AB INITIO CALCULATION OF THE KCl PHONON FREQUENCIES

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Abstract

We have calculated the phonon frequencies of KCl along symmetry directions
using an approach which is a combination of the frozen phonon and force constants
methods. We also calculated Grüneisen parameters for all modes at X and L points
in the Brillouin zone. Finally, the slope of acoustic dispersion curves around zone
center were used to calculate the three independent elastic coefficients c_{11}, c_{44}, c_{12} as
well as the Bulk modulus. Our *ab initio* calculations are based on pseudopotential
density functional theory within the local density approximation.

Introduction

Although many phenomena in condensed matter physics
can be understood on the basis of a static lattice model with
atoms distributed on a fixed, immobile periodic array,
there are also considerable numbers of physical properties
of solids which can not be explained other than in the
framework of lattice dynamics. As an example, to study
phase transitions between different crystal structures under
temperature and pressure, the phonon spectrum must be
known in order to calculate Gibbs free energy. Phonon
dispersion spectra are interesting not only for their relevance
to properties of pure materials, but also as ingredients of
approximate calculations for complex systems, such as
crystals containing impurities, alloys, and quantum
microstructures [1]. Traditionally, empirical methods have
been used to calculate dispersion curves, but in the past few
years *ab initio* approaches based on density functional
theory have become manageable by using powerful
computers [2,3].

Ionic systems, and in particular alkali halides, because
of their wide-ranging importance in condensed matter
physics, have historically attracted considerable attention
for theoretical and experimental studies. But in spite of
their importance, most theoretical studies are confined to
model calculations and few attempts have been made to

determine their vibrational and structural properties based
on first principle calculations. *Ab initio* calculations of the
phonon spectra for alkali halides will not only give an
accurate database for related constituent substances, but
also provide stringent tests of various empirical models.

We report here the results of a phonon frequency
calculation for KCl as a prototype, using an approach
which is a combination of frozen phonon [4] and force
constant [5] methods. Additionally, by investigating the
variation in phonon frequencies at X and L points with
pressure, the Grüneisen parameters for different modes
were estimated. Finally, by calculating low energy
acoustical phonon velocities around zone center the three
independent elastic coefficients of the solid were calculated
and compared with experimental results. The calculations
are based on pseudopotential-density functional theory
with local density approximation (LDA) [1,6].

The paper is organized as follows: Section II contains
the computational details. Results and discussion are
presented in section III.

Computational Details

In order to calculate phonon frequencies we need to
calculate the forces on individual atoms in the solid. *Ab
initio* force calculations can be done using the Hellman-
Feynman theorem which connects the derivative of the
quantum mechanical expectation value of the total energy

to electrostatic forces. To calculate the forces for every ionic displacement, the valence electrons are allowed to adjust themselves self-consistently to this new environment through an iteration technique based on conjugate gradient. The attainment of the electronically self-consistent ground state in this approach is treated as a global minimization problem, in which the total energy functional is minimized with respect to the plane-wave coefficients of the occupied orthonormal orbitals [2]. Using the Hellman-Feynman theorem formulated for pseudopotential method the total force on each atom is calculated [4,7]. It contains two terms. One is the force contributed from other ions and the second term is the force contribution from the valence electrons. The first term is calculated using Ewald sum [8]. For the second term, the valence electrons distribution is calculated using density functional theory with LDA. Once the force is calculated for each atom for a given displacement, the force constants can be obtained.

There are two commonly used approaches in lattice dynamics to calculate phonon frequencies using force components on atoms: frozen phonon and force constants. In the frozen phonon method, the ions in the solid are displaced corresponding to a particular normal mode, and the increase in energy or forces are measured to give frequency for that phonon, while in the force constants method, one atom at a given time is displaced and the forces exerted on all atoms are measured to find the force constants. As in the frozen phonon method, the phonon polarizations obtainable from group theory serve as a prerequisite for frequency calculations, hence this method can only be used for highly symmetric points in the Brillouin zone. On the other hand, in the force constants method what we have to do is to calculate all the interatomic force constants in the crystal. We can either diagonalize the resulting dynamical matrix directly to get all the frequencies and eigenvectors simultaneously or form the Fourier transformed dynamical matrix (FTDM) for every wavevector and diagonalize a much smaller size matrix to get the frequencies at that wavevector. This method, even by using FTDM, has the disadvantage of requiring large amounts of cpu-time; hence we used a method which is a combination of frozen phonon and force constants and is described in detail below:

To find the phonon modes of a lattice, we need to solve the equations of motion of N interacting atoms, each of which has three degrees of freedom. Let's assume that an infinite crystal is divided into L primitive cells (labeled by l), each containing r atoms (labeled by k) having mass m_k. Using a similar notation to that of Bruesch [9], the equilibrium position of each atom is given by:

$$\vec{x}\begin{pmatrix} l \\ k \end{pmatrix} = \vec{x}_l + \vec{x}_k$$

As the lattice vibrates, each atom is displaced from equilibrium by an amount $\vec{u}$. Consider an atom k in the lth primitive unit cell, using harmonic approximation we have:

$$m_k \ddot{u}_\alpha \begin{pmatrix} l \\ k \end{pmatrix} = - \sum_{\beta l' k'} \Phi_{\alpha\beta} \begin{pmatrix} l & l' \\ k & k' \end{pmatrix} u_\beta \begin{pmatrix} l' \\ k' \end{pmatrix}$$

where

$$\Phi_{\alpha\beta} \begin{pmatrix} l & l' \\ k & k' \end{pmatrix} = \frac{\partial^2 E}{\partial u_\alpha \begin{pmatrix} l \\ k \end{pmatrix} \partial u_\beta \begin{pmatrix} l' \\ k' \end{pmatrix}}$$

E is the total energy of the unit cell. For the above equation we expect solutions of the form:

$$\vec{u}_\alpha \begin{pmatrix} l \\ k \end{pmatrix} = \vec{\varepsilon}_\alpha \begin{pmatrix} l \\ k \end{pmatrix} e^{i(\vec{q} \cdot \vec{x} \begin{pmatrix} l \\ k \end{pmatrix} - \omega t)}$$

$\vec{q}$ is the wavevector.

On substituting this into the previous equation we find:

$$-m_k \omega^2 \vec{\varepsilon} = D(\vec{q}) \vec{\varepsilon}$$

where the Fourier transformed dynamical matrix is given by

$$D_{\alpha\beta}(kk' \mid \vec{q}) = \sum_{l'} \Phi_{\alpha\beta} \begin{pmatrix} 0 & l' \\ k & k' \end{pmatrix} e^{i\vec{q} \cdot \left[\vec{x} \begin{pmatrix} l' \\ k \end{pmatrix} - \vec{x} \begin{pmatrix} 0 \\ k \end{pmatrix} \right]}$$

The eigenvalues of $D(\vec{q})$ give the frequencies of normal modes with wavevector $\vec{q}$, and the eigenvectors give the polarization vectors of each mode. Hence, if all the force constants of the structure are known, then the phonon modes at any point in the Brillouin zone can be calculated. However, the above theory requires knowledge of interactions between atoms separated by distances up to infinity, in an infinite crystal, and this is not manageable. Because of computational limitation, our *ab initio* calculations can only simulate one or a few primitive cells, so we can only obtain a small number of the force constants. Since the code employs periodic boundary conditions, this obstacle can be overcome by using elongated supercell and defining effective force constants. Let's assume we have a supercell containing l_1 primitive cells in one direction. Using cyclic boundary conditions we have:

$$\vec{u}\begin{pmatrix} l \\ k \end{pmatrix} = \vec{u}\begin{pmatrix} l + nl_1 \\ k \end{pmatrix}$$

where n is an integer. The forces exerted on the atoms in our supercell are therefore given by:

$$\vec{F}\begin{pmatrix} l \\ k \end{pmatrix} = \sum_{l'=1}^{h} \sum_{k'} \sum_{n=-\infty}^{+\infty} \vec{u}\begin{pmatrix} l'+nl_1 \\ k' \end{pmatrix} \Phi\begin{pmatrix} l & l'+nl_1 \\ k & k' \end{pmatrix}$$

Then we could alternatively define effective force constants which only relate to atoms within the supercell by writing:

$$\vec{F}\begin{pmatrix} l \\ k \end{pmatrix} = \sum_{l'=1}^{h_1} \sum_{k'} \Psi\begin{pmatrix} l & l' \\ k & k' \end{pmatrix} \vec{u}\begin{pmatrix} l' \\ k' \end{pmatrix}$$

$$\Psi\begin{pmatrix} l & l' \\ k & k' \end{pmatrix} = \sum_{n=-\infty}^{+\infty} \Phi\begin{pmatrix} l & l'+nl_1 \\ k & k' \end{pmatrix}$$

If we use a wavevector $\vec{q}$ which gives the same periodicity in an infinite crystal as these cyclic boundary conditions impose, then we can use Ψ and the atoms in the supercell only, instead of Φ and an infinite number of atoms. This condition on the wavevector can be written:

$$\vec{e}\begin{pmatrix} l+nl_1 \\ k \end{pmatrix} = \vec{e}\begin{pmatrix} l \\ k \end{pmatrix} exp\left\{ i\vec{q}. \left[\vec{x}_{l+nl_1} - \vec{x}_l \right] \right\} = \vec{e}\begin{pmatrix} l \\ k \end{pmatrix}$$

and hence the Fourier transformed dynamical matrix becomes:

$$D(kk' \mid \vec{q}) = \sum_{l=1}^{h_1} exp\left[i\vec{q}. (\vec{x}_l - \vec{x}_0) \right] \Psi\begin{pmatrix} 0 & l \\ k & k' \end{pmatrix}$$

We can thus obtain the exact phonon frequencies by treating our supercell as an isolated system of r atoms, connected by springs with force constants given by the simulation, instead of as an infinite crystal; r is the number of atoms in the supercell.

The calculations were done using the CASTEP code, which has been documented in detail elsewhere [2]. It solves the Kohn-Sham equations by expanding the wavefunctions in a plane wave basis set with periodic boundary conditions. We used a norm-conserving, non-local pseudopotential of the Kleiman-Bylander type, generated by Lin [9] using the method of Kerker [11]. Plane waves up to a kinetic-energy cutoff of 300 eV are used, further increase did not change the results significantly. The calculation is done self-consistently by using four special k points in the irreducible Brillouin zone [12].
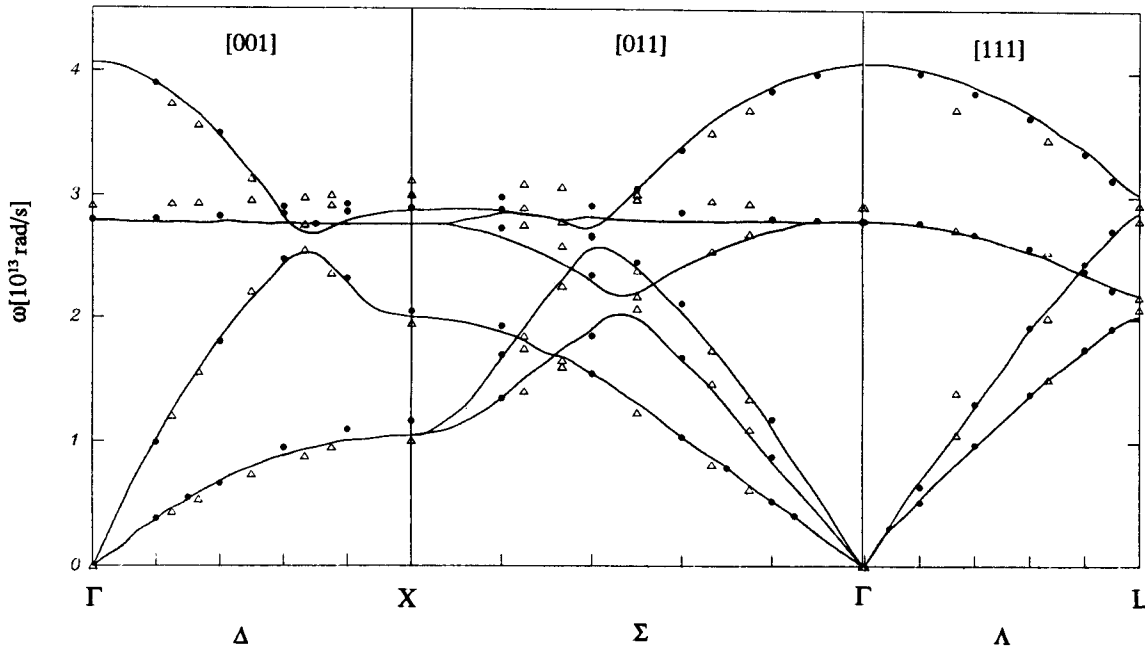

Figure 1. Phonon frequencies obtained are theoretically compared with experimental results; triangles are our data, filled circles are experimental data, and solid lines are dispersion curves obtained by using the breathing shell model [13].

Results And Discussion

The phonon frequencies calculated along symmetry directions [001], [011], and [111] are shown in Figure 1 and Table I. Our calculated results are shown in Figure 1 as triangles. The dots indicating the experimental values and the dispersion curves are obtained by using the breathing shell model borrowed from reference 13. It can be seen that our results are in excellent agreement with those of others; the deviation at most is less than 5%. This discrepancy can partly be attributed to the fact that our theoretical calculations are done at 0 K, while the experimental data are obtained at 80 K. Using harmonic approximation, a limited number of K-points, and low energy cutoff may be considered as other sources of error in our calculations. Yin *et al.* [4], using the frozen phonon method, have calculated phonon frequencies for Si and Ge. Their results for LTO at Γ point are not consistent with experimental data. They could remove this discrepancy by adding a third order anharmonic term to the energy as a function of amplitude. Although the possibility exists for a similar source of error in KCl, substantial discrepancy between our calculated LO(Γ) frequency and experimental results need a different explanation. G. Giannozzi *et al.* [1] have shown that in polar semiconductors the macroscopic electric field due to the long-range character of the Coulomb forces present in the LO(Γ) mode are responsible for such a discrepancy. Kunc *et al.* [14] using similar arguments have explained the result for LO(Γ) mode of GaAs. To obtain a rough estimation for LO(Γ) we fitted our data along Σ direction with tenth order polynomials. By extrapolating the dispersion curve we obtained $\omega_{LO}(\Gamma)$= 3.935 (in units

of 10^{13} rads^{-1}) and ratio $\frac{\omega_{LO}}{\omega_{TO}}$ = 1.347. The experimental values are 4.06 and 1.448, respectively [13].

In order to investigate the effect of pressure on the phonon modes, we have calculated the Grüneisen parameter for all modes at X and L points. This parameter, which is a measure of the anharmonicity of the interatomic potential and is important in predicting the thermal properties of materials, can be calculated as follows:

$$\gamma_s = \frac{\partial ln\omega_s}{\partial lnV}$$

where s labels the phonon to be considered and V is the volume of the unit cell. The results are shown in Figure 2 and Table II. It is clearly seen that at X-point, the acoustical modes, contrary to optical modes, are softening under pressure which means that the effective force constants for these modes are weakened. To our knowledge, no experimental values for the mode Grüneisen parameters of KCl at X and L points have been presented, hence our results serve as a prediction.

Finally, we can use the zone-center acoustical velocities to calculate some of the elastic constants. These velocities are associated with c_{11}, c_{44} and c_{12} by [15]:

$$\left(\frac{d\omega}{dk}\right)_{LA} = \sqrt{\frac{c_{11}}{\rho}} \qquad \text{[100] direction}$$

$$\left(\frac{d\omega}{dk}\right)_{TA} = \sqrt{\frac{c_{44}}{\rho}} \qquad \text{[100] direction}$$

Table I. Phonon frequencies calculated along symmetry directions (10^{13}rad/s)

| Direction	$a/2\pi(q_x,q_y,q_z)$	LO	T_1O	T_2O	LA	T_1A	T_2A
[0 0 1] $\Gamma \rightarrow X$	(0.0 0.0 0.0)	-	2.921		0.0	0.0	
	(0.0 0.0 1/4)	3.737	2.933		1.208	0.419	
	(0.0 0.0 1/3)	3.565	2.939		1.569	0.520	
	(0.0 0.0 1/2)	3.131	2.962		2.210	0.729	
	(0.0 0.0 2/3)	2.765	2.985		2.556	0.879	
	(0.0 0.0 3/4)	2.922	3.003		2.360	0.951	
	(0.0 0.0 1.0)	3.121	3.004		1.955	1.007	
[0 1 1] $\Gamma \rightarrow X$	(0.0 1/4 1/4)	3.698	2.697	2.944	1.357	1.105	0.606
	(0.0 1/3 1/3)	2.558	2.964	3.510	1.754	1.484	0.815
	(0.0 1/2 1/2)	2.178	3.016	2.974	2.389	2.079	1.241
	(0.0 2/3 2/3)	2.595	3.070	2.793	2.259	1.666	1.615
	(0.0 3/4 3/4)	2.902	2.766	3.094	1.857	1.415	1.762
[1 1 1] $\Gamma \rightarrow L$	(1/6 1/6 1/6)	3.707	2.738		1.414	1.068	
	(1/3 1/3 1/3)	3.464	2.560		2.015	1.526	
	(1/2 1/2 1/2)	2.940	2.181		2.813	2.084	
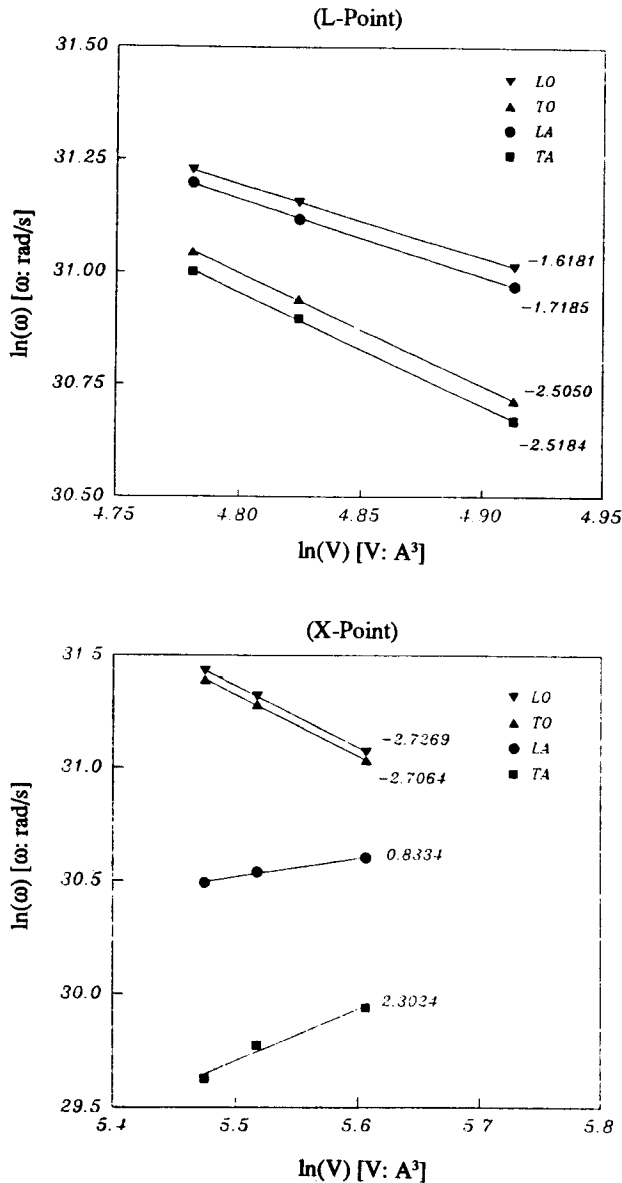
Figure 2. Variation of frequencies of phonons with size cell, to give Grüneisen parameters at X and L points. The numbers indicate slope of the lines.

$$\left(\frac{d\omega}{dk}\right)_{LA} = \sqrt{\frac{c_{11} + 2c_{12} + 4c_{44}}{3\rho}} \quad [111]\ direction$$

where ρ is the mass density.

Applying the slope of the low frequency acoustical dispersion curves at appropriate points in the above relations we calculated the three independent elastic constants. The calculated values of c_{11}, c_{44}, and c_{12} are compared with the experimental data in Table III. The agreement is excellent.

Table II. Grüneisen parameters at X and L points

Point	TA	LA	TO	LO
X-Point	-2.197	-0.836	2.714	2.727
L-Point	2.518	1.719	2.505	1.619

Table III. *Ab initio* calculated values for elastic constants (10^{11}Pa) and Bulk modulus (10^9Pa) compared with experimental results

	c_{11}	c_{44}	c_{21}	B_0
This work	0.435	0.056	0.057	18.28
Exp. [14]	0.403	0.063	0.066	19.7
Other cal. [16]	—	—	—	18.6

Additionally, the Bulk modulus for a cubic crystal is [15]:

$$B_0 = \frac{1}{3}\left(c_{11} + 2c_{12}\right)$$

Using the elastic coefficients we calculated the Bulk modulus, and the results are shown in Table III. Alternatively, to obtain zero pressure Bulk modulus we also plotted the total structural energy as a function of volume and fitted the data with Parsafar *et al.* equation of state [6,7]. The results are shown in Table III. It is seen that the value of the Bulk modulus obtained using elastic coefficients is in reasonable agreement with the experimental result.

Acknowledgements

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