

Change in the bulk modulus at the *B1-B2* phase transition

C. E. Sims, N. L. Allan, and T. H. K. Barron

School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 ITS, United Kingdom

(Received 23 December 1998)

Ab initio Hartree-Fock calculations for NaCl are used to derive the changes across the *B1-B2* phase transition in both the bulk modulus (ΔK_T) and the transverse infrared frequency ($\Delta \nu_{TO}$). ΔK_T is found to be positive but very small, and $\Delta \nu_{TO}$ negative and relatively large ($\approx 20\%$). In contrast, using a relationship based on lattice dynamics with rigid ions and short-range repulsion only between nearest neighbors, Hofmeister [Phys. Rev. B **56**, 5835 (1997)] has recently deduced from the observed drop in ν_{TO} , itself in good agreement with the Hartree-Fock calculations, that there should be a marked drop in K_T . We have, therefore, also calculated ΔK_T and $\Delta \nu_{TO}$ for NaCl using lattice dynamics, with a shell model that incorporates short-range potentials between both first and second neighbors, obtaining good agreement with the Hartree-Fock calculations. This calls into question the use at high pressures of a semiempirical relation between infrared frequencies and K_T , based on a model which includes only nearest-neighbor short-range interactions. Similar calculations for CaO give a much larger increase in the bulk modulus across the phase boundary, still accompanying a dramatic drop in ν_{TO} . [S0163-1829(99)13125-4]

Considerable experimental and theoretical attention has been paid to the pressure-induced phase transition from the *B1* (NaCl) to the *B2* (CsCl) structure,¹⁻³ which serves as an important model for other structural phase transformations such as those important in geophysics. Recently, in the course of extensive infrared (IR) measurements on the alkali halides up to pressures of 42 GPa, Hofmeister⁴ found that the principal IR frequencies dropped sharply when the phase changed from *B1* to *B2*. She went on to suggest that these results indicated that the bulk modulus K_T would also drop sharply at the transition, using a semiempirical relation between K_T and the principal infrared frequencies. This relation is based on a rigid-ion model with a repulsive short-range pair potential between nearest neighbors, and has been verified empirically to a good approximation at 1 atm. Hofmeister⁴ estimated that, for NaCl, K_T decreases by $16 \pm 3\%$ at the *B1-B2* transition pressure of 32 GPa.

Although a decrease in K_T has also been proposed by Heinz and Jeanloz,⁵ this result is most surprising. A change of such magnitude is not in agreement with most previous theoretical studies. For example, the Hartree-Fock studies of Aprà *et al.*⁶ predict a small increase in K_T at the transition, and similar results have been obtained in the linearized augmented-plane-wave calculations of Feldman *et al.*⁷ and the local-density-approximation based calculations of Bukowski and Aidun.⁸ A previous simulation study⁹ of NaCl, based on electron-gas pair potentials¹⁰ and including vibrational effects via quasiharmonic lattice dynamics, concluded that the bulk moduli for the two phases are very similar.

The behavior of K_T is crucial for many approximate models and equations of state. Accordingly in this work we extend our earlier work⁹⁻¹² on the *B1-B2* phase transition to investigate this discrepancy. We check the *ab initio* results by making simultaneous Hartree-Fock calculations of transverse IR frequencies as well as of K_T , and we check the semiempirical relation used by Hofmeister by using a more fully developed lattice-dynamical model to calculate K_T and

phonon frequencies as well as to estimate thermal effects. We concentrate on NaCl and, for comparison, CaO, since, as noted by ourselves and others,^{4,9,13} binary halides may not serve as good model systems for binary oxides.

As elsewhere,¹² *ab initio* periodic Hartree-Fock calculations were carried out using the CRYSTAL 95 code,^{14,15} with extended Gaussian basis sets appropriate for the solid state taken from previous work on NaCl.¹⁶ *A posteriori* correlation corrections¹⁷ were based on the correlation-only density functional of Lee, Yang, and Parr.¹⁸ For the *B1* and *B2* structures the unit cell is described by a single lattice parameter a , so that the equilibrium structure at applied pressure P_{ext} can be found by minimizing the availability²¹ $\tilde{G} = F + P_{\text{ext}}V$ directly with respect to a . All electronic structure calculations are in the static limit in which the Helmholtz free energy equals Φ_{stat} . The derivatives $d\Phi_{\text{stat}}/dV (= -P)$ were evaluated numerically. At equilibrium $P = P_{\text{ext}}$, and the availability equals the Gibbs energy. At the thermodynamic transition pressure P_{trans} , the Gibbs energies of the two phases are equal. The bulk modulus at any pressure $(= -d\Phi_{\text{stat}}/dV)$ was calculated from $V(d^2\Phi_{\text{stat}}/dV^2)$.

In the static limit the calculated Hartree-Fock thermodynamic transition pressure P_t for NaCl is 38 GPa. This is somewhat larger than the experimental values of 27 GPa (Ref. 19) and 32 GPa (Ref. 4), but the calculated transition pressure drops to 27 GPa with the inclusion of *a posteriori* correlation corrections based on the Lee-Yang-Parr functional¹⁸ (see Table I). At P_t , the Hartree-Fock bulk modulus increases from 164 to 165 GPa. When correlation corrections are included, this slight increase is enhanced (Table I). At pressures ± 5 GPa from the respective transition pressures the difference in bulk modulus between the two phases (*B2-B1*) remains positive; all the calculated values are collected together in Table I. Even if the observed transition pressure from *B1* to *B2* was as much as 5 GPa above the thermodynamic transition pressure due to kinetic effects, our Hartree-Fock and Hartree-Fock+correlation calculations do not support a decrease of 16% in K_T at the phase change.

TABLE I. Calculated thermodynamic $B1$ - $B2$ transition pressures and bulk moduli for NaCl at a range of pressures from Hartree-Fock calculations and Hartree-Fock calculations including *a posteriori* correlation corrections.

	HF		HF + correlation ^a	
	$B1$	$B2$	$B1$	$B2$
P_t (GPa)	38.2		27.2	
K_T (GPa) (at $P_t + 5$ GPa)	181	181	164	168
K_T (GPa) (at P_t)	164	165	142	146
K_T (GPa) (at $P_t - 5$ GPa)	147	149	123	127

^aLee, Yang, and Parr functional (Ref. 18).

We have calculated phonon frequencies at the Γ point using the frozen-phonon approximation as described previously.²⁰ Coulomb terms were summed using the Ewald summation; thus no macroscopic fields are generated and the Γ -point distortion corresponds to the transverse-optic (TO) mode. The calculated Hartree-Fock values, reported in Table II, are somewhat higher than experiment, consistent with previous experience that molecular and periodic Hartree-Fock calculations tend to overestimate vibrational frequencies.²⁰ However, the variation in the TO frequency for the $B1$ phase with pressure is similar to that observed by Hofmeister,⁴ and so is the negative change in this frequency ($\approx -19\%$) from the $B1$ to the $B2$ phase at P_t . For NaCl, therefore, periodic Hartree-Fock calculations indicate the bulk modulus increases only slightly across the $B1$ - $B2$ phase transformation, but there are pronounced drops in the infrared phonon frequencies in agreement with Hofmeister's measurements.⁴

We estimate the vibrational contributions to the bulk moduli of the two phases by means of pair-potential calculations. We use lattice statics and quasiharmonic lattice-dynamics methods,²¹ and the set of two-body shell-model potentials for NaCl are taken from Ref. 22. They include nearest-neighbor and next-nearest-neighbor short-range interactions. The vibrational contribution F_{vib} to the Helmholtz free energy is given by

$$F_{\text{vib}} = \sum_{\mathbf{q},j} \left\{ \frac{1}{2} h \nu_j(\mathbf{q}) + kT \ln[1 - \exp(-h \nu_j(\mathbf{q})/kT)] \right\}$$

where the $\nu_j(\mathbf{q})$ are the normal mode frequencies for wave vector \mathbf{q} and k is Boltzmann's constant; the $\nu_j(\mathbf{q})$ are thus explicit functions of the crystallographic parameters but not of the temperature T . We sum over uniform grids of \mathbf{q} vectors,²³ using successively finer grids until convergence is achieved. In the static limit F_{vib} is zero. Given F , equations of state, transition pressures and bulk moduli are determined as in the *ab initio* calculations.

TABLE II. Calculated Hartree-Fock transverse-optic mode frequencies (THz) at the Γ point for NaCl.

Pressure	$P_t - 5$ GPa	P_t	$P_t + 5$ GPa
$B1$	11.4	11.9	12.4
$B2$	9.1	9.6	9.8

We have carried out pair-potential calculations for NaCl at $T=0$ and $T=300$ K. At $T=0$ we find $P_t=34.0$ GPa, with a very small increase in bulk modulus from 188 GPa ($B1$) to 190 GPa ($B2$). At 300 K, K_t has dropped slightly to 33.3 GPa, and the bulk moduli of the phases are virtually identical at 181 GPa. These values suggest that the inclusion of the vibrational terms does not significantly alter ΔK_T at the phase transition. At both temperatures, and for both phases, changing the pressure by ± 5 GPa from P_t changes K_T by ± 20 GPa with consequently no change in ΔK_T .

The calculated decreases in the infrared vibrational frequencies during the $B1$ - $B2$ transition are in good agreement with experiment. The change in the bulk modulus deduced from these frequencies using the semiempirical relation⁴ is in much poorer agreement both with the *ab initio* calculations and with the lattice-dynamical model. Hofmeister⁴ states that these drops in vibrational frequencies are "due to the decrease in bond strength as ionic separation increases, and strongly suggest that the bulk modulus K_T generally decreases during the transition." This argument is incomplete, largely due to the neglect of next-nearest-neighbor interactions.

At P_t the volume of the $B2$ phase is smaller than that of $B1$. However, although ΔV is negative, the nearest-neighbor distance increases, from 2.48 to 2.66 Å in our pair-potential calculations, with a corresponding lowering of force constants for the nearest-neighbor interactions. In contrast, the next-nearest-neighbor distance decreases from 3.51 to 3.07 Å and the force constants for the next-nearest-neighbor interactions are likely to increase. With no change in force constants the change in the bulk modulus would simply reflect the increased coordination number. The actual change reflects the balance between these contributions.

The bulk modulus depends both on the nearest-neighbor and next-nearest-neighbor interactions. In contrast, the atomic displacements corresponding to the $\mathbf{q}=0$ optic modes do not change the next-nearest-neighbor distance. In a pair-potential model, therefore, the change in infrared frequencies from one phase to the other will indeed be governed largely by the increased coordination number and the change in nearest-neighbor force constant. The decrease in this force constant provides a simple physical explanation for the observed marked decrease in the IR frequencies across the transition, whereas the bulk modulus may increase or decrease. The model also indicates that not *all* phonon frequencies will decrease from the $B1$ to $B2$ phase, as is clear from Fig. 1(a), which shows vibrational densities of states for NaCl at 300 K derived by averaging over the entire Brillouin zone. Whereas the high-frequency optic modes decrease in frequency across the phase boundary, other modes may increase in frequency; at lower frequencies there is a marked shift to higher frequencies. Similar variations are observed in both rigid-ion and shell-model calculations. Finally our lattice-dynamics calculations reveal imaginary frequencies for the $B2$ structure of NaCl at pressures less than 2.5 GPa. This not only prohibits lattice-dynamical calculations but also implies that the $B2$ structure is unstable at these lower pressures, confirming Hofmeister's suggestion.⁴

Our results thus call into question the use at high pressures (as in Ref. 4) of a semiempirical relation based upon a

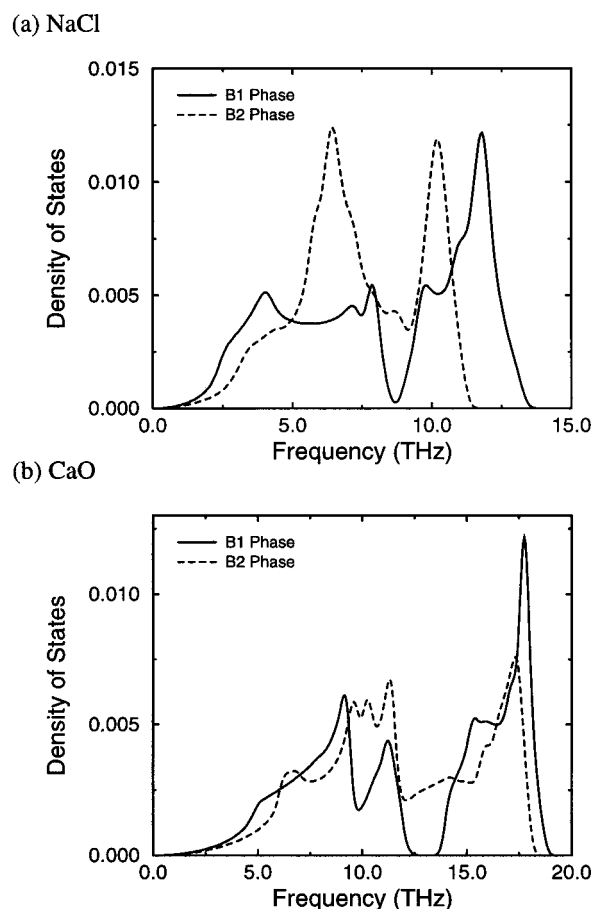


FIG. 1. Shell model vibrational densities of states at 300 K and the calculated thermodynamic transition pressure for the *B1* and *B2* phases of (a) NaCl and (b) CaO.

model that includes only nearest-neighbor short-range interactions and verified only at atmospheric pressure.

Finally, we examine the drop in infrared frequencies and the change in the bulk modulus at the *B1*-*B2* phase change

in CaO, which is a possible “invisible” component of the Earth’s lower mantle.²⁴ Using the extended basis set from previous work,²⁵ Hartree-Fock calculations and Hartree-Fock calculations including correlation corrections indicate an increase in K_T of ≈ 10 GPa at P_t . A pair-potential shell model, using the set of potentials from Ref. 26, also indicates a comparable increase in bulk modulus at the phase transition, both in the static limit and at 300 K. Vibrational contributions are small, as for NaCl. The marked increase in K_T for CaO confirms suggestions^{4,9,13} that the equations of state of halides and of oxides need not follow the same behavior. Indeed, as pointed out in Ref. 4, the alkali halides themselves show a wide range of behavior. Despite the increase in bulk modulus at P_t , in CaO, as in NaCl, the transverse and longitudinal optic modes *decrease* markedly in frequency; the TO mode decreases by $\approx 20\%$ from the *B1* to the *B2* phase in our pair-potential model. The vibrational densities of states for the *B1* and *B2* phases, calculated using this model and shown in Fig. 1(b), show the same qualitative differences between the two phases as NaCl, and are consistent with our simple force-constant argument.

In conclusion, for NaCl we have presented a range of *ab initio* and lattice-dynamical calculations in which there is no marked decrease in bulk modulus across the *B1*-*B2* transition accompanying the drop of the infrared active frequencies. We have presented a simple physical model to explain this in terms of next-nearest interactions. Our results call into question the use at high pressures of a semiempirical relation between the bulk modulus and the infrared frequencies based on a model which includes only nearest-neighbor short-range interactions. Analogous calculations for CaO indicate a marked increase in the bulk modulus across the phase boundary.

This work was supported by EPSRC Grant No. GR/L31340. C.E.S. wishes to thank EPSRC and ICI Explosives for financial support.

¹For example, P. W. Bridgman, *The Physics of High Pressure* (Dover, New York, 1970).

²A. Martín Pendás, V. Luaña, J. M. Recio, M. Flórez, E. Francisco, M. A. Blanco, and L. N. Kantorovich, *Phys. Rev. B* **49**, 3066 (1994), and references therein.

³For example, B. B. Karki, L. Stixrude, S. J. Clark, M. C. Warren, G. J. Ackland, and J. Crain, *Am. Mineral.* **82**, 51 (1997).

⁴A. M. Hofmeister, *Phys. Rev. B* **56**, 5835 (1997).

⁵D. L. Heinz and R. Jeanloz, *Phys. Rev. B* **30**, 6045 (1984).

⁶E. Aprà, M. Causà, M. Prencipe, R. Dovesi, and V. R. Saunders, *J. Phys.: Condens. Matter* **5**, 2969 (1993).

⁷J. L. Feldman, M. J. Mehl, and H. Krakauer, *Phys. Rev. B* **35**, 6395 (1987).

⁸M. S. T. Bukowinski and J. Aidun, *J. Geophys. Res.* **90**, 1794 (1985).

⁹N. L. Allan, M. Braithwaite, D. L. Cooper, B. Petch, and W. C. Mackrodt, *J. Chem. Soc., Faraday Trans.* **89**, 4369 (1993).

¹⁰For example, N. L. Allan and W. C. Mackrodt, *Philos. Mag.* **B 69**, 871 (1994).

¹¹N. L. Allan, M. Braithwaite, D. L. Cooper, W. C. Mackrodt, and S. C. Wright, *J. Chem. Phys.* **95**, 6792 (1991).

¹²C. E. Sims, G. D. Barrera, N. L. Allan, and W. C. Mackrodt, *Phys. Rev. B* **57**, 11 164 (1998).

¹³For example, O. L. Anderson and J. E. Nafe, *J. Geophys. Res.* **70**, 3951 (1965).

¹⁴C. Pisani, R. Dovesi, and C. Roetti, *Hartree-Fock Ab Initio Treatment of Crystalline Systems* (Springer-Verlag, Berlin, 1988).

¹⁵R. Dovesi, V. R. Saunders, C. Roetti, M. Causà, N. M. Harrison, R. Orlando, and E. Aprà, *CRYSTAL 95*, User Manual, Università di Torino and CCLRC Daresbury Laboratory, 1996.

¹⁶E. Aprà, M. Causà, M. Prencipe, R. Dovesi, and V. R. Saunders, *J. Phys.: Condens. Matter* **5**, 2969 (1993).

¹⁷For example, see M. Causà and A. Zupan, *Chem. Phys. Lett.* **220**, 145 (1994); *Int. J. Quantum Chem.* **S28**, 633 (1995).

¹⁸C. Lee, W. Yang, and R. G. Parr, *Phys. Rev. B* **37**, 785 (1988).

¹⁹S. Froyen and M. L. Cohen, *J. Phys. C* **19**, 2623 (1986).

²⁰M. D. Towler, N. L. Allan, N. M. Harrison, V. R. Saunders, W. C. Mackrodt, and E. Aprà, *Phys. Rev. B* **50**, 5041 (1994).

- ²¹M. B. Taylor, G. D. Barrera, N. L. Allan, and T. H. K. Barron, Phys. Rev. B **56**, 14 380 (1997).
- ²²M. J. L. Sangster and R. M. Atwood, J. Phys. C **11**, 1541 (1978).
- ²³D. J. Chadi and M. L. Cohen, Phys. Rev. B **8**, 5747 (1973).
- ²⁴R. Jeanloz and T. J. Ahrens, Geophys. J. R. Astron. Soc. **62**, 505 (1980).
- ²⁵W. C. Mackrodt, N. M. Harrison, V. R. Saunders, N. L. Allan, M. D. Towler, E. Aprà, and R. Dovesi, Philos. Mag. A **68**, 653 (1993).
- ²⁶M. J. L. Sangster and A. M. Stoneham, Philos. Mag. B **43**, 597 (1981).