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# *Ab initio* calculations of static lattice properties for NaCl and a test of the Decker equation of state

J. L. Feldman, M. J. Mehl, L. L. Boyer, and N. C. Chen
*Naval Research Laboratory, Washington, D.C. 20375-5000*

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Calculations of the equilibrium volume and bulk modulus at the equilibrium volume are made for Gordon-Kim based theories of NaCl and used in the Decker approach for calculating the equation of state. Generally the resultant "Decker equation of state" is in excellent agreement with the exact calculations. However, for one theory a 9% discrepancy is obtained for the highest $B1$-phase pressures, i.e., $p=30$ GPa. Results of the application of this analysis to recent linear augmented-plane-wave calculations, which make no approximation beyond the local-density approximation, are also presented and give added support to the validity of the Decker procedure. It is also shown that a five-parameter Birch formula, where tested rigorously, is an excellent representation of crystal-energy versus volume calculations. Finally, results of the second pressure derivative of the bulk modulus, evaluated at zero pressure, are found to be in fair agreement with a recent experimental determination.

## I. INTRODUCTION

The chief purpose of this paper is to consider the validity of the Decker equation of state (EOS) for sodium chloride in its $B1$ structural form, as the Decker[1] EOS plays an important role in high-pressure physics since it is the primary pressure calibrant in the region $0 \leq p \leq 30$ GPa. Using the quasiharmonic approximation, Decker fitted three parameters of a semiempirically derived expression for the pressure to the room-temperature isothermal bulk modulus and equilibrium volume, and, only approximately, to the temperature dependence above room temperature of both the bulk modulus and the thermal expansivity. Thus the Decker EOS was intended for use over a wide range of temperatures as well as pressures. Two of these fitted parameters are interatomic potential parameters. In this paper we will be concerned with the potential-energy term alone and a review of Decker's treatment of that term will be given in the following paragraph. While it is not possible to test rigorously the accuracy of the Decker EOS, we can examine how well the Decker *procedure* works when applied to results of *ab initio* theories of the properties of NaCl; in particular, the Gordon-Kim (GK) theory[2] and later refinements of it,[3-5] as well as first-principle calculations[6] within the local-density approximation[7] (LDA). These theories contain approximations which could give rise to either too close an agreement or too large a discrepancy between the theoretical EOS and the associated "Decker EOS." On the other hand, good agreement between the two would give additional confidence in the Decker procedure. An advantage of theoretical tests over experimental ones is that the latter generally must contend with the problem of nonhydrostatic pressures at high pressures.

The volume derivative of the potential energy in Decker's expression for the pressure is the static lattice contribution and it is of interest to study it alone. Decker expressed the crystal potential energy as

$$\psi=N_0(-Aq^2/r-C/r^6-D/r^8+6be^{-r/\rho}+6b_+e^{-\sqrt{2}r/\rho_+}+6b_-e^{-\sqrt{2}r/\rho_-}) , \tag{1}$$

where $r$ is the nearest-neighbor interatomic distance, $N_0$ is Avogadro's number, $q$ is the unit electron charge, $A$ is the Madelung constant, and $C$ and $D$ are van der Waals constants. Further, the Born-Mayer potential parameters, $\rho_+$ and $b_+$, were considered fixed ratios of $\rho$ and $b$. A reasonable physical approximation was made for the ratios $\rho_\pm/\rho$, i.e., Pauling ionic radii were used, but an admittedly[1] rather arbitrary choice was made for the ratios $b_\pm/b$. In this work we fit the appropriate expressions for the bulk modulus and equilibrium volume based on Eq. (1) to the results of our calculations, using the same two adjustable interatomic potential parameters, i.e., $\rho$ and $b$, as did Decker. We also use Decker's values for all fixed quantities.

## II. APPROXIMATIONS

The motivation for including Gordon-Kim based theoretical results here is partly computational feasibility. It is necessary to calculate the bulk modulus and equilibrium volume to a high degree of accuracy within the theory, because the Decker equation is based on experimental values of those quantities, which are accurately known. The basic description of the Gordon-Kim theory is given elsewhere.[2] However, particular features of our calculations are the following: The kinetic-energy term is of the Thomas-Fermi form, as originally proposed by GK. The exchange and correlation term is of the Hedin-Lundqvist (HL)[8] form, as is often used in electron-energy band and total energy calculations, and which can be shown to agree well with more recent results for exchange and correlation energy of a homogeneous interacting electron gas. The isolated ion electron densities are calculated within the effective one-electron theory, with use of the HL form of exchange and correlation energy, and with use of orbital-averaged[9] self-interaction corrections (SIC). Only pair overlap interactions are considered and we included up to third-nearest-neighbor atoms for each type of interaction, i.e., $Na^+$-$Na^+$, $Na^+$-$Cl^-$, $Cl^-$-$Cl^-$, in order to insure that all possibly significant two-body overlap contributions are included.

Finally, we briefly discuss calculations based on the potential-induced breathing (PIB) model,[3] also to be presented in this paper. The PIB model makes use of Watson spheres[10] for determining the variation of the ion electron densities (which are overlapped) with volume and *no* SIC is made for the calculations presented.[11] It is also necessary to mention an additional uncertainty which is present only in the PIB model: The energy is written as the sum of three terms, (a) one which is determined solely by the overlap of electron densities, (b) one which is given by applying an LDA energy functional expression to the single-ion electron densities, and (c) the Madelung term; within term (b) we consider both the Thomas-Fermi form and the more exact Kohn-Sham form for the kinetic-energy contribution. Just as in the GK calculations the Thomas-Fermi form for the kinetic energy is used in the overlap term, as methods for evaluating the Kohn-Sham kinetic energy for this term have not yet been developed. Additional features of the calculations were also the same as those for GK as described above.

## III. NUMERICAL PROCEDURE

The total energy was calculated at numerous volumes using our *ab initio* theories, and the results were then fit to a parametrized functional form. Several functional forms for the energy were tried including three-, four-, and five-parameter Birch and four-parameter Murnaghan forms.[12] However, among these formulas, the five-parameter Birch form generally gave statistically best fits over large volume ranges and, even for the volume range including the equilibrium volume and the lowest $B1$ phase volume, yielded results to within the precision of the calculations. In addition, by accurately fitting *ab initio* calculations over small volume ranges it was possible to insure that results such as the equilibrium volume and bulk modulus were reasonably independent of the particular fitting function used. We mention also that the precision of Gordon-Kim-type theoretical results is primarily dependent on the radial mesh over which the charge density is computed and this mesh size was varied to yield especially high-precision results over small volume regions about the equilibrium volume.

While these parametrizations were clearly done for the purpose of obtaining accurate derivatives of the total energy with respect to volume they might have some interest from the point of view of pressure calibration. For example, since the Birch five-parameter expression was found to yield agreement with all of our results it is of course a most suitable form to use for pressure calibration on the basis of our *ab initio* calculations. On the other hand the use of this Birch form requires a knowledge of two additional adjustable parameters than are needed for the Decker EOS. We stress, however, that the main purpose of this paper is to consider the Decker EOS and not to provide intercomparisons of different empirical EOS's.

## IV. RESULTS AND DISCUSSION

### A. Equilibrium properties

We present results in Table I for the equilibrium properties of special importance in employing the Decker procedure as well as results for the cohesive energy based on the Decker procedure. The results given in the first row are based on the use of Decker's own parameters in his potential-energy expression and may, therefore, be regarded as experimentally extracted results in the case of $V_0$ and $B_0$. The experimentally extracted results of Pautama,[13] Decker,[1] Spetzler, Sammis, and O'Connell[14] are based on both different experiment results and different analyses of data; e.g., Spetzler and co-workers[14] linearly extrapolated high-$T$ results to $T=0$ K. The PIB model with the use of Thomas-Fermi (Kohn-Sham) kinetic energy in the single-ion term is denoted PIB1 (PIB2) in this and succeeding tables. It is seen that both sets of PIB calculations are in closer agreement with experiment than are the more theoretically rigorous linear augmented-plane-wave (LAPW) calculations, but it must be recalled that many-body overlap interactions have been ignored in these PIB calculations and that the Wigner correlation[15] yields a value of $V_0$, in LDA calculations, which is only 2–3 % too small.[6,16]

TABLE I. Static lattice equilibrium properties of NaCl.

| | $V_0$ ($\text{Å}^3$/unit-cell) | $B_0$ (GPa) | $E_0$ (eV/unit-cell) |
|---|---|---|---|
| Decker | 43.300 | 27.92 | −8.11 |
| GK | 40.825 | 33.37 | −8.41 |
| De-GK | 40.825[a] | 33.37[a] | −8.36 |
| PIB1 | 42.658 | 26.1 | |
| De-PIB1 | 42.658[a] | 26.1[a] | −8.08 |
| PIB2 | 42.100 | 29.9 | |
| De-PIB2 | 42.100[a] | 29.9[a] | −8.22 |
| LAPW[b] | 40.96 | 31.4 | |
| De-LAPW | 40.96[a] | 31.4[a] | −8.30 |
| Pautama[c] (Expt.) | 43.221 | 27.6 | |
| Spetzler *et al.*[d] (Expt.) | 43.16 | 28.47 | |

[a] Input parameters.
[b] Reference 6. Results for Hedin-Lundqvist exchange and correlation.
[c] Reference 13.
[d] Reference 14.

TABLE II. Pressures at selected unit-cell volumes.

| | | $V=38.283$ Å$^3$ | $V=34.148$ Å$^3$ | $V=28.521$ Å$^3$ |
|---|---|---|---|---|
| Decker | $P$ (GPa) | 4.60 | 11.62 | 31.22 |
| | $-dV/V_0$ | 0.1158 | 0.2680 | 0.3413 |
| GK | $P$ (GPa) | 2.51 | 9.17 | 28.34 |
| | $-dV/V_0$ | 0.0623 | 0.1636 | 0.3014 |
| De-GK | $P$ (GPa) | 2.52 | 9.29 | 29.17 |
| PIB1 | $P$ (GPa) | 3.67 | 10.997 | 28.11 |
| | $-dV/V_0$ | 0.1026 | 0.1995 | 0.3314 |
| De-PIB1 | $P$ (GPa) | 3.61 | 9.61 | 26.06 |
| PIB2 | $P$ (GPa) | 3.60 | 10.43 | 29.95 |
| | $-dV/V_0$ | 0.0907 | 0.1889 | 0.3225 |
| De-PIB2 | $P$ (GPa) | 3.58±0.09 | 10.36±0.27 | 29.67±0.93 |
| LAPW[a] | $P$ (GPa) | 2.53 | 9.02 | 27.84 |
| | $-dV/V_0$ | 0.0653 | 0.1663 | 0.3037 |
| De-LAPW | $P$ (GPa) | 2.50±0.08 | 8.86±0.31 | 27.21±1.14 |

[a] Reference 6. Results for Hedin-Lundqvist exchange and correlation.

The static lattice cohesive energy $E_0$ was directly computed only for the GK theory, but the results for $E_0$ based on the Decker fits (denoted De-GK, etc.) yield approximate values of $E_0$ for all of the theories considered (see Table I). We point out that the use of Decker's values for the parameters yield excellent agreement with experiment for the cohesive energy.[1]

It is also of interest to briefly compare our work with that of Boyer.[17] While our GK calculation is quite similar to his, the two differ in that Boyer made use of potentials based on the overlap of Hartree-Fock free-ion electron densities, and he included only nearest-neighbor interactions for each ion-pair type. The effect in our results of including further interactions is quite small as indicated by comparing the GK results in Table I with the values 41.281 Å$^3$ and 32.7 GPa for $V_0$ and $B_0$, respectively, where the latter were obtained by ignoring interactions other than nearest-neighbor ones for each atom-pair type. For comparison, we obtain $V_0=44.1$ Å$^3$ from Figure 1 of Boyer.[16]

### B. Equation of state

In Table II we compare results for the pressure at a few selected volumes. In the table, $dV/V=(V-V_0)/V_0$ where the appropriate values of $V_0$ are found in Table I. Certain of these results are seen to differ from each other markedly, although perhaps the discrepancies can be attributed largely to the various equilibrium volumes $V_0$ obtained.[17] Nevertheless, upon following the above-mentioned "Decker" procedure we obtain a much closer agreement, which is also shown in Table II, between appropriate results, i.e., De-GK and GK, etc. (The uncertainties shown in the table correspond to the effect of estimated 2% and 3% numerical uncertainties in the PIB2 and LAPW[6] results for $B_0$, respectively; the numerical uncertainties in the PIB1 and GK bulk moduli are 1% and 0.3%, respectively, and the corresponding uncertainties in the pressures are, therefore, quite small.) A discrepancy between the PIB1 and De-PIB1 results of about 9% in the pressure at the highest $B1$ phase pressures ($\sim 30.0$ GPa) is obtained and this is somewhat greater than the uncertainty generally associated with the Decker EOS, although a discrepancy of similar magnitude is predicted[18] on the basis of Keane's EOS.[19] It is important to note that for pressures at which the Decker EOS has been tested[1] by direct measurement, i.e., $p \leq 5$ GPa, the difference between the PIB1 and De-PIB1 results is $\sim 2-3\,\%$ in the pressure, which is only slightly outside Decker's estimate of error based on the uncertainty in the input experimental parameters which he used. Thus at pressures for which the Decker EOS is known to be valid the PIB1 and De-PIB1 results are in satisfactory agreement with each other, and hence the above-mentioned 9% discrepancy is meaningful as an uncertainty estimate in the Decker EOS at $p=30$ Gpa.

It might be argued that the Decker EOS has already been satisfactorily tested by other theoretical results[4,16,20] which have yielded excellent agreement with experimental equilibrium properties and with the Decker EOS. However, those calculations involve various assumptions which could render that agreement somewhat fortuitous. Indeed, in a previous article it was shown that first principle calculations within local-density-functional theory do not yield precise agreement with the room-temperature Decker EOS.[6] It should also be mentioned that, for convenience, we have considered the static lattice case alone whereas Decker's procedure incorporated lattice-vibrational effects. Nevertheless, we believe a test of Decker's static lattice term as we have done here is of interest, although it should not preclude similar studies in which lattice-vibrational effects are included.

### C. Pressure dependence of bulk modulus

In addition, we have also examined the pressure dependence of the bulk modulus, as recent attempts to experimentally extract its second pressure derivative $B''$ have been made.[18,21] Our results (see Table III) for $B'$ and $B''$ were obtained directly from the five-parameter Birch fit to our results for total energy versus volume over large volume ranges. The ability of the Birch formula to represent total energy versus $V$ is perhaps indicated by the fact that corresponding to our GK results, which represent our most precise results, the standard deviation of the least-squares fit was 0.05 meV over a volume range $0.661 < V/V_0 < 1.175$, which indeed is considered to be the precision of those results. Accurate least-squares fits were made over large volume ranges in the case of our PIB and LAPW[6] calculations as well, but those calculations were performed only to about 1- or 2-meV precision, which is state-of-the-art precision in LAPW calculations. In the latter cases the range of results for $B'$ and $B''$ among the calculations also represents our estimate of uncertainty, as indicated in Table III. (It is noted that the results quoted in Table I corresponding to PIB and GK were based on least-squares fits to various fitting functions, over narrow volume ranges, of higher-precision energy calculations than the above-mentioned precisions.) Also compared in Table III are results obtained on the basis of the Decker static lattice expression. These latter results reasonably compare with those[12] based on the room-temperature Decker EOS. Finally, Hart and Greenwood[21] made ultrasonic measurements of the elastic moduli of single crystals of the sodium halides at pressures up to 1.5 GPa and analyzed their results in terms of a linear plus quadratic pressure dependence. They obtained the values 5.05 and $-0.14\ \mathrm{GPa}^{-1}$ for $B'$ and $B''$, respectively, and it should be noted that they represent room-temperature measurements. The admittedly rather crude agreement among the values for $B''$ shown in this paper is encouraging as comparisons with earlier determinations[22] of $B''$ are much poorer due to the difficulty in experimentally determining $B''$.

TABLE III. Static lattice results for $B'$ and $B''$.

| | GK | PIB1, PIB2, LAPW | Decker[a] |
|---|---|---|---|
| $B'$ | 4.84 | (4.7,5.1) | 4.73 |
| $B''$ ($\mathrm{GPa}^{-1}$) | $-0.18$ | $(-0.25,-0.17)$ | $-0.20\pm0.02$ |

[a] Based on potential-energy parameters given in Ref. 1.

## V. CONCLUSIONS

We have considered a few *ab initio* methods chiefly for the purpose of investigating the validity of the Decker phenomenological extrapolation procedure for determining the equation of state of NaCl. Generally, we have found the Decker procedure to be quite reliable. In the course of this study it has also been shown that the five-parameter Birch energy expression is an excellent representation of *ab initio* calculations over a wide range of volumes—at least covering the range for which the $B1$ phase of NaCl is stable.

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[1] D. L. Decker, J. Appl. Phys. **42**, 3239 (1971).

[2] R. G. Gordon and Y. S. Kim, J. Chem. Phys. **56**, 3122 (1972).

[3] L. L. Boyer, M. J. Mehl, J. L. Feldman, J. R. Hardy, J. W. Flocken, and C. Y. Fong, Phys. Rev. Lett. **54**, 1940 (1985); **57**, 2331(E) (1986); M. J. Mehl, R. J. Hemley, and L. L. Boyer, Phys. Rev. B **33**, 8685 (1986).

[4] R. J. Hemley and R. G. Gordon, J. Geophys. Res. **90**, 7803 (1985).

[5] C. Muhlhausen and R. G. Gordon, Phys. Rev. B **23**, 900 (1981).

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

[7] W. Kohn and L. J. Sham, Phys. Rev. A **140**, 1133 (1965).

[8] L. Hedin and B. I. Lundqvist, J. Phys. C **4**, 2064 (1971).

[9] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[10] R. E. Watson, Phys. Rev. **111**, 1108 (1958).

[11] Application of SIC decreases the value of $V_0$ by about 8%, in bad agreement with experiment.

[12] See F. Birch, J. Geophys. Res. **83**, 1257 (1978), for a thorough comparison of parametrized equations of state.

[13] Y. Pautama, Ann. Acad. Sci. Fenn., Ser. A **6**, 129, 1 (1963).

[14] H. Spetzler, C. G. Sammis, and R. J. O'Connell, J. Phys. Chem. Solids **33**, 1727 (1972).

[15] E. Wigner, Trans. Faraday Soc. **34**, 678 (1938), and corrected in D. Pines, Solid State Phys. **1**, 375 (1955).

[16] S. Froyen and M. L. Cohen, Phys. Rev. B **29**, 3770 (1984).

[17] L. L. Boyer, Phys. Rev. B **23**, 3673 (1981).

[18] L. C. Chhabildas and A. L. Ruoff, J. Appl. Phys. **47**, 4182 (1976).

[19] A. Keane, Aust. J. Phys. **7**, 322 (1954).

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

[21] S. Hart and P. H. Greenwood, Solid State Commun. **46**, 161 (1983).

[22] See Refs. 20 and 21 for thorough reviews of the experimental literature.