

Viewpoint Paper

First principles phonon calculations in materials science

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ABSTRACT

Phonon plays essential roles in dynamical behaviors and thermal properties, which are central topics in fundamental issues of materials science. The importance of first principles phonon calculations cannot be overly emphasized. *Phonopy* is an open source code for such calculations launched by the present authors, which has been world-widely used. Here we demonstrate phonon properties with fundamental equations and show examples how the phonon calculations are applied in materials science.

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1. Introduction

Application of first principles calculations in condensed matter physics and materials science has greatly expanded when phonon calculations became routine in the last decade. Thanks to the progress of high performance computers and development of accurate and efficient density functional theory (DFT) codes, a large set of first principles calculations are now practical with the accuracy comparable to experiments using ordinary PC clusters. In addition to electronic structure information, a DFT calculation for solids provides energy and stress of the system as well as the force on each atom. Equilibrium crystal structures can be obtained by minimizing residual forces and optimizing stress tensors. When an atom in a crystal is displaced from its equilibrium position, the forces on all atoms in the crystal raise. Analysis of the forces associated with a systematic set of displacements provides a series of phonon frequencies. First principles phonon calculations with a finite displacement method (FDM) [1,2] can be made in this way. An alternative approach for phonon calculations is the density functional perturbation theory (DFPT) [3,4]. The present authors have launched a robust and easy-to-use open-source code for first principles phonon calculations, *phonopy* [5–20]. This can handle force constants obtained both by FDM and DFPT. The number of users is rapidly growing world-wide, since the information of

phonon is very useful for accounting variety of properties and behavior of crystalline materials, such as thermal properties, mechanical properties, phase transition, and superconductivity. In this article, we show examples of applications of the first principles phonon calculations.

In Sections 2–4, we take FCC-Al as examples of applications of first principles phonon calculations. For the electronic structure calculations, we employed the plane-wave basis projector augmented wave method [21] in the framework of DFT within the generalized gradient approximation in the Perdew–Burke–Ernzerhof form [22] as implemented in the VASP code [23–25]. A plane-wave energy cutoff of 300 eV and an energy convergence criteria of 10^{-8} eV were used. A $30 \times 30 \times 30$ *k*-point sampling mesh was used for the unit cell and the equivalent density mesh was used for the supercells together with a 0.2 eV smearing width of the Methfessel–Paxton scheme [26]. For the phonon calculations, supercell and finite displacement approaches were used with $3 \times 3 \times 3$ supercell of the conventional unit cell (108 atoms) and the atomic displacement distance of 0.01 Å.

2. Harmonic approximation

In crystals, it is presumed that atoms move around their equilibrium positions $\mathbf{r}(lk)$ with displacements $\mathbf{u}(lk)$, where *l* and *κ* are the labels of unit cells and atoms in each unit cell, respectively. Crystal potential energy Φ is presumed to be an analytic function of the displacements of the atoms, and Φ is expanded as

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$$\begin{aligned}
\Phi = & \Phi_0 + \sum_{l\kappa} \sum_{\alpha} \Phi_{\alpha}(l\kappa) u_{\alpha}(l\kappa) \\
& + \frac{1}{2} \sum_{l'\kappa'} \sum_{\alpha\beta} \Phi_{\alpha\beta}(l\kappa, l'\kappa') u_{\alpha}(l\kappa) u_{\beta}(l'\kappa') \\
& + \frac{1}{3!} \sum_{l''\kappa''} \sum_{\alpha\beta\gamma} \Phi_{\alpha\beta\gamma}(l\kappa, l'\kappa', l''\kappa'') \times u_{\alpha}(l\kappa) u_{\beta}(l'\kappa') u_{\gamma}(l''\kappa'') + \dots
\end{aligned} \quad (1)$$

where α, β, \dots are the Cartesian indices. The coefficients of the series expansion, Φ_0 , $\Phi_{\alpha}(l\kappa)$, $\Phi_{\alpha\beta}(l\kappa, l'\kappa')$, and, $\Phi_{\alpha\beta\gamma}(l\kappa, l'\kappa', l''\kappa'')$, are the zeroth, first, second, and third order force constants, respectively. With small displacements at constant volume, the problem of atomic vibrations is solved with the second-order terms as the harmonic approximation, and the higher order terms are treated by the perturbation theory.

With a force $F_{\alpha}(l\kappa) = -\frac{\partial\Phi}{\partial u_{\alpha}(l\kappa)}$, an element of second-order force constants $\Phi_{\alpha\beta}(l\kappa, l'\kappa')$ is obtained by

$$\frac{\partial^2\Phi}{\partial u_{\alpha}(l\kappa)\partial u_{\beta}(l'\kappa')} = -\frac{\partial F_{\beta}(l'\kappa')}{\partial u_{\alpha}(l\kappa)}. \quad (2)$$

Crystal symmetry is utilized to improve the numerical accuracy of the force constants and to reduce the computational cost. The more details on the calculation of force constants are found in Refs. [8,9].

As found in text books [27–30], dynamical property of atoms in the harmonic approximation is obtained by solving eigenvalue problem of dynamical matrix $D(\mathbf{q})$,

$$D(\mathbf{q})\mathbf{e}_{\mathbf{q}j} = \omega_{\mathbf{q}j}^2\mathbf{e}_{\mathbf{q}j}, \quad \text{or} \quad \sum_{\beta\kappa'} D_{\kappa\kappa'}^{\alpha\beta}(\mathbf{q})e_{\mathbf{q}j}^{\beta\kappa'} = \omega_{\mathbf{q}j}^2 e_{\mathbf{q}j}^{\alpha\kappa}, \quad (3)$$

with

$$D_{\kappa\kappa'}^{\alpha\beta}(\mathbf{q}) = \sum_{\Gamma} \frac{\Phi_{\alpha\beta}(\mathbf{0}\kappa, l'\kappa')}{\sqrt{m_{\kappa}m_{\kappa'}}} e^{i\mathbf{q}\cdot[\mathbf{r}(l'\kappa')-\mathbf{r}(\mathbf{0}\kappa)]}, \quad (4)$$

where m_{κ} is the mass of the atom κ , \mathbf{q} is the wave vector, and j is the band index. $\omega_{\mathbf{q}j}$ and $\mathbf{e}_{\mathbf{q}j}$ give the phonon frequency and polarization vector of the phonon mode labeled by a set $\{\mathbf{q}, j\}$, respectively. Since $D(\mathbf{q})$ is an Hermitian matrix, its eigenvalues, $\omega_{\mathbf{q}j}^2$, are real. Usually $D(\mathbf{q})$ is arranged to be a $3n_a \times 3n_a$ matrix [30], where 3 comes from the freedom of the Cartesian indices for crystal and n_a is the number of atoms in a unit cell. Then $\mathbf{e}_{\mathbf{q}j}$ becomes a complex column vector with $3n_a$ elements, and usually $\mathbf{e}_{\mathbf{q}j}$ is normalized to be 1, i.e., $\sum_{\alpha\kappa} |e_{\mathbf{q}j}^{\alpha\kappa}|^2 = 1$. $\mathbf{e}_{\mathbf{q}j}$ contains information of collective motion of atoms. This may be understood as a set of atomic displacement vectors,

$$[\mathbf{u}(l1), \dots, \mathbf{u}(l\kappa)] = \left[\frac{A}{\sqrt{m_1}} \mathbf{e}_{\mathbf{q}j}^1 e^{i\mathbf{q}\cdot\mathbf{r}(l1)}, \dots, \frac{A}{\sqrt{m_{n_a}}} \mathbf{e}_{\mathbf{q}j}^{n_a} e^{i\mathbf{q}\cdot\mathbf{r}(l\kappa)} \right], \quad (5)$$

where A is the complex constant undetermined by Eq. (3), and $\mathbf{e}_{\mathbf{q}j}^{\kappa T} = (e_{\mathbf{q}j}^{\alpha\kappa}, e_{\mathbf{q}j}^{\beta\kappa}, e_{\mathbf{q}j}^{\gamma\kappa})$.

As a typical example, the phonon band structure and phonon density of states (DOS) of Al are shown in Fig. 1. The phonon DOS is defined as

$$g(\omega) = \frac{1}{N} \sum_{\mathbf{q}j} \delta(\omega - \omega_{\mathbf{q}j}), \quad (6)$$

where N is the number of unit cells in crystal. Divided by N , $g(\omega)$ is normalized so that the integral over frequency becomes $3n_a$. The phonon band structure can be directly comparable with experimental data by neutron or X-ray inelastic scattering. They often show reasonable agreements [20,31,32]. Frequency data by Raman and infrared (IR) spectroscopy can also be well reproduced [12,33].

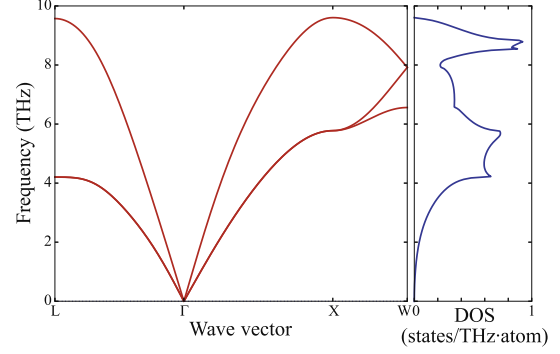


Fig. 1. Phonon band structure and DOS of Al.

Irreducible representations of phonon modes, which can be used to assign Raman or IR active modes, are calculated from polarization vectors [12,34]. Atom specific phonon DOS projected along a unit direction vector $\hat{\mathbf{n}}$ is defined as

$$g_{\kappa}(\omega, \hat{\mathbf{n}}) = \frac{1}{N} \sum_{\mathbf{q}j} \delta(\omega - \omega_{\mathbf{q}j}) \left| \hat{\mathbf{n}} \cdot \mathbf{e}_{\mathbf{q}j}^{\kappa} \right|^2. \quad (7)$$

This $g_{\kappa}(\omega, \hat{\mathbf{n}})$ can be directly compared with that measured by means of nuclear-resonant inelastic scattering using synchrotron radiation. In Ref. [17], phonon calculations of L1₀-type FePt projected along the c -axis and basal plane are well comparable to experimental ⁵⁷Fe nuclear-resonant inelastic scattering spectra measured at 10 K in the parallel and perpendicular geometries, respectively.

Once phonon frequencies over Brillouin zone are known, from the canonical distribution in statistical mechanics for phonons under the harmonic approximation, the energy E of phonon system is given as

$$E = \sum_{\mathbf{q}j} \hbar\omega_{\mathbf{q}j} \left[\frac{1}{2} + \frac{1}{\exp(\hbar\omega_{\mathbf{q}j}/k_B T) - 1} \right], \quad (8)$$

where T , k_B , and \hbar are the temperature, the Boltzmann constant, and the reduced Planck constant, respectively. Using the thermodynamic relations, a number of thermal properties, such as constant volume heat capacity C_V , Helmholtz free energy F , and entropy S , can be computed as functions of temperature [30]:

$$C_V = \sum_{\mathbf{q}j} C_{\mathbf{q}j} = \sum_{\mathbf{q}j} k_B \left(\frac{\hbar\omega_{\mathbf{q}j}}{k_B T} \right)^2 \frac{\exp(\hbar\omega_{\mathbf{q}j}/k_B T)}{[\exp(\hbar\omega_{\mathbf{q}j}/k_B T) - 1]^2}, \quad (9)$$

$$F = \frac{1}{2} \sum_{\mathbf{q}j} \hbar\omega_{\mathbf{q}j} + k_B T \sum_{\mathbf{q}j} \ln [1 - \exp(-\hbar\omega_{\mathbf{q}j}/k_B T)], \quad (10)$$

and

$$\begin{aligned}
S = & \frac{1}{2T} \sum_{\mathbf{q}j} \hbar\omega_{\mathbf{q}j} \coth [\hbar\omega_{\mathbf{q}j}/2k_B T] \\
& - k_B \sum_{\mathbf{q}j} \ln [2 \sinh(\hbar\omega_{\mathbf{q}j}/2k_B T)].
\end{aligned} \quad (11)$$

The calculated F , C_V , and S for Al are shown in Fig. 2.

3. Mean square atomic displacements

With the phase factor convention of the dynamical matrix used in Eq. (4), an atomic displacement operator is written as,

$$\hat{u}_{\alpha}(l\kappa) = \sqrt{\frac{\hbar}{2Nm_{\kappa}}} \sum_{\mathbf{q}j} \frac{\hat{a}_{\mathbf{q}j} + \hat{a}_{-\mathbf{q}j}^{\dagger}}{\sqrt{\omega_{\mathbf{q}j}}} e_{\mathbf{q}j}^{\alpha\kappa} e^{i\mathbf{q}\cdot\mathbf{r}(l\kappa)}, \quad (12)$$

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