Structural properties of NaCl

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A theoretical description of the static structural, vibrational, and solid-solid phase-transition properties of alkali halides is presented. The description is *ab initio* involving pseudopotentials and density-functional theory. Using NaCl as a prototypical example, we conclude that properties of alkali halides can be computed accurately using this first-principles approach.

Since the early work of Madelung[1] and Ewald,[2] the alkali halides and in particular NaCl, have been the focus of a large number of detailed studies. The use of the Madelung constant[3] for the long-range part of the Coulomb interaction and a short-range repulsive potential (e.g., $\lambda e^{-r/R_0}$ where R_0 is the nearest-neighbor distance) give some reasonable estimates of bonding properties. However, as the experimental data base has grown, the simple models have required considerable amending and in some cases have become complex with many adjustable parameters. A similar situation exists for the lattice vibrational properties of these systems.[4] The simple structure of rocksalt has been used extensively as the model system for phonon studies. Despite the central role of these materials in condensed matter physics, few attempts[5] have been made to determine their vibrational and structural properties from a fundamental basis.

We report here the results of a study of NaCl in which we have determined several structural and dynamical properties using the pseudopotential approach[6,7] within a local-density theory.[8] This approach has been applied successfully to semiconductors and metals[7,9,10] to compute structural and dynamical properties. The application of this approach to highly ionic materials is an important test of this theory, since it is generally considered to be most suited to metallic systems where the electron density is slowly varying. As will be described, the approach is surprisingly successful as demonstrated by excellent predictions for the zero-temperature lattice constant, bulk modulus, pressure-induced solid-solid phase transition, and some selected phonon frequencies.

The calculations are based on a determination of the total structural energy,[11] E_{tot}, as a function of volume or lattice constant and structure. The ionic *ab initio* pseudopotentials[12] are generated using the atomic number as input; this approach has been shown[13] to be successful for partially ionic solids. For NaCl, the pseudopotentials are generated using the approach of Kerker[14] with a nonlinear core correction for Na.[15] Nonlocal potentials (*s*, *p*, and *d* symmetry) are used and tested to give the correct atomic wave functions, energy levels, and excitation energies for several atomic configurations. A plane-wave expansion is used and the localized nature of the Cl orbitals requires a large number of waves for convergence of the charge density and cohesive energy. Plane waves up to a kinetic-energy cutoff, E_{pw}, of 30 Ry (1000 plane waves) are used for the static properties and $E_{pw} = 20$ Ry for the dynamical properties. All plane waves are treated exactly[16] without perturbation

theory. Extrapolation to infinite E_{pw} yields a 0.5-eV error estimate in the cohesive energy for $E_{pw} = 30$ Ry. However, the differences in E_{tot} for different structures is estimated to be accurate to ≤ 1.5 mRy. Reducing E_{pw} from 30 to 12 Ry gives a 0.1% change in the lattice constant and a 4% change in the bulk modulus.

The calculation is done self-consistently[9,10] by evaluating the charge density at 10 special k points[17] in the irreducible Brillouin zone. Exchange and correlation are treated within the local density formalism[8] using Wigner's interpolation formula.[18] This will be discussed further later.

Figure 1 contains the calculated total energies E_{tot} for NaCl in the $B1$ (rocksalt) and $B2$ (CsCl) phase as a function of volume normalized to the $T = 0$ experimental volume V_0.[19] The diamonds and squares are the calculated points and the lines are fits using the Birch[20] equation of state. From the equation of state we obtain the lattice constant and bulk modulus given in Table I. The lattice con-
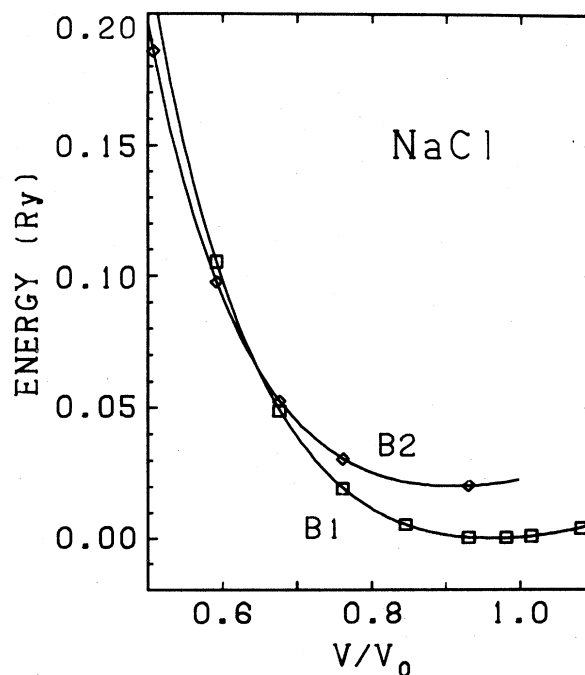

FIG. 1. Calculated total energies per unit cell for NaCl in the structures indicated as a function of volume. The solid lines are fits to the calculated points. The experimental cell volume, V_0, at $T = 0$ and atmospheric pressure is 43.81 Å^3.

TABLE I. Lattice constant and bulk modulus for NaCl at $T = 0$. The column labeled "Corr." has been corrected for zero-point motion as described in the text.

	Calc.	Corr.	Expt.
a_0 (Å)	5.52	5.56	5.60[a]
B_0 (GPa)	31.2	28.4	26.6[b]

[a]Reference 19.   [b]Reference 23.

stant is somewhat smaller, and the bulk modulus larger, than the experimental values. This discrepancy can be reduced by including the effect of zero-point motion. Since the lattice becomes stiffer when compressed, increasing the zero-point energy, the effect of the zero-point motion can be viewed as a negative pressure. This pressure is estimated by the Debye temperature and the assumption that the phonon frequencies scale with the elastic constants. The zero-point energy is then proportional to the square root of the bulk modulus. With $B_0' = \partial B_0/\partial p$, we obtain to first order

$$p_{zero} = \frac{\partial E_{zero}}{\partial V} = -\frac{E_{zero}B_0'}{2V_0} , \qquad (1)$$

and

$$\frac{\Delta V}{V_0} = -\frac{p_{zero}}{B_0} = \frac{E_{zero}B_0'}{2V_0B_0} . \qquad (2)$$

For NaCl, $B_0' \sim 5$,[21,22] $E_{zero} \sim 4.6$ mRy/molecule [calculated using the Debye model with $\Theta_D = 320$ K (Ref. 23)], which gives $\Delta V/V_0 = 2\%$. Correcting for B_0 using the above B_0', we obtain the values labeled "corrected" in Table I.

The value obtained for the bulk modulus depends to some degree on how the fit to the calculated points is made. This leads to uncertainties of the order 5% which can be reduced by computing more points around the energy minimum. We also emphasize that our results depend on the form chosen for the local density correlation express. The Wigner interpolation formula used here gives better static properties than other forms. The formalism of Hedin and Lundqvist[24] generally gives lattice constants that are smaller[13,15] for NaCl by approximately 1.2%. The parametrization[25] of the recent results by Ceperly and Alder seems to give results intermediate between the other two.

At a pressure of approximately 30 GPa, NaCl transforms from the $B1$ to the $B2$ structure.[22,26,27] Our calculated pressure for this transformation is 27 GPa. In Table II we give calculated and experimental values for the transition volumes. Including zero-point energy will only modify these values slightly. Again we can estimate the shifts using the Debye model. From the measured entropy difference, ΔS, across the transition, we obtain an approximation for the ratio of the Debye temperatures. With $\Delta S = 0.76k_B$ per unit cell,[26] we find $\Theta_{D(B1)}/\Theta_{D(B2)} \sim 1.13$. Furthermore, assuming scaling as above, we obtain a zero-point energy of 10 mRy for the $B1$ phase at the transition volume. Thus, in going from the $B1$ to the $B2$ phase, the zero-point energy drops by 1.3 mRy. This leads to a decrease in the transition pressure of 2 GPa and an increase in the transition volumes of 2%. For comparison with room-temperature experiments, the effects of finite temperature on the free energy will be to further increase these shifts.

TABLE II. Transition pressures and transition volumes for the $B1-B2$ phase transformation in NaCl. The volumes are given as fractions of the room-temperature zero-pressure volume (44.86 Å³/molecule).

	Calc.	Expt.
p (GPa)	27	30[a] 29[b,c]
v_{B1}	0.646	0.643[a] 0.650[b] 0.63–0.70[c]
v_{B2}	0.617	0.606[a] 0.618[b] 0.60–0.64[c]
$\dfrac{\Delta v}{v_{B1}}$ (%)	−4.5	−5.8[a,c] −5.0[b]

[a]Reference 26.   [c]Reference 22.
[b]Reference 27.

Sato-Sorensen[22] has very recently published pressure versus volume data for NaCl up to 70 GPa. Her data are reproduced in Fig. 2 where we also show the results from differentiating the equations of state from Fig. 1. In order to make possible the comparison, V_0 is taken to be the experimental room-temperature normal volume. We have adjusted our results for finite temperature (and zero-point pressure) by adding a small *ad hoc* constant pressure.[28] There appears to be a systematic deviation at high pressures which may indicate nonhydrostatic effects in the experiment.[29] Indeed, Bassett, Takahashi, Mao, and Weaver's[26] older data show good agreement with our calculation for the volume at their transition pressure, 30 GPa.

Finally, we have investigated the dynamic properties of NaCl.[30] Using the frozen phonon formalism,[9,10] we have calculated the frequencies of the phonon modes at Γ and X. The results are tabulated in Table III. Uncertainties are estimated based on several calculations with different displace-
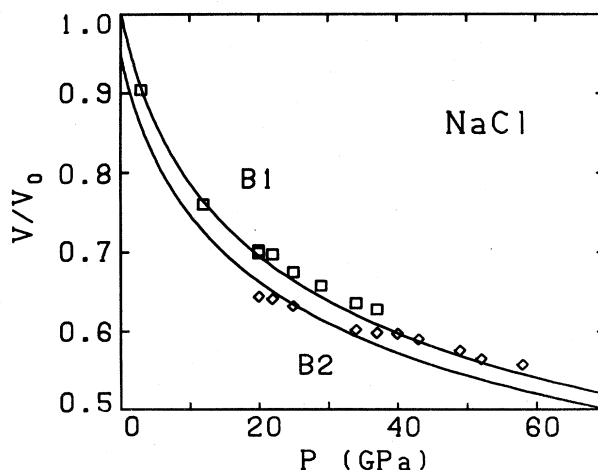

FIG. 2. Experimental and calculated pressure-volume curves for NaCl. The experimental values, represented by the squares and diamonds, are taken from Ref. 22 and the solid lines are the results of our calculations. The room-temperature normal volume is $V_0 = 44.86$ Å³, and our calculated results have been adjusted as described in the text.

TABLE III. Phonon frequencies for selected modes in NaCl (in units of 10^{13} rad sec^{-1}).

	Theory $T = 0$ K	Experiment $T = 80$ K[a]
TO(Γ)	3.09(0.10)	3.25(0.02)
LO(X)	3.48(0.15)	3.62(0.015)
TO(X)	3.26(0.10)	3.39(0.01)
LA(X)	2.58(0.15)	2.67(0.015)
TA(X)	1.53(0.10)	1.64(0.01)

[a]Reference 30.

ments and varying basis size. The percentage uncertainties are larger for the acoustical modes mainly because they involve differences between numbers of the same magnitude. The agreement with experiment is good although the calculated frequencies seem to be systematically somewhat softer than experiment.

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