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Dielectric screening and zone-center phonons in Si

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We present a microscopic calculation of the zone-center phonon frequencies of silicon. The electronic contributions to the phonons are fully incorporated into the dynamical matrix via the dielectric matrix $\epsilon_{\vec{G},\vec{G}}$. The acoustic sum rule is shown to be satisfied.

The dielectric-function approach to study the lattice dynamics of simple metals has proven to be very successful. Using pseudopotentials and the diagonal part of the nearly-free-electron dielectric matrix, the phonon spectrum of many metals containing only s and p screening electrons can now be calculated quite accurately with only minor errors resulting from uncertainties in the treatment of exchange and correlation effects.[1] The situation for semiconductors and insulators is however very different.[2,3] Although the microscopic theory[4,5] was formulated in the late 1960's, a truly first-principles phonon calculation for these materials is still lacking. The main difficulty lies in the evaluation of the full dielectric matrix for solids with localized valence electrons. In this note we present results for such a first-principles calculation for the $\vec{q}=0$ phonons in silicon.

In the microscopy theory of phonons, the dynamical matrix can be decomposed into [4,5]

$$D_{ss'}^{\alpha\beta}(\vec{q}) = D_{ss'}^{(I)\alpha\beta}(\vec{q}) + D_{ss'}^{(e)\alpha\beta}(\vec{q}), \tag{1}$$

where α, β are Cartesian components and s, s' label the atoms in the unit cell. The phonon frequencies $\omega_\lambda(\vec{q})$ and polarization vectors $\hat{e}_\lambda(\vec{q})$ are then the eigenvalues and eigenvectors of D. The first term $D^{(I)}$ contains the direct Coulomb interaction between the ion cores in the crystal and can be evaluated straightforwardly using the Ewald method. The second term $D^{(e)}$ arises from the additional contribution to the effective ion-ion interaction resulting from electronic screening. This term which contains the detailed information on the electron-phonon interaction is given by

$$D_{ss'}^{(e)\alpha\beta}(\vec{q}) = \frac{1}{(M_s M_{s'})^{1/2}} \left(C_{ss'}^{\alpha\beta}(\vec{q}) - \delta_{ss'} \sum_{s''} C_{ss''}^{\alpha\beta}(0) \right), \tag{2}$$

where M_s is the nuclear mass of the sth atom in the unit cell. In the pseudopotential formulation the force constants are defined by

$$\begin{aligned} C_{ss'}^{\alpha\beta}(\vec{q}) = \frac{\Omega_a}{4\pi e^2} \sum_{\vec{G}\vec{G}'} (\vec{q}+\vec{G})^\alpha V_s(\vec{q}+\vec{G}) e^{i\vec{G}\cdot\vec{R}_s} |\vec{q}+\vec{G}|^2 \\ \times [\epsilon_{\vec{G},\vec{G}'}^{-1}(\vec{q}) - \delta_{\vec{G}\vec{G}'}](\vec{q}+\vec{G}')^\beta \\ \times V_{s'}(\vec{q}+\vec{G}') e^{-i\vec{G}'\cdot\vec{R}_{s'}}, \end{aligned} \tag{3}$$

where $\vec{G}$ is the reciprocal-lattice vector, Ω_a is the atomic volume, $\vec{R}_s$ is the position vector of the ion cores, V_s is the bare ion pseudopotential, and $\epsilon_{\vec{G}\vec{G}'}^{-1}(\vec{q})$ is the inverse of the static part of the full dielectric matrix calculated in the pseudopotential framework.

A first-principles calculation of the phonon spectrum in this formulation thus involves the determination of the bare ion pseudopotentials and the inverse of $\epsilon_{\vec{G}\vec{G}'}(\vec{q}, \omega=0)$. In the standard random phase approximation, the expression for ϵ is[6]

$$\begin{aligned} \epsilon_{\vec{G}\vec{G}'}(\vec{q},\omega) = \delta_{\vec{G}\vec{G}'} - \frac{4\pi e^2}{\Omega|\vec{q}+\vec{G}|^2} \\ \times \sum_{\vec{k}nn'} \frac{f_0(E_{n'}(\vec{k}+\vec{q})) - f_0(E_n(\vec{k}))}{E_{n'}(\vec{k}+\vec{q}) - E_n(\vec{k}) + \hbar\omega + i\hbar\alpha} \\ \times \langle \vec{k}+\vec{q}, n' | e^{i(\vec{q}+\vec{G})\cdot\vec{r}} | \vec{k}, n \rangle \\ \times \langle \vec{k}, n | e^{-i(\vec{q}+\vec{G}')\cdot\vec{r}} | \vec{k}+\vec{q}, n' \rangle, \end{aligned} \tag{4}$$

where Ω is the crystal volume, f_0 is the Fermi-Dirac distribution function, and $|\vec{k}, n\rangle$ and $E_n(\vec{k})$ are electronic eigenstates and eigenvalues of the perfect crystal. For insulating materials, because of the localized nature of the wave functions of the valence electrons, the off-diagonal elements of $\epsilon_{\vec{G}\vec{G}'}$ are not negligible compared to the diagonal elements. Furthermore the dielectric constant tends to a finite value in the limit $\vec{q}\to 0$ resulting in an incomplete screening of the long-range Coulomb fields set up by the displaced ion core charges if only the diagonal part of ϵ is considered.

Since translational invariance required that $\lim_{\vec{q}\to 0} \omega(\vec{q}) \to 0$ for all acoustical modes, one can derive the so-called acoustical sum rule[5]

$$\lim_{\vec{q}\to 0} \sum_{s,\vec{G}\neq 0} \epsilon^{-1}(\vec{q},\vec{q}+\vec{G})\,|\vec{q}|\,(\vec{q}+\vec{G})^{\beta}\, V_s(\vec{q}+\vec{G})e^{-i\vec{G}\cdot\vec{R}_s}$$

$$=\lim_{\vec{q}\to 0} -\sum_{s} \epsilon^{-1}(\vec{q},\vec{q})\,|\vec{q}|\,\vec{q}^{\beta} V_s(\vec{q}), \quad (5)$$

which provides a partial relation between the matrix elements of ϵ^{-1}. In previous microscopic calculations[7-10] this sum rule has been used extensively to set constraints on the otherwise uncertain ϵ^{-1} and V_s.

In the present calculation for the zone-center phonon frequencies, we have made use of the dielectric matrix elements $\epsilon_{\vec{G}\vec{G}'}(\vec{q}_x\to 0,\omega)$ calculated by Louie, Chelikowsky, and Cohen[11] in their analysis of the optical spectrum of Si. A 59 × 59 matrix, containing $\vec{G}$ vectors through the set (222), was calculated using Eq. (4) and wave functions and energies from an accurate empirical pseudopotential band calculation. The effect of electron-hole interaction was however not included in these matrix elements. A recent study by Takeshima[12] indicated that the consequence of such an interaction on the $\vec{q}$-dependent dielectric function of semiconductors is to enhance the polarizability by a relatively constant factor and thus produce a static dielectric constant closer to the measured values. We, therefore, adopt the following rather simple model to include the effect of electron-hole interaction. We set

$$\epsilon_{\vec{G}\vec{G}'}(\vec{q}) = \lambda[\epsilon^{\mathrm{cal}}_{\vec{G}\vec{G}'}(\vec{q}) - \delta_{\vec{G}\vec{G}'}] + \delta_{\vec{G}\vec{G}'}, \quad (6)$$

with λ determined by the condition that the static dielectric constant

$$\epsilon_{\mathrm{stat}} = \lim_{\vec{q}\to 0} \frac{1}{\epsilon^{-1}_{\vec{0}\vec{0}}(\vec{q})}$$

to be equal to the experimentally measured value. Following this procedure we obtained $\lambda = 1.3$. For the Si-ion pseudopotential we have used a local approximation of a Abarenkov-Heine atomic model potential which can be expressed in the following four-parameter form:

$$V(q) = (a_1/q^2)[\cos(a_2 q) + a_3]e^{a_4 q^4}, \quad (7)$$

with $a_1 = -0.57315$, $a_2 = 0.79065$, $a_3 = -0.35201$, and $a_4 = -0.01807$. The potential is normalized to an atomic volume of 137.6 (a.u.)^3 with units in Ry if q is measured in a.u. This ion pseudopotential has been shown to yield successful results in a number of self-consistent bulk, surface, and impurity calculations involving Si.[13]

The calculated results are presented in Table I. We have examined the separate influence of the various parts of the dielectric matrix on the phonon frequencies. The first row in Table I was obtained by setting ϵ equal to the identity matrix. These results therefore correspond to those of Si^{4+} bare ions in a diamond structure with a background of a nonresponding electron sea. As expected, the transverse-acoustical (TA) modes have zero frequency. Also, because of the lack of screening, the frequency for the longitudinal-acoustical (LA) mode is just given by the ion plasma frequency

$$\Omega_p = (4\pi e^2 z^2/\Omega_a M)^{1/2},$$

and the values for the optical modes are all $\Omega_p/\sqrt{3}$. We obtained the results in the second row when only the diagonal part of the dielectric matrix was used. The LA phonon frequency is now reduced by screening to a value of $\Omega_p[\epsilon^{-1}_{00}(\vec{q}=0)]^{1/2}$ and the optical phonon frequencies are also reduced but in a more subtle way involving the higher components of $\epsilon^{-1}_{\vec{G}\vec{G}}(\vec{q}=0)$. Finally, the results for the full screening matrix are given in the third row and the experimental values[14] are given in the fourth row.

TABLE I. Phonon frequencies for Si at $\vec{q}=0$ in units of 10^{13} Hz. Experimental values are from Ref. 14.

	TA	LA	LO,TO
$\epsilon = \delta_{\vec{G}\vec{G}'}$	0.0	3.54	2.04
$\epsilon = \delta_{\vec{G}\vec{G}'}\epsilon_{\vec{G}\vec{G}'}$	0.0	0.96	1.62
$\epsilon = \epsilon_{\vec{G}\vec{G}'}$	0.0	0.06	1.81
Experiment	0.0	0.0	1.55
Acoustical sum rule	RHS	0.124	
$\vec{q}_x \to 0$	LHS	0.117	

With the inclusion of the off-diagonal elements, the LA phonon frequency is drastically reduced to a value very close to zero. This thus demonstrates clearly that the off-diagonal elements are essential in obtaining the correct screening of the long-range Coulomb fields set up by the ion core motions. Furthermore, as seen from Table I, the acoustical sum rule is very well satisfied without any adjustable parameters in the calculation. Expressed in units of Ry/(Bohr radius)^2, the left-hand side (LHS) of Eq. (5) is only different from the right-hand side (RHS) by about 5%. A number of factors may contribute to why the calculated LA phonon frequency is not exactly zero and the sum rule not completely satisfied. One is the finite truncation of our dielectric matrix size. Another is that, since an empirical pseudopotential was used in Ref. 11, the ionic potential employed here is not exactly the same potential used in generating the band structure and hence $\epsilon_{\vec{G}\vec{G}'}$. Finally, we remark that the optical-phonon frequencies are slightly higher when the off-diagonal elements are included indicating some stiffening of the Si-Si bonds through the umklapp processes.

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