Sodium chloride structural properties:
Linearized augmented-plane-wave calculations and pressure calibration

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Results of calculations, performed to a high degree of accuracy within the local-density approximation (LDA), of the compressive and B_1-B_2 transition properties of NaCl are presented. Results for the equation of state appear to have significance as a pressure calibrant. The linearized augmented-plane-wave method is used and calculations are performed for both Wigner and Hedin-Lundqvist exchange-correlation formulas in order to estimate uncertainties within the LDA.

Pressure calibration is critical in all static high-pressure studies, and NaCl is of central importance in this regard. As a result, in part, of its large compressibility and its much studied equilibrium ($p = 0$) properties, NaCl has been used as a primary pressure calibrant. The semi-empirical equation of state (EOS) for NaCl obtained by Decker[1] has been utilized in this regard. Given the importance of obtaining accurate pressure calibrations, especially in light of renewed interest in high-pressure research,[2] here we report theoretical studies of the EOS of NaCl using the general potential all-electron linearized augmented-plane-wave (LAPW) method. No uncontrolled approximations are made other than the local-density approximation[3] (LDA) for exchange and correlation (XC) and the neglect of spin-orbit effects in the electron band states.[4] Using these theoretical results, we give a representation of pressure versus volume for NaCl at high pressures in the B_2 phase which we believe to be highly accurate.

The Decker EOS calibration is limited to $p \lesssim 30.0$ GPa because, for higher pressures at room temperature, NaCl has transformed to the CsCl (B_2) structure and the Decker parametrization of interatomic forces is no longer valid.[5] It should also be noted that EOS pressure calibration is less accurate at high pressures than at low pressures due to the nature of the nonlinearity of p versus V, i.e., the bulk modulus increases with pressure. Above 30.0 GPa the ruby fluorescence scale, which is an empirical scale originally calibrated[6] at $p \leq 19.5$ GPa against the room-temperature Decker EOS, is generally used. Other calibrations[7] of the ruby scale to much higher pressures than 19.5 GPa have been based on analyses of shock data.

The Decker EOS has been rigorously tested by direct measurement only below 5.0 GPa but can be seen to be supported by other semiempirical treatments.[8] Ideally, one would like to have an EOS based on an *ab initio* theory, with as few approximations as possible, which accurately predicts all equilibrium structural and thermoelastic properties, and B_1-B_2 transition properties [e.g., $(V_2 - V_1)/V_1$] as well. In recent years the Hohenberg-

Kohn[9] density-functional theory within the LDA has been found to yield quite accurate results for bulk equilibrium properties of solids.[10] Calculations within the density-functional framework for NaCl have been varied. They have been based on the *ab initio* pseudopotential method,[11] the APW method using the muffin-tin approximation,[5] the augmented-spherical-wave method,[12] and on variations of the Gordon-Kim method of superposing individual ion electron densities.[13,14] Recently, following the completion of the present calculations, a calculation based on the LAPW method has also appeared.[15] Furthermore, various forms of homogeneous-electron-gas exchange-correlation energy have been used. Our discussion and comparisons of previous calculations will be limited here to those which make few approximations beyond the LDA. In view of the fact that (i) Froyen and Cohen[11] used Wigner[16] correlation and that (ii) of all currently used forms (e.g., Wigner, Hedin-Lundqvist,[17] Lundqvist-Lundqvist,[18] and Ceperly-Alder[19]) of XC, the Wigner form differs most from the remaining ones, we performed calculations for Wigner (W) as well as for Hedin-Lundqvist (HL) XC. This should provide an estimate of the uncertainty in results due to variations in the local form of XC.

In our calculations we use the special **k**-point method for performing Brillouin-zone summations, and we treat Cl $3s$, Cl $3p$, and Na $2p$ states as band states. The remaining lower-energy states can be treated as (*unfrozen*) core states[4] to an excellent approximation for the volume range of interest. Several aspects of the calculations were specifically monitored. These include the number of LAPW basis functions ($k_{max} \leq 4.3$ a.u.), the LAPW energy parameters, the number of special **k** points ($\leq 32, B_2$; $\leq 10, B_1$), and the number of LAPW energy windows (≤ 3). The accuracy achieved for the total energy is believed to be better than 0.3 mRy/(atom pair) on this basis. Finally, the *ab initio* total energies at different volumes were least-squares fitted to the five-parameter Birch[8] energy function.

What is calculated through our LDA total energies are

TABLE I. B_1 static-lattice equilibrium properties and B_1-B_2 transition pressure P_t.

	Exchange and correlation	a (Å)	B (GPa)	dB/dp	P_t (GPa)
This work	Hedin-Lundqvist	5.472±0.1%	31.4±3%	5.0±6%	21.4
This work	Wigner	5.535±0.1%	28.7±3%	5.0±6%	21.4
Froyen and Cohen	Wigner	5.52	31.2		27
Jansen and Freeman	Hedin-Lundqvist	5.64	30.4		
Expt.		5.5708[a]	27.6[a]	4.88[b]	29—30[c]
		5.568[b]	28.47[b]		

[a]Reference 20.
[b]Reference 21.
[c]Room-temperature values (Ref. 24).

"static-lattice" values of properties; in general, thermal and zero-point effects must be estimated for comparison with experiment. However, approximate experimental static-lattice values of equilibrium volume and of the bulk modulus and its pressure derivative have been extracted through analyses of data,[20,21] and comparisons with our results are made in Table I. In the case of the B_1 structural EOS we use a previous estimate[22] for the room-temperature thermal pressure, and in accord with the approximations of Ref. 1, the zero-point pressure is

$$p_z = p_{z,r}(V/V_r)^{A-1}\exp[(\gamma_r - \gamma)/A] ,$$

where $p_{z,r} = 9Nk\gamma_r\Theta_r/(4V_r) = 0.33$ GPa, $\gamma = \gamma_r(V/V_r)^A$, $\gamma_r = 1.71$, $\Theta_r = 279$ K, and $A = 0.93$. Here Θ_r and γ_r are, respectively, a Debye temperature and Grüneisen parameter[22] evaluated at the reference volume V_r, chosen to be the room-temperature equilibrium volume. The result is that the combined thermal and zero-point pressure, i.e., $p - p_{static}$, at room temperature can be well represented by the (volume-independent) value, 1.0 GPa. Interestingly, approximately the same result was also obtained on the basis of ab initio theoretical calculations by Hemley and Gordon.[14,23] For the B_2 structural EOS, due to the absence of thermal data, we must rely on theoretical calculations of zero-point and room-temperature thermal effects by Hemley and Gordon.[13,23] Again, to within a small (~ 0.1 GPa) uncertainty these latter results can be simply represented. In this case $p - p_{static}$ is given by 1.4 GPa, for $p < 23.8$ GPa, and by $1.4 + 6.4 \times 10^{-4}(p - 23.8)$ GPa for $p \leq 23.8$ GPa.

Figure 1 shows the room-temperature (RT) EOS for both B_1 and B_2 structures. It is found that B_1 equilibrium volumes at room temperature are $V_{HL}/V_{RT} = 0.948$ and $V_W/V_{RT} = 0.981$, where V_{RT} is the experimental value of 44.85 Å^3/(unit cell). A brief comparison to other results is in order here. Froyen and Cohen[11] made use of an ad hoc constant combined thermal and zero-point pressure shift, and it appears that they chose that shift to yield $V_W/V_{RT} = 1$. We disagree with the thermal correction which they chose. Our results, using the Wigner correlation, and those of Froyen and Cohen for the static-lattice value of the equilibrium volume can be seen (Table I) to be in agreement with each other to within $\sim 0.6\%$. We also mention that Bukowinski and Aidun,[5] who used the Lundqvist-Lundqvist[18] XC and the muffin-

tin approximation, obtained exact agreement with experiment.

What is especially interesting is the fact that the ratio $(p_{Decker} - p_W)/(p_W - p_{HL})$ in the B_1 phase, is found to be nearly independent of volume. This suggests that perhaps in order to obtain the "true" equation of state in the B_2 phase one ought to adopt this relation. Thus, we have made use of the formula

$$p(V) = p_W(V) + C[p_W(V) - p_{HL}(V)] , \qquad (1)$$

where C is the constant 0.57, which we obtained by setting $p = 0$ at the experimental B_1 equilibrium volume. The results for $V(p)$ are shown in Fig. 2. In the B_1 phase, deviations from the Decker EOS are at most 0.2 GPa and excellent agreement with experiment is obtained for $(V_1 - V_2)/V_1(\equiv \Delta V/V)$ at the experimental transition[24] to the B_2 phase, i.e., we obtain $\Delta V/V = 0.047$ at $p \approx 30.0$ GPa in comparison to the "averaged" experimental value of 0.047 ± 0.005 obtained by Liu and Bassett.[25] We also show (Fig. 3) static-lattice results for bulk moduli
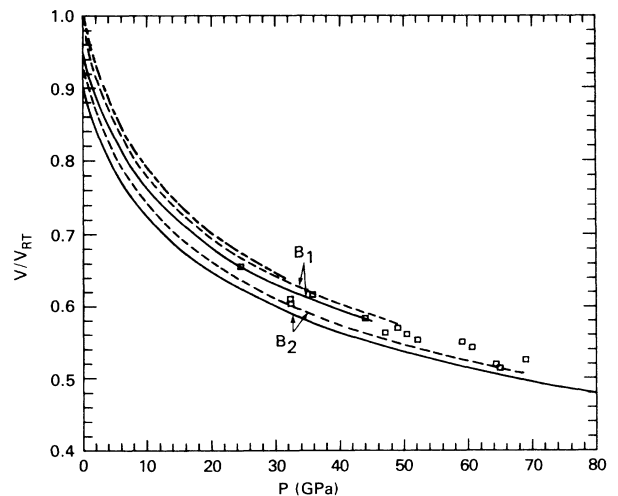

FIG. 1. Theoretical LDA results for the room-temperature equation of state. Solid (evenly dashed) lines correspond to the use of Hedin-Lundqvist (Wigner) XC. The unevenly dashed line corresponds to the Decker EOS (Ref. 1) and the data points are for the B_2 structure (Ref. 26).
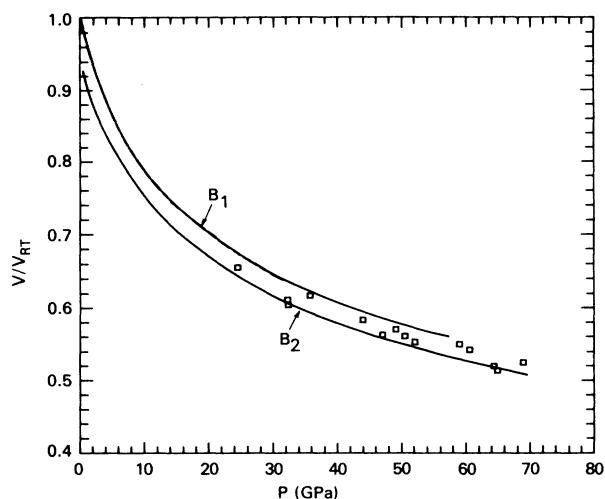
FIG. 2. Room-temperature equation of state. Solid lines correspond to the application of our extrapolation procedure (see text) to our LAPW results. For $p \leq 30.0$ GPa, the Decker EOS (Ref. 1) is also represented by the B_1 curve, to within the thickness of the line. The data points are for the B_2 structure (Ref. 26).
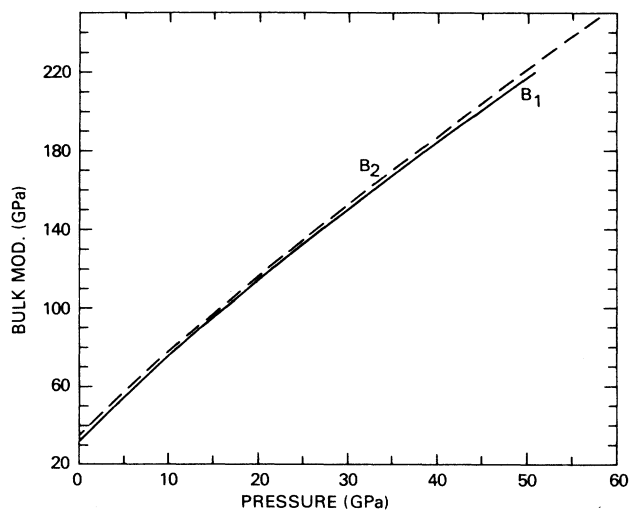

FIG. 3. Theoretical results for the pressure dependence of the bulk modulus for NaCl. Results are based on Hedin-Lundqvist XC. No zero-point or thermal vibrational effects are included.

versus p with use of Hedin-Lundqvist XC. Similar results were obtained using Wigner correlation. The nearness of B_1- and B_2-phase bulk moduli at any given pressure, is very much in accord with the fact that it has not been clearly determined *experimentally* which structure has the larger bulk modulus at the transition.[26] Finally, for the transition pressure, we obtain no difference in results between the two forms of the XC potential used and hence that the LDA yields disagreement with experiment (see Table I). The inclusion of thermal effects will only worsen this disagreement.[14] On the other hand, Froyen and Cohen obtained a transition pressure which is only slightly below the room-temperature experimental value. It is physically reasonable that the valence electron charge density in NaCl is more readily represented by LAPW basis functions than plane-wave basis functions. (This is reflected in the relatively large estimated uncertainty in absolute total energy, as distinguished from the estimated uncertainty in volume or structural dependences, of the calculation of Froyen and Cohen.[27]) Thus, we tentatively attribute the difference in results for the transition pressure between our calculation and the *ab initio* pseudopotential calculation to basis-set limitations of the latter. It should also be noted that the transition pressure is a very "sensitive" property. For example, upon increasing the total energy $E(V)$ by merely a constant 1 mRy for the B_2 structure alone, the transition pressure is increased by 1.36 GPa.

The calculation procedures used by Jansen and Freeman[15] to obtain the B_1 equilibrium volume and bulk modulus are very closely related to ours. However, there exists disagreement between our results and theirs for the

equilibrium volume (see Table I) which is outside our estimate of combined uncertainties of these calculations. We attribute this disagreement to the fact that Jansen and Freeman performed only one diagonalization of the secular equation to simultaneously obtain the Cl $3p$, $3s$, and Na $2p$ states[28] at each $\mathbf{k}$ point (i.e., one energy window was used). We performed three separate diagonalizations (three energy windows) at each $\mathbf{k}$ point using different LAPW energy parameters for each diagonalization.

To summarize, we believe the calculations reported herein represent the most accurate ones available, within the LDA of Kohn and Sham, for compressive and transition properties of NaCl. It is evident from this study that the LDA yields results which differ from experiment, even with account taken of the possible uncertainty in the form of the exchange-correlation function, and it would be interesting to include approximate energy contributions beyond LDA such as those of Langreth and Mehl[29] in further work. Furthermore, we have found that results based on Hedin-Lundqvist and Wigner exchange-correlation expressions can be simply extrapolated to yield remarkable agreement with the Decker EOS in the B_1 phase which suggests that our results corresponding to the B_2 phase can be utilized as a NaCl pressure calibrant beyond $p = 30.0$ GPa.

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