Ab initio Force-Constant Method for Phonon Dispersions in Alkali Metals

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The force-constant matrix and the phonon dispersion curves are calculated for metals (Li, Na, K) by the fully self-consistent direct *ab initio* supercell approach based on the local-density approximation and on norm-conserving pseudopotentials. Apart from a constant scale factor for each material there is a very good agreement between theoretical and experimental data for the dispersion curves.

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There are basically two approaches for a calculation of phonon dispersion curves of crystalline solids from first principles, the *linear response approach* and the *direct approach.* In the linear response approach the dynamical matrix is obtained from the modification of the electronic density resulting from the phonon displacements of the atoms. The linear modification may be obtained, for instance, via the inverse dielectric matrix. (For a review, see Ref. [1].) The dielectric matrix is calculated from the eigenfunctions and energy levels of the unperturbed system, which requires cumbersome summations over many unoccupied conduction bands. Alternatively, various methods have been introduced to calculate the linear modification of the density directly (i.e., not via the dielectric matrix), either from different variants of a perturbation theory [2] or from a minimization of the second-order perturbation of the total energy [3]. Via a Fourier transformation of the dynamical matrix the force constants can be obtained.

In the direct approach the perturbed system is treated on the same footing as the unperturbed one, and the required information is obtained from a comparison of the two systems. Thereby, in the so-called frozen-phonon calculations [4], the total energy is evaluated for a system with a displacement pattern according to a snapshot of the phonon movement, and from the energy as a function of the displacement amplitude the phonon frequency is obtained. The method is straightforward, but it is restricted to wave vectors for which the phonon displacement pattern is commensurate to the supercells used in the calculations (i.e., only short-wavelength phonons can be considered for reasonable supercell sizes). A second type of direct supercell calculation considers the forces related to the displacements of the atoms in the supercell rather than the energies. From the forces obtained by the use of the Hellmann-Feynman theorem (see, for instance, Ref. [5]) the elements of the force-constant matrix are calculated. Then the dynamical matrix is determined by a Fourier transformation, and the phonon frequencies for arbitrary wave vectors are evaluated by a diagonalization of this matrix. By displacing entire planes of atoms the interplanar force constants and hence the dispersion relations for the corresponding directions in the phonon Brillouin zone can be obtained [6]. Because the planar force constants are linear combinations of the elements of the force-constant matrix, the latter ones may be obtained [7] from a limited set of planar force constants. In both cases the set of coupling constants must be confined by discarding interactions outside a certain spatial range, and the convergence of the results with respect to the size of this range must be checked.

In the present Letter the *direct force-constant approach* is applied for the first time to the case of metals, namely the alkali metals Li, Na, and K in the body-centered cubic phase. These materials are often perceived as being among the simplest nearly free electron metals (which seems to be justified for Na and K but definitely not for Li). Most of the phonon calculations for these simple metals (Ref. [8], and references therein) therefore introduced pseudopotentials for the electron-ion interaction and approximated the electronic response due to an atomic displacement by the one of a homogeneous electron gas [9]. In most of these papers the influence of the various assumptions entering this type of theory (for instance, the form of the screening function of the homogeneous electron gas, the conduction-band–core-electron exchange approximation and the construction of the pseudopotential) is discussed extensively. Because the results sometimes depend critically on these assumptions, a direct *ab initio* approach which depends only on the form of the exchange-correlation potential is clearly superior. The present direct calculations are part of a project to determine the vacancy formation entropies in alkali metals (related to the modification of the phonon spectrum by the vacancy) which certainly requires going beyond the linear response theory.

In our calculations we considered periodically arranged supercells and displaced the basis atom κ in the supercell by a small displacement vector, $\vec{u}(\kappa) = \{u_\alpha(\kappa)\}$, where the Greek index labels the Cartesian coordinates. From the calculated Hellmann-Feynman forces [5], $\vec{F}(\kappa') = \{F_\alpha(\kappa')\}$, on the basis atoms κ' we then can determine one column of the force-constant matrix

$$\phi_{\alpha\beta}(\kappa;\kappa') := -\frac{\partial F_\beta(\kappa')}{\partial u_\alpha(\kappa)} \approx -\frac{F_\beta(\kappa')}{u_\alpha(\kappa)}, \qquad (1)$$

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where we have adopted a harmonic approximation. Taking symmetry arguments into account, it becomes obvious that for a bcc crystal the displacement of the central atom of the supercell, in fact, does not only allow one to determine just one column of the force-constant matrix, but all single elements. The only limitations are given by the size of the supercell. First, because of the periodic arrangement of supercells we can calculate in principle only the couplings between the atoms in the same supercell. Second, even the force constants linking atoms in the same supercell are influenced by the superposition of the forces from the displaced atoms in the periodically arranged supercells. Therefore, in order to obtain reliable results for those coupling constants, the supercell size should exceed the spatial range of the forces. We determined the couplings up to the fifth nearest neighbor couplings. Of course, we cannot exclude that the couplings, for instance, to the fourth or fifth neighbors are affected by the above discussed superposition. To exclude this, calculations for even larger supercells are needed, which is beyond our present computational capability. However, we do not expect that the neglect of couplings to further distant neighbors and the possible uncertainty for the couplings to the fourth and fifth neighbors have an effect on the phonon spectrum for the following two reasons: First, we repeated the calculations by setting the couplings to the fifth neighbors zero, and there was virtually no effect on the phonon spectra. Second, we performed frozen-phonon calculations for the H point in Li, which automatically and exactly include all the couplings up to infinity, yielding an almost identical result as from the dynamical matrix (see below) obtained by use of the couplings up to the fifth neighbor. Although we used a rather small displacement of $\delta = 0.015a$ (a = elementary lattice constant), the calculations include slight anharmonicities, which are corrected for along the lines given in Ref. [10].

The calculations were performed in local-density approximation (LDA). Nonlocal, nonlinear [11], optimally smooth norm-conserving pseudopotentials [12] were used, allowing a rather small energy cutoff for the plane wave basis set. From frozen-phonon calculations at the H point $[\vec{q} = (0, 0, \frac{2\pi}{a})]$ we found that a cutoff of $E_c = 8.5$ Ry was sufficient which we then used in all later calculations. We confirmed that special $\vec{k}$ point meshes with 120 $\vec{k}$ points in the simple cubic two-atom supercell and corresponding sets in the larger supercells are sufficient. The calculations were performed using our theoretical values for equilibrium lattice constants obtained in the LDA, which are 6.34 a.u. for Li, 7.65 a.u. for Na, and 9.62 a.u. for K, in accordance with previous LDA results [13].

TABLE I. The nonvanishing elements $\phi_{\alpha\beta}(0, \kappa')$ of the force-constant matrix in Li, Na, and K.

$\kappa'\alpha\beta$	Li (N/m)	Na (N/m)	K (N/m)
$1xx$	3.001	1.442	0.835
$1xy$	2.709	1.585	0.954
$2xx$	1.046	0.490	0.454
$2yy$	0.408	0.143	0.048
$3xx$	−0.636	−0.088	−0.053
$3xy$	−0.415	−0.073	−0.041
$3zz$	−0.059	0.006	0.000
$4xx$	0.219	0.055	0.025
$4xy$	−0.049	0.003	0.005
$4yy$	−0.085	0.001	0.004
$4yz$	0.051	0.009	0.000
$5xx$	0.120	0.012	−0.001
$5xy$	0.158	0.011	0.001

From Table I it becomes obvious that the coupling constants in real space decay much faster in Na and K than in Li. According to the above discussion we can, of course, not exclude that the couplings to the fourth or fifth neighbors are affected by superposition effects. However, this holds for Li as well as for Na and K. The fact that Li behaves differently from Na and K means that either the interaction ranges are different or that the analytical forms of the interaction as a function of the distance are different. We think that the first assumption is more likely. With the force-constant matrix $\phi(\kappa; \kappa')$ the dynamical matrix

$$D_{\alpha\beta}(\vec{q}) = \sum_{\kappa'} \frac{1}{M} \phi_{\alpha\beta}(0; \kappa') e^{i\vec{q}\cdot\vec{R}_{\kappa'}} \qquad (2)$$

is obtained where M is the atomic mass and $\vec{R}_{\kappa'}$ is the position vector of the atom κ'. The diagonalization of $D(\vec{q})$ then yields the phonon dispersion curves $\omega(\vec{q})$ which are represented in Figs. 1–3 for three high-symmetry directions in the phonon Brillouin zone.

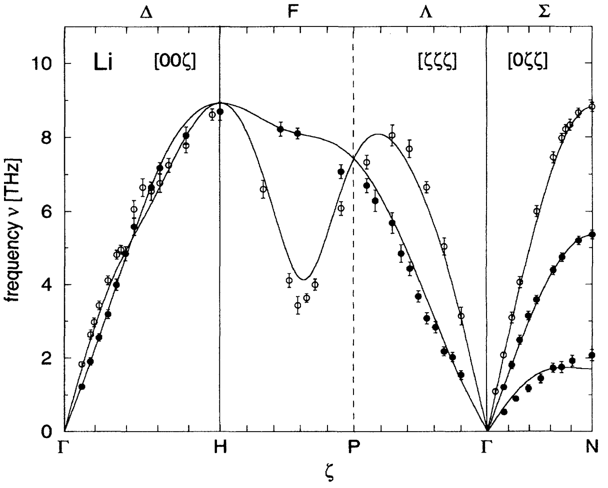

FIG. 1. Theoretical phonon dispersion curves (scaled at the N point, see text) for Li. For the Brillouin zone notation, see Ref. [15]. The open and full circles represent the results from inelastic neutron scattering [15] at 293 K for the longitudinal and the transverse branches.

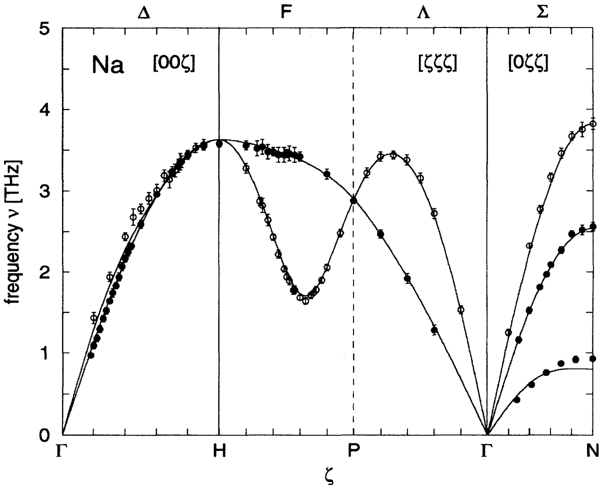

FIG. 2. Theoretical phonon dispersion curves (scaled at the N point, see text) for Na. The open and full circles represent the results from inelastic neutron scattering [16] at 90 K for the longitudinal and the transverse branches.

In all materials the calculated phonon frequencies at the zone boundaries were larger than the experimental phonon frequencies. For instance, the calculated frequencies of the longitudinal branch at the N point of Li, Na, and K exceeded the experimental frequencies by a factor of 1.16, 1.10, and 1.05, respectively. According to the above discussion it has been already demonstrated that this does not result from the neglect of couplings to further distant neighbors or a possible uncertainty for the couplings to the fourth and fifth neighbors. To make sure that the discrepancy to the experiment has nothing to do with the use of pseudopotentials we have redone the frozen-phonon calculations for the H point in Li using the full-potential linearized-augmented-plane-wave method, again with the same result. It must be admitted that the reason for this discrepancy is not known. Part of the discrepancy might arise from the fact that the lattice constants of the alkali metals are exceptionally strongly underestimated [13] by the local-density approximation. To demonstrate that, apart from the discrepancy for the absolute values, the functional form of the experimental dispersion curves is very well reproduced by our calculations, we scaled the theoretical data by the factors found for the longitudinal N point frequencies and given above.

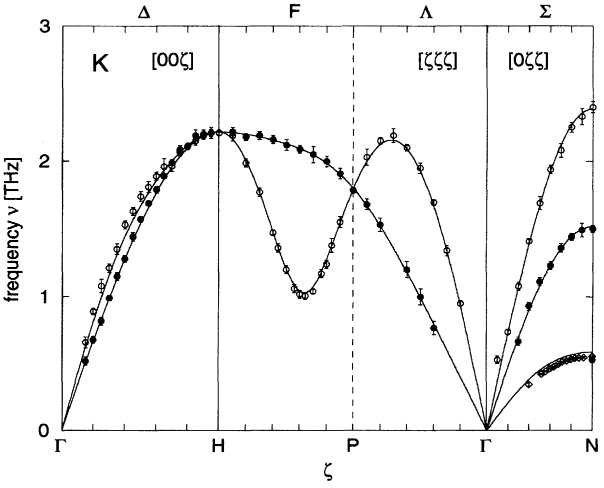

FIG. 3. Theoretical phonon dispersion curves (scaled at the N point, see text) for K. The open and full circles represent the results from inelastic neutron scattering [17] at 9 K for the longitudinal and the transverse branches. The open diamonds represent experimental data at 4.3 K [18].

It becomes obvious from Figs. 1–3 that there is nearly perfect agreement between theory and experiment for Na and especially for K. For Li, which is electronically more complicated (see above), the agreement is still quite good. It should especially be noted that the crossing between the longitudinal and the transverse branch for the $[00\zeta]$ direction is perfectly reproduced, as well as the plateaulike behavior of the transverse branch in $[\zeta\zeta\zeta]$ direction. For K there is no phonon anomaly in the low-frequency transverse branch along the $[0\zeta\zeta]$, in disagreement with the theory of Dagens *et al.* [8] but in line with the experimental data of Dolling and Meyer [18] at $T = 4.3$ K.

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