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Theoretical study of the elastic and thermodynamic properties of sodium chloride under pressure

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We have calculated the pressure-volume relationship at 293 K, the pressure dependence of the elastic constants, and some other thermodynamic properties of sodium chloride, using two rigid-ion models. Monte Carlo simulations, anharmonic perturbation theory, and quasiharmonic theory were used as appropriate. Special care has been taken to make sure that the numerical results are of benchmark quality—they accurately reflect the predictions of the models used. The results show the necessity of including a second-neighbor interaction between like ions. Without this interaction the $B1$-$B2$ phase transition occurs at much too low a pressure. We find good agreement with experiment at high pressures except for the deviation from the Cauchy relation. We use our results to extract quantitative predictions on the volume dependence of three-body forces in NaCl.

I. INTRODUCTION

We recently calculated the thermodynamic properties of a very simple rigid-ion model of sodium chloride,[1] using a combination of Monte Carlo and anharmonic perturbation-theory techniques. Our principal aim in that work was to present benchmark-quality results for a simple model with long-range Coulomb forces. The results along the zero-pressure isotherm were in very good agreement with experiment considering the simplicity of the model. Since much experimental information is available for nonzero-pressure conditions, where sodium chloride has for many years been used as a standard,[2] it seemed to us worthwhile to extend our calculations to the moderate- and high-pressure regimes, again making sure that the numerical reliability of our work was of benchmark quality.

We quickly recognized that this regime presented a difficult challenge to the model, which incorporates a single short-range potential, represented by a Born-Mayer formula, acting between unlike ions only. A number of calculations have been made in the past with similar models, usually using a static energy formalism,[3] and they show that the model becomes unstable at a pressure well inside the observed range of stability of the $B1$ phase, the instability being caused by C_{44} going to zero as a function of pressure.

Our original model has many inadequacies that may be responsible for this instability problem. The effects of ionic polarizability are completely neglected in the rigid-ion formalism. A shell model[4] is often used to include these effects, but the basic premise of this model has recently been brought into question.[5,6] In any case, in a centrosymmetric crystal the elastic properties do not depend on the polarizability, at least in the harmonic approximation. The Born-Mayer form of the short-range potential may not be sufficiently accurate for small separations. We cannot rule this out as a reason for the difficulty, but a major change would be needed to stabilize the model at high pressures. A third possibility is that three-body forces become important at small interionic distances. We know that three-body forces are present because of the failure of the Cauchy relation, $C_{12}=C_{44}$, even at low temperatures. It seems plausible that this contribution becomes more important as the crystal is compressed. However, we do not believe there is a well-justified formalism for completely including these effects at the present time. Indeed, we shall use our results to try to extract from the experimental results some information about the volume dependence of the three-body forces.

One remaining deficiency of the model that is relatively easily corrected is the neglect of the second-neighbor forces. A careful analysis of these has been given by Catlow, Diller, and Norgett.[7] They give, as their model 2, a form of the Cl-Cl potential that should be valid for all the alkali chlorides. if we include this potential in our model, with the parameter values given by Catlow *et al.*, it is necessary to make adjustments to the two parameters of the Born-Mayer nearest-neighbor potential so that the volume and bulk modules at 0 K and zero pressure are once more correctly reproduced. We have carried out the calculations described in this paper both for our original nearest-neighbor model called model 1, and for the model incorporating this Cl-Cl second-neighbor interaction called model 2.

The experiments with which we wish to make contact consist of (1) shock-wave data that can be converted to a single isotherm up to a pressure of 320 kbar,[8] (2) measurements of the room-temperature elastic constants up to a pressure of ~80–90 kbar,[9,10] and (3) measurements of the elastic constants at pressures up to 10 kbar over a wide range of temperatures.[3] We find that the two-parameter model accounts quite well for most of these properties, and that the inclusion of the second-neighbor

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Cl-Cl interaction removes most of the discrepancies. The only discrepancy remaining between theory and experiment is the deviation from the Cauchy relation.

II. COMPARISON WITH SHOCK-WAVE DATA

From measurements of the propagation of a shock wave through a material, the pressure-volume-temperature relationship along the Hugoniot can be determined, and the pressure-volume relationship along an isotherm can be calculated from this. Fritz, Marsh, Carter, and McQueen[8] have presented data for the 293 K isotherm in sodium chloride for pressures up to 320 kbar. Representative data are shown as the solid line in Fig. 1. At the highest pressure, the volume is reduced to 64% of its zero-pressure volume, so that these data sample the interionic potential over a wider range of nearest-neighbor distances than any other measurement we are aware of. Measurements of the pressure-volume relationships can also be made by static methods, though generally the pressures realized are lower. Results for sodium chloride that are in good agreement with the shock-wave measurements have been given by Vaidya and Kennedy.[11]

The free energy F of the crystal can be written as the sum of the energy of the static lattice plus a vibrational contribution, and for the simple models we have used the static energy that consists of short-range contributions from nearest and second-nearest neighbors and the Madelung electrostatic energy:

$$\begin{aligned} F &= \phi_{\mathrm{st}} + F_{\mathrm{vib}} \\ &= N(6V_0 e^{-r/\rho} + 6\phi_{\mathrm{Cl\text{-}Cl}} - \alpha_M e^2/r) + F_{\mathrm{vib}} \; . \end{aligned} \tag{1}$$

Here r is the nearest-neighbor distance, and the values of V_0 and ρ are $3.221\,774\,3\times10^{-9}$ erg and 0.295 01 Å, respectively, for the model with only nearest-neighbor forces, and $1.333\,327\,6\times10^{-9}$ erg and 0.335 90 Å when second-neighbor forces are included. In that case $\phi_{\mathrm{Cl\text{-}Cl}}$ was taken from Catlow *et al.*[7] It consists of a van der Waals potential at large distances, a rather smooth polynomial just outside the minimum, a steeply rising polynomial inside the minimum, and a Born-Mayer potential at very small separations (which are not reached even in the compressed solid). N is the number of unit cells and α_M is the Madelung constant. The simplest calculation we can make is to ignore the vibrational contribution to the free energy. This leads to the triangles in Fig. 1 when the two-neighbor potential is used. The comparable result for the nearest-neighbor model is identical at zero pressure, and 1.6% smaller at the highest pressure. Clearly this property is not sensitive to the potential model.

A number of authors have made similar calculations, and have also included the vibrational contributions by using the Mie-Grüneisen or Hildebrand equations of state.[2] It is not difficult to calculate the free energy exactly in a quasiharmonic approximation as a sum of contributions from the individual normal modes

$$F_{\mathrm{vib}} = \sum_{\mathbf{q}j} \{\hbar\omega_{\mathbf{q}j}/2 + kT \ln[1-\exp(-\hbar\omega_{\mathbf{q}j}/kT)]\} \; . \tag{2}$$

Once the form of the interatomic potential is chosen, the quasiharmonic frequencies, and hence the vibrational free energy, are completely determined. It is inconsistent to treat, for example, the Debye temperature and Grüneisen parameter as independent quantities. We have calculated the sum over the Brillouin zone for a range of volumes, at a temperature of 293 K, and found the volume-pressure relationship by suitable interpolation. The result is represented by the open circles in Fig. 1. Again this curve is calculated for the model including second-neighbor interactions. The model with only nearest-neighbor short-range interactions gives an almost identical result, except that it terminates at a pressure of 220 kbar (the volume being 1.8% smaller), because the crystal becomes unstable (certain quasiharmonic frequencies become imaginary). We have also made Monte Carlo calculations at several compressed volumes. These are shown as the closed and open squares in Fig. 1, and are in excellent agreement with the quasiharmonic results for both models studied. We would expect, in general, that a solid becomes less anharmonic as it is compressed. To verify this, we have also calculated the free energy using anharmonic perturbation theory, and find that the results, which are not very different from the quasiharmonic values at zero pressure, become indistinguishable at high pressures. Our Monte Carlo calculations become

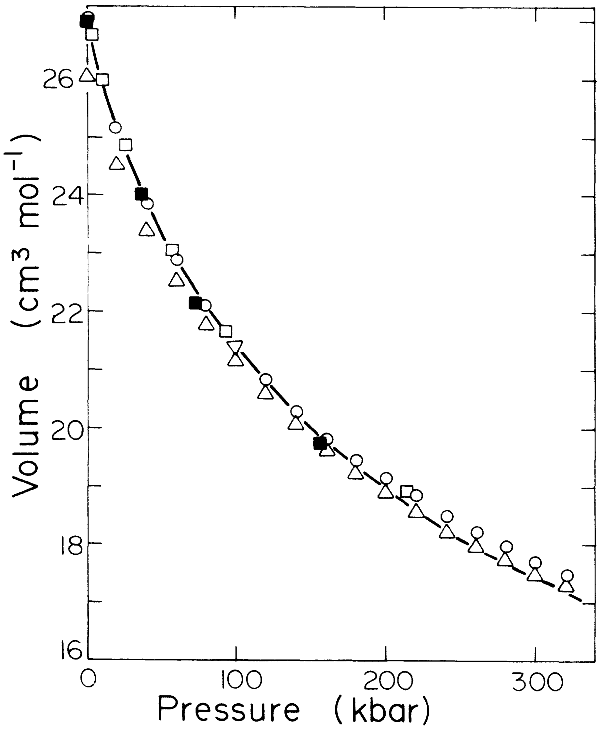

FIG. 1. Volume-pressure relationship for NaCl at 293 K. The triangles are the static energy calculation, model 2; lattice dynamics, model 2, open circles; Monte Carlo, model 1, solid squares; Monte Carlo, model 2, open squares. The solid line represents experimental results from Ref. 8.

progressively less reliable at high pressures. At a temperature of 293 K, the quantum correction to our Monte Carlo results, which we calculate as the first term in the Wigner-Kirkwood expansion, is important, even at zero pressure. As the pressure increases, the vibration frequencies generally increase, and the quantum correction gets larger. if we wished to use Monte Carlo techniques in the high-pressure range we would need the quantum Monte Carlo formalism. However, since the crystal is becoming almost harmonic at these pressures this does not seem necessary here. We regard the agreement with experiment as generally excellent, but point out that this shows the unsuitability of this property for testing the potential. The equation of state results are listed in Table I.

A quantity that is required in the reduction of the shock-wave data is the Grüneisen parameter, γ. An empirical formula is usually used to represent its volume dependence.[8] We have calculated the volume dependence of γ, where $\gamma=\beta_p V/\chi_T C_V$, as predicted by our two potentials. There are, unfortunately, no experimental data available for comparison with our results. The results for the two models are shown in Fig. 2. The closed circles and squares are calculated for the model with only nearest-neighbor short-range forces using lattice dynamics and Monte Carlo, respectively. As the model becomes unstable its Grüneisen parameter drops precipitously. Since the real material does not become unstable near this point, we do not expect it to show this behavior. The corresponding results for our model 2 incorporating the Catlow potential for the Cl-Cl interaction are shown by the open circles and squares, respectively. Our results reveal an unexpected defect in the Catlow potential. The

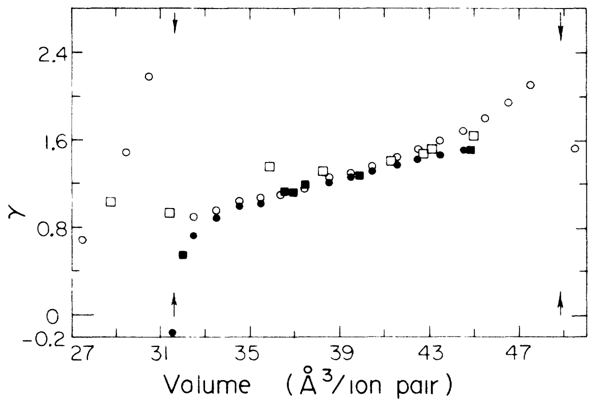

FIG. 2. Theoretical volume dependence of the Grüneisen γ at 293 K. Closed squares and circles are Monte Carlo and lattice-dynamical results for the nearest-neighbor model. Open squares and circles are for Monte Carlo and lattice-dynamical results for the model including second-neighbor forces. The one standard deviation random error in the Monte Carlo results is ±0.1, except at the volume discontinuity, where it is ±0.3. The pairs of arrows correspond to the two potential discontinuities discussed in the text.

TABLE I. Equation of state for NaCl, pressure in kbar, volume in cm^3/mole. The theory is based on the Catlow potential, Ref. 7, including second-neighbor Cl-Cl forces. The standard deviation random errors of the Monte Carlo results for the pressures are less than 1% for $p > 10$ kbar.

		Volume	
p	Experiment	Lattice dynamics	Monte Carlo
0	27.00	27.05	27.07
10	26.01		
13.8			25.71
20	25.18	25.14	
24.7			24.88
40	23.89	23.86	
58			23.02
60	22.90	22.87	
80	22.09	22.07	
92			21.65
100	21.40	21.38	
120	20.81	20.79	
140	20.27	20.27	
160	19.80	19.79	
180	19.36	19.43	
200	18.96	19.15	
216			18.89
220	18.59	18.85	
240	18.24	18.52	
260	17.99	18.22	
280	17.71	17.94	
300	17.45	17.68	
320	17.21	17.45	

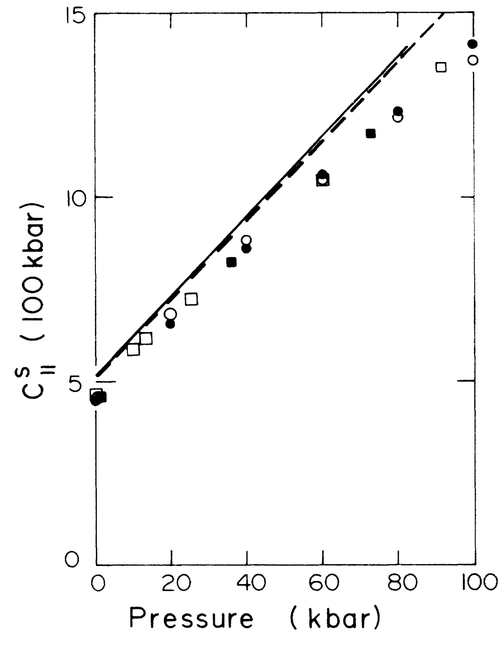

FIG. 3. c_{11} in NaCl under pressure. Solid and dashed lines are experimental results, from Refs. 9 and 10, respectively. Solid symbols, squares for Monte Carlo and circles for lattice dynamics, calculated for our model with only unlike neighbor short-range forces. Open symbols, squares for Monte Carlo and circles for lattice dynamics, calculated for our model including second-neighbor forces. The one standard deviation random error of the Monte Carlo results is about the size of the symbols used.

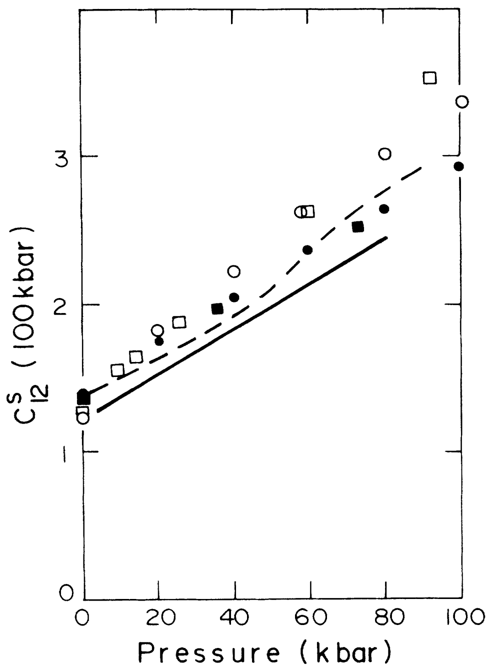

FIG. 4. c_{12} for NaCl under pressure. Symbols are as in Fig. 3.

large discontinuity, which occurs at a second-neighbor distance of 3.551 Å, is a direct consequence of a discontinuity in the third derivative of the potential at that separation. The potential, and its first and second derivatives, are constrained to be continuous, but that is not true of the higher derivatures. There is a similar, though smaller discontinuity at a second-neighbor distance of 4.103 Å, which is reached only at higher temperatures. We can reach this volume at room temperature by extending our calculations to negative external pressure. In view of this defect in the Catlow potential, we cannot rely on the detailed predictions of this model for γ, though it may well show the correct values for γ over a large range of volumes. It is interesting to note that the discontinuities observed using lattice dynamics are suppressed by the Monte Carlo method since the latter always samples the crystal over a range of separations.

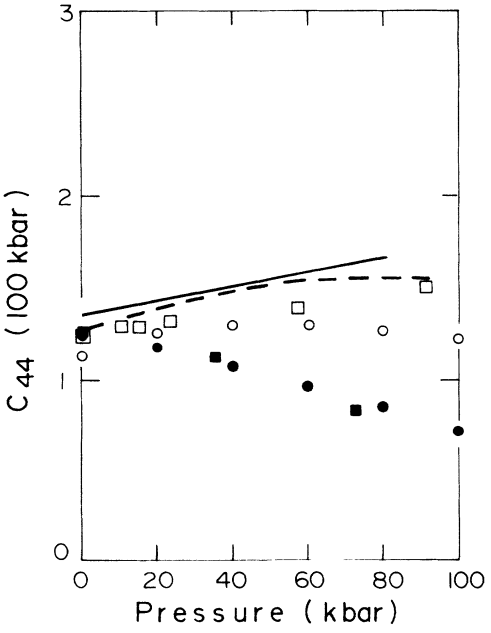

FIG. 5. c_{44} for NaCl under pressure. Symbols are as in Fig. 3.

III. ROOM-TEMPERATURE ELASTIC CONSTANTS

The elastic constants at room temperature have been measured up to a pressure of 80 kbar by Kinoshita, Hamaya, and Fujisawa,[9] and up to 90 kbar by Voronov, Chernysheva, and Goncharova.[10] The two sets of results are in good agreement, considering the difficulty of the experiment. Smooth lines through the two sets of results are shown as the solid and dashed lines, respectively, in Figs. 3, 4, and 5. The closed and open circles show the values calculated for the nearest-neighbor and two-neighbor models, respectively, from the strain derivatives of the quasiharmonic free energy. Our procedure was to calculate the sum over the normal modes for slightly distorted unit cells, and to find the derivatives by numerical differentiations. We also made a number of Monte Carlo runs, using both potential models, under various conditions of temperature and pressure. Some room-temperature results are shown as closed and open squares in the figures.

The two experimental lines for c_{11} are in good agreement with each other. The two sets of calculated values are also close together, and are less than 10% below the experiments. The models were fitted to the bulk modulus at 0 K, so that this 10% discrepancy at the highest pressure indicates a shortcoming of the potential models whose predictions are identical. However, the slopes of the calculated lines are close at the experimental slope.

In the case of c_{12} the experimental uncertainties are much larger, and the differences between the two sets of experimental data are not significant. It is interesting to note that our two models also predict different results at the highest pressures. The difference is currently of the same order as the experimental uncertainty.

The largest difference between the two model calculations occurs, as expected, in c_{44}. The value calculated for the model with only nearest-neighbor short-range forces falls sharply as the pressure increases, and in fact it reaches zero at a pressure of about 220 kbar. The value of c_{44} for the model including the second-neighbor potential is almost constant over the pressure range shown in Fig. 4, and it actually increases at higher pressures. It does not go to zero for pressures up to 320 kbar. We again note that our Monte Carlo results are less reliable than the lattice-dynamical results at the highest pressures because of the increasing quantum corrections. The pressure dependence of the elastic constants are presented in Table II.

IV. PRESSURE DEPENDENCES AT HIGH TEMPERATURES

Spetzler, Sammis, and O'Connell[3] have measured the elastic constants of sodium chloride at pressures up to 10 kbar and over a temperature range of 300–800 K. They have combined their results with the zero-pressure values for the heat capacity and thermal expansion to integrate the thermodynamic relationships for the various pressure derivatives. Unfortunately, the values they used for the heat capacity are old, and not in agreement with more recent values.

In view of the high temperatures involved, we have used the Monte Carlo technique to find the values of the thermodynamic properties of our models. Runs of about 4×10^6 configurations were performed at temperatures of 300, 550, and 800 K, and at pressures up to 10 kbar. In view of the statistical uncertainty in each quantity, it was not possible over this pressure range to distinguish any nonlinearity in the pressure dependence. We have therefore calculated average pressure derivatives over the range 0–10 kbar, and have processed the experimental values in the same way.

The results are shown in Table III. The uncertainties both for the calculated and experimental values are quite large. The values for the pressure derivative of C_p at 300 K are essentially zero, and for most values the uncertainties are probably about 20%. Bearing this in mind, we regard the agreement between the two sets of calculated values and the experimental values to be generally very satisfactory. The one major difference between the two model calculations is once again in the pressure dependence of c_{44}, which has, as expected, the wrong sign for the nearest-neighbor model.

V. THE ROLE OF SECOND-NEIGHBOR FORCES

In our earlier zero-pressure calculations a simple two-parameter rigid-ion model was shown to give excellent agreement with a wide range of thermodynamic properties of sodium chloride. In this work we have seen that the same model performs reasonably well in describing the properties of sodium chloride under pressure, except with regard to two related properties: c_{44} decreases strongly as the pressure increases, and the crystal becomes unstable at pressure well below the observed $B1$-$B2$ phase transition. Similar results to these have been noted previously by Voronov *et al.*[10] and by Spetzler *et al.*[3] who showed that the inclusion of a second-neighbor force could extend the range of stability of the $B1$ phase to above the observed transition, although c_{44} still decreased somewhat with pressure.

Two questions needed to be answered with regard to these results. First, could a suitable choice of second-neighbor potential more closely reproduce the experimentally observed pressure dependence of c_{44}? Second, why was our nearest-neighbor model so successful in the zero-pressure calculations? We have shown that the answers to both questions are indicated by the work of Catlow *et al.*[7] on the potentials acting between halogen ions in the alkali halides. As their model 2, they identify

TABLE II. Elastic constants (in units of 100 kbar) of NaCl as a function of pressure (in kbar). The theory is based on the Catlow potential, Ref. 7, including second-neighbor Cl-Cl forces.

	C_{11}^S				C_{12}^S				C_{44}			
	Experiment		Theory		Experiment		Theory		Experiment		Theory	
p	Ref. 9	Ref. 10	Lattice dynamics	Monte Carlo	Ref. 9	Ref. 10	Lattice dynamics	Monte Carlo	Ref. 9	Ref. 10	Lattice dynamics	Monte Carlo
0	5.1	5.03	4.43	4.64±0.01	1.22	1.41	1.22	1.29±0.01	1.36	1.27	1.13	1.214±0.003
10.1				5.82±0.01				1.58±0.01				1.281±0.004
13.8				6.13±0.01				1.637±0.003				1.268±0.002
20	7.34	7.22	6.80		1.53	1.62	1.77		1.44	1.38	1.26	
24.7				7.25±0.01				1.91±0.01				1.308±0.003
40	9.52	9.50	8.75		1.83	1.96	2.22		1.51	1.48	1.30	
58				10.40±0.02				2.69±0.01				1.40±0.01
60	11.70	11.59	10.51		2.14	2.40	2.63		1.59	1.54	1.30	
80	13.88	13.72	12.15		2.44	2.75	3.02		1.67	1.55	1.27	
90		14.67				2.92				1.55		
92.4				13.54±0.06				3.54±0.03				1.50±0.03
100			13.71				3.38				1.23	

four expressions for the potential, depending on the ionic separation. Outside a characteristic distance r_a, the potential is of the C/r^6, the van der Waals form. Between r_a and the distance r_m corresponding to the minimum of the potential, the potential is represented by a rather flat third-order polynomial. The values of r_m and r_a are 3.551 and 4.103 Å, respectively, for the Cl ion. At zero pressure the second-neighbor distance in sodium chloride varies from 3.956 Å at 0 K to 4.150 Å at 1050 K. Over most of this range the second-neighbor force constants are small. However, the room-temperature second-neighbor distance varies from 3.988 Å at zero pressure to 3.454 Å at 300 kbar. Over this range, the second-neighbor bond stretching force constant, calculated from the expressions given by Catlow *et al.*, increases substantially. Thus we could successfully ignore the second-neighbor potential in the zero-pressure calculations, but it must be included at the small ionic separations that occur at high pressure. We have shown that the small increase of c_{44} with pressure is correctly reproduced by this potential.

We find additional support for the quenching of the van der Waals interaction in calculations we have recently performed on potassium chloride.[12] There, the second-neighbor distance is always *greater* than r_a, and so it is necessary to include the C/r^6 interaction to get good agreement with experiment even at zero pressure.

The use of four separate expressions for the potential does lead to difficulties. Catlow *et al.* required that the potential and its first and second derivatives should be continuous, but not surprisingly the third and higher derivatives show large discontinuities at r_m and r_a. Properties that depend rather directly on the third derivatives are the thermal expansivity and the Grüneisen parameter, γ, and the values calculated for these quantities, including the Catlow *et al.* second-neighbor interaction, clearly show large and abrupt changes as the second-neighbor distance crosses the values r_a and r_m.

VI. THE CAUCHY RELATION DEVIATION

One discrepancy in our model that the inclusion of a second-neighbor interaction does nothing to correct is the experimentally observed deviation from the Cauchy relation

$$C^{\mathrm{st}}_{12}=C^{\mathrm{st}}_{44}\ , \tag{3}$$

where the C^{st}_{ij} are second derivatives of the static energy with respect to finite strain parameters. The C_{ij} are related to the c_{ij} found from speed of sound experiments by

$$\begin{aligned} c_{12}&=C_{12}+P\ ,\\ c_{44}&=C_{44}-P\ . \end{aligned} \tag{4}$$

A thorough discussion of these relations has been given by Wallace.[13] The deviation

$$\Delta C=C_{12}-C_{44} \tag{5}$$

can arise from three-body forces or from vibrational contributions to the elastic constants. In our model calculations, only the vibrational term is present, and the calculated ΔC is positive. At very low temperatures the vibrational contribution is negligible, and ΔC, which must arise entirely from three-body forces, is negative in sodium chloride. Experimentally, ΔC changes sign somewhat below room temperature, and we suppose that this arises from a cancellation between the two contributions.

We will assume that the two-body force models give a useful estimate of the vibrational contribution to ΔC and so we can estimate the three-body contribution as

$$\Delta C_{\text{three body}}=\Delta C_{\text{expt}}-\Delta C_{\text{theor}}\ , \tag{6}$$

and we would expect this to be basically a function of volume, or of nearest-neighbor distance.

In Fig. 6(a) we plot experimental values of ΔC, taken from three sources,[3,14,15] plotted versus the nearest-neighbor distance. The large scatter of the points shows clearly that ΔC is not a function simply of r, the nearest-neighbor distance.

In Fig. 6(b) we have subtracted the theoretical values of ΔC, to give an estimate of $\Delta C_{\text{three body}}$. On the scale of this graph both models for the two-body forces give the same results. The scatter of the points is reduced enormously and is within the experimental uncertainty. The positive values at large r_0 are probably not significantly different from zero. While the experimental uncertain-

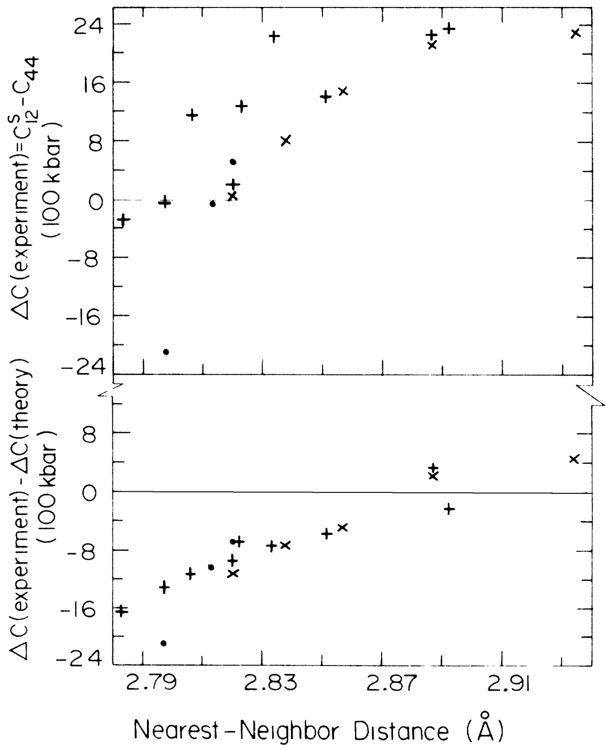

FIG. 6. (a) Cauchy deviation $\Delta C=C^S_{12}-C_{44}$ for NaCl. Experimental values from Refs. 14 (filled circles), 15 (multiplication symbols), and 3 (plus signs). (b) Difference between the experimental and calculated ΔC. Symbols as in (a).

TABLE III. Pressure derivatives of thermodynamic and elastic properties. Model 1 includes short-range forces only between unlike ions and model 2 includes the second-neighbor Cl-Cl forces. Experimental results are from Ref. 3.

Property	Temperature (K)	Model 1	Model 2	Experiment
$\partial C_p/\partial P$	300	-0.08	-0.05	-0.07
(J/mole K kbar)	550	-0.19	-0.04	-0.15
	800	-0.32	-0.17	-0.25
$\partial \beta_p/\partial P$	300	-2.6	-2.0	-2.2
(10^{-6}/K kbar)	550	-3.1	-2.8	-3.1
	800	-5.1	-4.0	-4.5
$\partial c_{11}^S/\partial P$	300	11.1	11.0	10.8
	550	11.2	11.4	10.9
	800	11.5	11.7	11.0
$\partial c_{12}^S/\partial P$	300	1.8	2.5	1.8
	550	2.2	2.7	2.2
	800	3.1	3.1	2.6
$\partial c_{44}/\partial P$	300	-0.39	0.55	0.33
	550	-0.17	0.46	0.44
	800	-0.05	0.56	0.58

ties, which are about 10 kbar in absolute uncertainty, do not permit us to extract a unique analytic form, the residual three-body contribution to ΔC is falling very rapidly to zero as the nearest-neighbor distance increases. We hope that these results will encourage a new examination of this very old problem.

VII. CONCLUSIONS

The two-parameter rigid-ion model that very successfully accounted[1] for the zero-pressure thermodynamic properties of sodium chloride is almost as successful in describing the corresponding properties under pressure. However, it cannot be regarded as giving reliable predictions of all properties because of the incorrect pressure dependence it gives for c_{44}. This particular discrepancy is remedied by the inclusion of a second-neighbor interaction. The form of Cl-Cl potential suggested by Catlow *et al.*[7] is fairly successful, but the discontinuities in the third derivative of that potential lead to unphysical discontinuities at high pressures in some properties that depend on that derivative, such as the Grüneisen constant, γ.

We have ignored three-body forces in our calculations. While several formalisms[16–18] have been proposed for these, none at the moment is capable of accurately predicting the deviation from the Cauchy relation. We have used our results to estimate for the first time what part of this deviation is caused by the three-body forces.

ACKNOWLEDGMENTS

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