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First-principles calculations of vibrational and thermodynamical properties of solids

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The presented first-principle phonon calculations make use of the standard DFT program, and the direct method. The procedure requires optimization of the structure, calculation of the forces, and construction of the dynamical matrix. This method has already been applied to a large number of crystalline systems to calculate the phonon dispersion curves, phonon density of states, and thermodynamic functions, which were required for a description of phase transitions.

Key words: *phonons; ab initio calculations; direct methods; vibrations in crystals*

1. Introduction

The dynamic and thermodynamic properties of solids depend upon the lattice vibrations related to phonons. Therefore, knowledge of phonon characteristics is required to describe the mechanical, acoustic, dynamic, spectroscopic and thermodynamic properties of crystals at finite temperature.

The possibility to calculate phonons directly from first-principles has existed for several years. The easiest and most convenient way to do it, is to use existing and well-tested DFT software [1–4], which can calculate crystalline structures, electronic bands, magnetic properties, and the so-called Hellmann–Feynman (HF) forces. To avoid surface effects, the DFT programs use supercells on which three-dimensional periodic boundary conditions are imposed.

The HF forces allow the atomic response forces for the displacement of any other atom to be found. To find harmonic phonons it is sufficient to convert the response HF forces to force constants and then to use the basic equations of the dynamical lattice theory. The last task has been coded in PHONON [5] software.

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2. Direct method

Traditionally, the ground state energy E (at $T = 0$) as a function of atomic positions $\mathbf{R}(\mathbf{n}, \mu)$, where $\mathbf{n}$ is the primitive unit cell index and μ is the atomic index, can be expanded over small displacements as

$$E\left(\mathbf{R}(\mathbf{n},\boldsymbol{\mu}),\ldots\ R(\mathbf{m},\boldsymbol{\nu}),\ldots\right) = E_0 + \frac{1}{2}\sum_{n,\mu,m,\nu} \boldsymbol{\Phi}(\mathbf{n},\boldsymbol{\mu},\mathbf{m},\boldsymbol{\nu})\mathbf{U}(\mathbf{n},\boldsymbol{\mu})\mathbf{U}(\mathbf{m},\boldsymbol{\nu}) \tag{1}$$

where the force constant matrix

$$\boldsymbol{\Phi}_{i,j}(\mathbf{n},\boldsymbol{\mu},\mathbf{m},\boldsymbol{\nu}) = \left.\frac{\partial^2 E}{\partial \mathbf{R}_i(\mathbf{n},\boldsymbol{\mu})\partial \mathbf{R}_j(\mathbf{m},\boldsymbol{\nu})}\right|_0 \tag{2}$$

is defined at the extremum configuration $(\partial E)/\partial \mathbf{R}_i(\mathbf{n},\boldsymbol{\mu})\,|_0 = 0$ at which all first order derivatives vanish.

The dynamical matrix is defined as

$$D(k;\boldsymbol{\mu},\boldsymbol{\nu}) = \frac{1}{\sqrt{M_\mu M_\nu}}\sum_m \Phi(0,\boldsymbol{\mu};\mathbf{m},\boldsymbol{\nu})\exp\{-2\pi i\mathbf{k}\left[\mathbf{R}(0,\boldsymbol{\mu}) - \mathbf{R}(\mathbf{m},\boldsymbol{\nu})\right]\} \tag{3}$$

Here, summation $\mathbf{m}$ runs over all atoms of the crystal, M_μ, M_ν are masses of atoms, and $\mathbf{k}$ is the wave vector. Eigenvalues of the dynamical matrix

$$\omega^2(\mathbf{k}, j)\mathbf{e}(\mathbf{k}, j) = D(\mathbf{k})\mathbf{e}(\mathbf{k}, j) \tag{4}$$

give the phonon frequencies $\omega^2(\mathbf{k}, j)$ and polarization vectors $\mathbf{e}(\mathbf{k}, j)$.

Any atomic displacement $\mathbf{U}(\mathbf{m}, \boldsymbol{\nu})$ generates HF forces

$$F(\mathbf{n},\boldsymbol{\mu}) = -\frac{\partial E}{\partial R(\mathbf{n},\boldsymbol{\mu})} \tag{5}$$

on all other atoms. Using the expansion of Equation (1), one finds

$$F_i(\mathbf{n},\boldsymbol{\mu}) = -\sum_{m,\nu,j} \Phi_{i,j}(\mathbf{n},\boldsymbol{\mu},\mathbf{m},\boldsymbol{\nu})U_j(\mathbf{m},\boldsymbol{\nu}) \tag{6}$$

which relates the generated forces with the force constant matrices and atomic displacement. The calculations of vibrational properties start from minimizing the total energy of the crystal with respect to the electronic part, lattice constants and atomic positions. At the minimized state all HF forces should vanish. Now, the HF forces should be calculated for configurations with a single atom displaced from the equilibrium position. The HF forces are calculated in the supercell with periodic boundary conditions, and that brings some modifications. Consider a supercell and displace an

atom ($\mathbf{m}, \nu$) by $\mathbf{U}(\mathbf{m}, \nu)$. Due to periodic boundary conditions this displacement causes the same displacements of corresponding atoms ($\mathbf{m} + \mathbf{L}, \nu$) in all images of the supercell.

Here, $\mathbf{L} = (L_a, L_b, L_c)$ are the indices of lattice constants of the supercell. Thus, according to Eq. (6), a displacement of a single atom ($\mathbf{m}, \nu$) in the original supercell generates a net force

$$F_i(\mathbf{n}, \mu) = -\sum_L \Phi_{i,j}(\mathbf{n}, \mu, \mathbf{m} + \mathbf{L}), \nu) U_j(\mathbf{m}, \nu) \tag{7}$$

We may introduce the cummulant force constant defined as

$$\Phi_{i,j}^{(\Sigma)}(\mathbf{n}, \mu, \mathbf{m}, \nu) = \sum_L \Phi_{i,j}(\mathbf{n}, \mu, \mathbf{m} + \mathbf{L}, \nu) \tag{8}$$

and the summation $\mathbf{L}$ runs over all supercell images. Thus, from the first-principle program one can only calculate the force constants $\Phi_{i,j}^{(\Sigma)}(\mathbf{n}, \mu, \mathbf{m}, \nu)$. The solution of Eq. (7) is the essence of the direct method [6, 7].

The program PHONON solves Eq. (7) with respect to cummulant force constants, Eq. (8), which, in turn, are introduced to the dynamical matrix. For wave vectors, which are commensurate with the supercell, the summation over all atoms of the crystal in Eq. (3) leads to an exact dynamical matrix, and hence it provides exact phonon frequencies and polarization vectors. The phonon frequencies, which do not belong to the commensurate wave vectors, could hold some uncertainties. But, if the supercell is so large that the force constants decay at half of the supercell linear size (i.e., they are three orders of magnitude smaller), then phonons at all wave vectors are correct. The program PHONON ensures that the force constants have the correct symmetry required by the crystal space group. It is also able to impose the translational-rotational invariance conditions causing the acoustic phonon modes to start at zero frequencies from the Brillouin zone centre.

Selection of the supercell shape is essential. It should have a form closest to a cube. Symmetry of the supercell should not break the crystal point group. Also it is necessary that all coordination shells defined within the supercell have a complete list of atoms. Supercells of other shapes could reduce the crystal symmetry since the supercell acts as an external field. Elongated supercell shapes can help to supplement the list of exact phonon frequencies calculated with the direct method in a particular crystal direction. For polar crystals the macroscopic electric field splits the infrared active phonon modes to LO and TO components. This splitting can be satisfactorily handled when knowing the Born effective charges and the dielectric constant.

3. First-principle phonons

The VASP [1, 2] and PHONON [5] programs have been applied to a number of crystalline systems. It was possible to confirm the soft mode at the *X* reciprocal lattice

point in the cubic zirconia ZrO_2 [6]. This soft mode transforms the crystal to the observed tetragonal phase. Calculations of phonon dispersion curves in cubic carbides TiC [8] and ZrC [9] showed that the calculations within the general gradient approximation lead to a slightly better agreement with the measured phonon branches. Other cubic systems studied were magnesium oxide MgO [10] and boron nitride BN [11]. Both possess the LO/TO splitting, which could have been quite successfully calculated by the elongated supercell method. Reduction of crystal symmetry increases the complexity of the calculation. The tetragonal rutile structures of tin oxide SnO_2 [12] and germanium oxide GeO_2 [13] have been studied. Their phonon dispersion relations, although having only 18 branches, were never measured. Under pressure both systems show soft modes of B_{1g} symmetries. These soft modes lead to a ferroelastic phase transition, seen also experimentally.

Of course, the calculations can be applied to lower-symmetry phases, like hexagonal GaN, having a wurzite structure [14]. It was optimized for rhombohedral symmetry, which lowers the wurzite space group. To restore the full wurzite space group symmetry some of the calculated force constants were additionally symmetrized. The calculated phonon dispersion curves were later measured by the inelastic X-ray scattering technique [15], and the agreement proved to be very good.

The phonon dispersion curves of zero-gap semiconductor HgSe have been computed and measured [16] and the agreement is very good. This crystal shows LO/TO splitting which quite strongly depends on the concentration of the charge carriers. The phonon dispersion curves of another semiconductor ZnTe at high-pressure has been calculated [17] and satisfactorily compared with the measured Raman data.

Some minerals are also interesting from the point of view of their stability. The optimization of a supercell within a given structure does not yet mean that this structure is the most stable. To state that a structure is dynamically stable all phonon frequencies should be positive. Under this guideline the phonon dispersion relation calculations for several structures of $MgSiO_3$ [18] and $CaTiO_3$ [19] have been undertaken. For these crystals the $Pm\bar{3}m$, *I*4/*mcm*, *Immm*, *P*4/*mbm* and *Pmnb* symmetries were checked. Except for *Pmnb* all the mentioned phases show soft modes. Therefore, the low-temperature space groups of these crystals are of the *Pmnb* type.

Especially interesting are the phonon calculations for the rhombohedral crystals. The phonon density of states of $FeBO_3$ has been measured by nuclear inelastic absorption of synchrotron radiation [20]. Since this compound is antiferromagnetic, it was necessary to include the magnetic interaction in the first-principle calculations in order to get an agreement between the measured and calculated phonon densities. In this case, the effect of magnetic interaction on the phonons is exceptionally large. The crystal is magnetostrictic and the magnetic interaction changes interatomic distances and hence the phonon force constants.

Another rhombohedral compound is $LiNbO_3$. It possesses a ferroelectric phase transition from *R*3*c* to $R\bar{3}c$. The phonon calculations [21] show that the paraelectric phase $R\bar{3}c$ has a soft mode of the same symmetry as the irreducible representation

which drives the phase transition to the ferroelectric phase $R3c$. The phonon dispersion curves of the ferroelectric phase do not have any soft mode. This is an example of how the phonon calculations could clarify the nature of phase transitions.

First-principle calculations have also been used to find the phonon dispersion curves, and phonon density of states for a number of chalcopyrites such as $AgGaS_2$ [22], $AgGaSe_2$ [23], $AgGaTe_2$, $CuInS_2$ [25], $CuInSe_2$ [24] and $ZnSnP_2$ [26]. These are body-centred tetragonal structures with 8 atoms in the primitive unit cells. The $AgGaSe_2$ [27] and $CuInSe_2$ [28] belong to the most complex crystals for which the phonon dispersion curves have ever been measured. The agreement of these experimental data with our calculated phonon branches is very good. The $CuInSe_2$ material [29] shows a special property. It crystallizes in two structures: the chalcopyrite and of AuCu-type. The ground state energies and phonon calculations show that the free energies of both polymorphic phases are equal over the whole temperature interval. Moreover, the lattice constants of the two phases match perfectly, therefore these two phases coexist.

The first-principle phonon calculations are limited to $T = 0$ K. However, quantities in which harmonic phonons play a leading role can also be calculated within the so-called quasiharmonic approximation. As an example we quote the γ-Mg_2SiO_4 system [30, 31]. The phonon dispersion curves of this cubic crystal have been calculated for several positive and negative pressures P, and for each P the harmonic free energy F has been plotted. The minimum of F as a function of the lattice constant gives a lattice constant at a given temperature. Hence, one obtains thermal expansion as a function of temperature, a quantity which has been calculated ab initio and which agrees with the experimental data.

Special attention has been devoted to the shape memory alloy NiTi [32]. This crystal has a high-temperature cubic austenite phase and a low-temperature monoclinic martensite phase. The transition between the phases is accompanied by the appearance of a hexagonal R-phase, and incommensurate state. The ab initio phonon dispersion curves revealed a soft mode in the austenite phase, which is able to drive NiTi to the orthorhombic phase, and to the R-phase. But the monoclinic phase can be attained only by condensation of two order parameters. However, for the R-phase, orthorhombic and monoclinic phases all have positive phonon frequencies, hence one may calculate the free energies for each of these phases. Knowing also the ground state energies one find that below the phase transition temperature T_c the free energy of the monoclinic phase is the lowest, while above T_c the R-phase has minimal free energy. The orthorhombic phase never becomes stable, and indeed it has not been observed for the stoichiometric composition of NiTi.

In the second order structural tetragonal to orthorhombic phase transition of $CaCl_2$ the free energy of one phase changes continuously into the free energy of the other phase. Then, the usual procedure with the intersection of two free energies cannot be used. However, since at constant volume the harmonic phonon frequencies do not depend on temperature, one may find the critical volume, at which the phase transition takes place, even at $T = 0$ K. The second order phase transition temperature is

then defined at a point where the minimum of the free energy as a function of volume coincides with the critical volume determined at $T = 0$ K [33].

4. Discussion

The direct method has some advantages and disadvantages.

- A great advantage is that it could use the data calculated by any standard DFT program, which is able to calculate the HF forces. One should, however, ensure that the forces are calculated with high accuracy to an order of 0.0001 eV/Å.
- Calculation of HF forces is not time-consuming since it needs only electronic optimization for a fixed ionic configuration.
- A small regular supercell provides exact phonon frequencies at the Γ point.
- For complex crystals for which the supercell is as big as the unit cell, and for which the interaction range is confined to the supercell, the phonon frequencies are exact for any wave vector. One may check the decay of the force constants parameters before calculating the phonon dispersion relations.
- Anharmonic effects and molecular dynamic calculations can be treated within the same framework.

There are also some disadvantages:

- Crystals having small unit cells must be represented by larger supercells.
- During calculations of the HF forces the displaced atom usually breaks the symmetry of the system. This changes the Brillouin zone integration in the DFT code.
- Within the direct method it is not easy to calculate the LO/TO splitting. It could be performed when the ionic effective Born charges and electronic dielectric constant are known.
- The largest error of phonon frequencies is expected for the low-energy modes. The error will still enlarge with the increasing dimension of the dynamical matrix, i.e. with increasing the number of atoms in the unit cell.

Only results for three-dimensional periodic systems have been referred to above. With a similar effort one may calculate phonons for other objects. Constructing several layers in a supercell one can study phonons on the surface. Placing an atom on the surface one may find the vibration spectrum of the adsorbed atoms. In a similar way multilayers can be treated. Another direction of research is to replace, within a suitable sized supercell, an atom by a vacancy or another atom, and thereby form a defect. One then may carry out the first-principle phonon calculations for point defects, pairs of defects, and clusters of defects. These calculations require, however, larger computer power, since all these systems possess less symmetry, and hence, the number of independent parameters to be found by the first-principle program is greater.

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