different volumes. The units are in $(10^{13}\ \text{rad/sec})^2$, and relative contributions (i.e., ω_i^2/ω^2, $i=$kin, *e-i*, etc.) are shown in parenthesis. We will examine these contributions by term

(1) ω_{kin}^2. The electron kinetic energy (KE) gives a positive contribution to the phonon frequency. This can be understood very simply in the density-functional formalism. The KE is given by

$$E_{\mathrm{kin}}=C_0\int\rho^{5/3}d^3r+C_1\int\frac{|\nabla\rho|^2}{\rho}d^3r+\cdots\ . \tag{18}$$

C_0 and C_1 are positive. In a metallic close-packed structure the electron density is reasonably uniform compared to covalent and ionic solids. Any distortion will create oscillations in the electronic density, and hence increase the KE through the gradient term. Actually, the increase in KE is also manifest in the first term. Because the exponent (5/3) is greater than unity, the increase in KE in the high-density region is more than the decrease in the low-density region. Quantitatively, the phonon distortion causes some regions to have a higher density than the average density, $\rho_0+\Delta\rho$, and some regions to have a lower density than the average density, $\rho_0-\Delta\rho$. The kinetic-energy increase caused by the distortion given by the first term in Eq. (18) is

$$\Delta E_{\mathrm{kin}}=\tfrac{1}{2}[C_0(\rho_0+\Delta\rho)^{5/3}+C_0(\rho_0-\Delta\rho)^{5/3}]-C_0\rho_0^{5/3} \tag{19}$$

$$=+\tfrac{1}{2}C_0\tfrac{5}{3}\tfrac{2}{3}\rho_0^{5/3}\left[\frac{\Delta\rho}{\rho_0}\right]^2+O\left[\frac{\Delta\rho}{\rho_0}\right]^4+\cdots\ . \tag{20}$$

If the exponent in the first term of Eq. (18) were less than unity, then the coefficient of $(\Delta\rho/\rho_0)^2$ in Eq. (20) would be negative. The above argument applies only to structures with approximately uniform density such as Al. For open structures such as Si, the phonon distortion could cause the density to be more uniform giving a negative contribution, for example, the TA mode at $(100)2\pi/a$ of Si.[14]

TABLE IV. Various contributions to the phonon frequencies at two different volumes $0.97V_0$ and $1.03V_0$, for the longitudinal mode. V_0 is the equilibrium volume. Units are in $(10^{13}\ \text{rad/sec})^2$. Relative contributions are in parentheses.

	$L(\frac{1}{2}\frac{1}{2}\frac{1}{2})$		$L(100)$		$L(\frac{1}{2}00)$	
	$0.97V_0$	$1.03V_0$	$0.97V_0$	$1.03V_0$	$0.97V_0$	$1.03V_0$
ω_{kin}^2	+124.40 (2.85)	+105.25 (3.10)	+107.03 (2.46)	+100.48 (2.84)	+54.79 (2.41)	+49.39 (2.65)
$\omega_{e\text{-}i}^2$	−599.91 (−13.72)	−565.24 (−16.63)	−422.94 (−9.73)	−406.78 (−11.49)	−587.47 (−25.83)	−551.96 (−29.58)
$\omega_{e\text{-}e}^2$	+217.89 (4.98)	+209.48 (6.16)	+137.34 (3.16)	+133.13 (3.76)	+259.09 (11.39)	+242.50 (13.00)
ω_{xc}^2	−35.89 (−0.82)	−32.28 (−0.95)	−29.52 (−0.68)	−28.31 (−0.80)	−16.95 (−0.75)	−16.08 (−0.86)
ω_e^2	−293.48 (−6.71)	−282.81 (−8.32)	−208.09 (−4.79)	−201.48 (−5.69)	−290.53 (−12.78)	−276.16 (−14.80)
$\omega_{i\text{-}i}^2$	+337.19 (7.71)	+316.79 (9.32)	+251.52 (5.79)	+236.87 (6.69)	+313.27 (13.78)	+294.82 (15.80)
ω^2	+43.71 (1.00)	+33.98 (1.00)	+43.43 (1.00)	+35.39 (1.00)	+22.74 (1.00)	+18.66 (1.00)
ω_{pot}^2	−80.69 (−1.85)	−71.27 (−2.10)	−63.60 (−1.46)	−65.09 (−1.84)	−32.05 (−1.41)	−30.73 (−1.65)
$\left\lvert\frac{\omega_e^2}{\omega_{i\text{-}i}^2}\right\rvert$	0.87	0.89	0.83	0.85	0.93	0.94
$\left\lvert\frac{\omega_{\text{kin}}^2}{\omega_{\text{pot}}^2}\right\rvert$	1.54	1.48	1.68	1.54	1.71	1.61

The kinetic-energy term is larger for the smaller volume. If we assume $\Delta\rho/\rho_0$ is independent of volume, then it is clear from Eq. (20) that this is so because ρ_0 is larger at smaller volume. Actually, $\Delta\rho/\rho_0$ is not independent of volume but decreases slightly with volume; however, the $\rho_0^{5/3}$ factor dominates causing a net increase in the kinetic-energy term. Although the absolute magnitude of this term is much larger for the longitudinal modes than the transverse modes, the relative contributions are quite similar indicating that the kinetic-energy term is just as important for the transverse modes as for the longitudinal modes.

(2) $\omega_{e\text{-}i}^2$. The *e-i* interaction contributes negatively to the restoring force because a phonon distortion tends to dimerize the atoms causing an increase in the *e-i* interaction, which is negative. The magnitude of this term increases as the volume decreases for the longitudinal modes, but it is quite insensitive to the volume change for the transverse modes. For some transverse modes the magnitudes get smaller when the volume is decreased. This term measures the degree of covalency. As the volume decreases, the degree of covalency increases for the longitudinal modes but may possibly decrease for some transverse modes.

(3) $\omega_{e\text{-}e}^2$. Dimerization causes an increase in *e-e* Coulomb repulsion; hence this term gives a positive contribution. The volume dependence of this term is similar to that of $\omega_{e\text{-}i}^2$.

(4) ω_{xc}^2. The correlation energy is a very slowly varying function of the density; thus it does not contribute significantly to the phonon frequency. This term, therefore, contributes mainly through

TABLE V. Same as Table IV except this is for the transverse mode.

	$T(\frac{1}{2}\frac{1}{2}\frac{1}{2})$		$T(100)$		$T(\frac{1}{2}00)$	
	$0.97V_0$	$1.03V_0$	$0.97V_0$	$1.03V_0$	$0.97V_0$	$1.03V_0$
$\omega^2_{\rm kin}$	+11.51 (1.33)	+10.78 (1.66)	+37.29 (2.38)	+36.54 (3.28)	+18.40 (2.05)	+16.96 (2.32)
$\omega^2_{e\text{-}i}$	−20.38 (−2.96)	−21.00 (−3.24)	−92.21 (−5.89)	−92.99 (−8.35)	−42.35 (−4.73)	−41.27 (−5.64)
$\omega^2_{e\text{-}e}$	+3.20 (0.37)	+3.40 (0.52)	+20.91 (1.34)	+21.37 (1.92)	+9.05 (1.01)	+9.33 (1.28)
$\omega^2_{\rm xc}$	−2.48 (−0.29)	−2.47 (−0.38)	−10.04 (−0.64)	−10.01 (−0.90)	−5.02 (−0.56)	−4.93 (−0.63)
ω^2_e	−8.15 (−0.95)	−9.31 (−1.43)	−44.06 (−2.82)	−45.09 (−4.05)	−19.93 (−2.22)	−19.91 (−2.72)
$\omega^2_{i\text{-}i}$	+16.78 (1.95)	+15.80 (2.43)	+59.71 (3.82)	+56.23 (5.05)	+28.90 (3.22)	+27.22 (3.72)
ω^2	+8.63 (1.00)	+6.49 (1.00)	+15.65 (1.00)	+11.14 (1.00)	+8.97 (1.00)	+7.31 (1.00)
$\omega^2_{\rm pot}$	−2.88 (−0.33)	−4.29 (−0.66)	−21.64 (−1.38)	−25.40 (−2.28)	−9.43 (−1.05)	−9.65 (−1.32)
$\left\lvert\frac{\omega^2_e}{\omega^2_{i\text{-}i}}\right\rvert$	0.49	0.59	0.74	0.80	0.69	0.73
$\left\lvert\frac{\omega^2_{\rm kin}}{\omega^2_{\rm pot}}\right\rvert$	4.03	2.52	1.72	1.44	1.95	1.76

its exchange component. Since E_x is proportional to $-\rho^{4/3}$ with a negative coefficient, it has the opposite effect of the $\rho^{5/3}$ term in the kinetic energy and is decreased by the phonon distortion. The volume dependence of this term is quite weak for both longitudinal and transverse modes because it is not strongly dependent on the density.

(5) $\omega^2_{i\text{-}i}$. This is an electrostatic energy term which has a minimum for a symmetrical arrangement of ions. Phonon distortions always increase the *i-i* term for a close-packed structure. The *i-i* interaction scales with the inverse of the lattice constant; consequently, this term increases as the volume decreases.

(6) ω^2_e. This term is negative, which indicates that the effect of the electron motion is to reduce the *i-i* interaction. The effectiveness of this screening can be measured by the absolute value of the ratio of ω^2_e to $\omega^2_{i\text{-}i}$. The screening seems to be very effective for the longitudinal modes and slightly less effective for some transverse modes (see Tables IV and V). For the longitudinal modes, ω^2_e approaches $-\omega^2_{i\text{-}i}$ as $q \to 0$ thus giving $\omega \to 0$ as $q \to 0$. As the volume decreases, the screening becomes less effective, see $|\omega^2_e/\omega^2_{i\text{-}i}|$.

(7) $\omega^2_{\rm pot}$. This term is negative indicating that the potential energy alone would be unstable against any phonon distortion. The increase in the electron kinetic energy is an essential contribution to the restoring force. The absolute value of the ratio of $\omega^2_{\rm kin}$ to $\omega^2_{\rm pot}$ is also shown in Tables IV and V. This ratio is larger for smaller volume because the kinetic-energy term becomes more dominant at small volume.

It is difficult to isolate one major contribution to the restoring force. As we can see from Tables IV and V several components have magnitudes many times larger than the net contribution. The phonon frequency is a result of many compensating effects. However, if we focus on the kinetic and potential energies only, we can state that it is the increase in the electron kinetic energy which provides the restoring force when a close-packed metal is distorted by a phonon mode. On the other hand, if we think in terms of ion-ion interactions ($\omega_{i\text{-}i}^2$) and electron screening (ω_e^2), then we would state that the restoring force is provided by the Coulomb interaction between ions which tends to restore the ions back to a symmetrical arrangement, and this restoring force is softened by the electron screening. At first sight these two pictures seem quite different, but they are related. If we do not consider the electron kinetic energy, then the electron screening would overcompensate the ion-ion interaction; the electron kinetic energy limits the electron screening, and thus gives a positive phonon frequency. Therefore, the importance of the electron kinetic energy is manifest in both pictures.

VI. CONCLUSIONS

We have demonstrated that it is possible to predict the phonon frequencies of Al with the atomic number and mass as the only input parameters and a well-defined formalism, that is, *ab initio* pseudopotentials, the density-functional method, and the frozen-phonon approach. Furthermore, this method enables us to examine the microscopic origins of the restoring vibrational forces. For a simple close-packed metal such as Al, we found that if we analyze the total energy in terms of electron kinetic energy and potential energy, it is the increase in the electron kinetic energy which contributes to the restoring force.

We expect that the present method can be applied to other solids. A systematic analysis of the restoring force for a series of materials should provide much information about vibrational forces and phonon modes.

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