

of  $Z$  among 12 compounds to be dramatic proof that eq. (1) is a good approximation to the interatomic forces in alkali halide crystals.

### 3. Comparison with experiment

Because explicit thermal corrections are made in these calculations, it is possible to compare theory to experiment over a wide range of temperatures. Of perhaps greatest interest is the Grüneisen parameter discussed in subsection 2.2. The Grüneisen parameter calculated from the normal mode spectrum of NaCl by eq. (5),  $\gamma_{th}$ , is compared with experimental results over a wide temperature range in fig. 1.  $\gamma_e$ , which occurs in

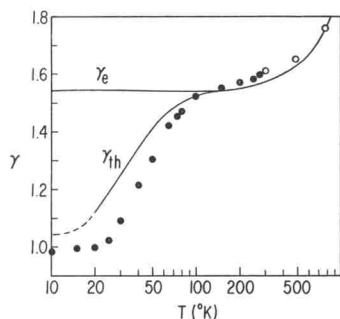


Fig. 1. Grüneisen parameter of NaCl versus temperature in NaCl. ● - WHITE (1965); ○ - SPETZLER *et al.* (1972); — - theoretical calculation.

the equation of state (eq. 3) is also shown. The 10% agreement with experiment approaches the accuracy of others, who have used much more detailed models than the present one, and whose calculations have been limited to zero pressure (for example, ACHAR and BARSCH, 1971a, b; NAMJOSHI *et al.*, 1971).

My theoretical calculation of the adiabatic and isothermal bulk moduli are compared with experimental data over a wide range of temperatures, in fig. 2. The agreement is excellent up to about 600 K. The calculated shear elastic constant  $C_{44}$  (not shown) is within 1 or 2% of experimental values up to at least 800 K.

The other shear elastic constant,  $C_s \equiv \frac{1}{2}(C_{11} - C_{12})$ , is the only elastic constant which is not used as an input parameter. Its value is determined essentially by the Cauchy relation,  $\tilde{C}_{12} - \tilde{C}_{44} = 2\tilde{P}$ , which is a result of the assumption of a potential based on two-body interactions. In NaCl, the calculated value of  $C_s$  differs from experiment by about 7%, while the pressure derivative is in error by 15%.

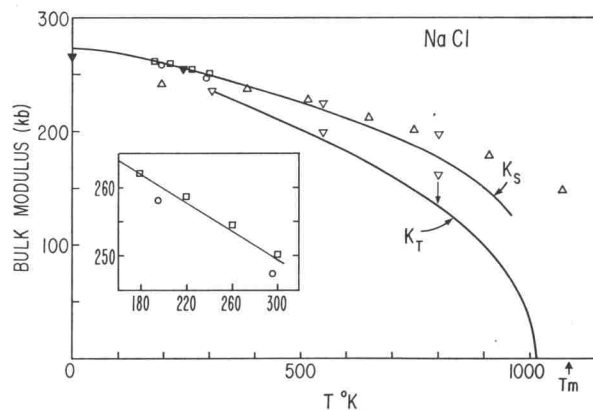


Fig. 2. Adiabatic and isothermal bulk moduli of NaCl versus temperature. □ - GHAFELEHBASHI *et al.* (1971); ○ - BARTELS and SCHUELE (1965); ▽ - SPETZLER *et al.* (1972); ▼ - LEWIS *et al.* (1962); △ - SLAGLE and MCKINSTRY (1967); — - theoretical calculation.

A comparison of the predicted pressure derivatives of  $K_s$  and  $C_{44}$  is given in fig. 3, over a wide temperature range. The agreement of  $dC_{44}/dP$  is fairly good over the entire temperature range. The predicted  $dK/dP$  rises above the experimental data at about 400 K, with the disagreement becoming serious above about 600 K. The unusually low value of  $dK/dP$  reported by GHAFELEHBASHI and KOLIWAD (1970) at 180 K is inconsistent with the earlier result of BARTELS and SCHUELE (1965) at 195 K, and is hard to explain in terms of the quasiharmonic approximation.

It is apparent that more sophisticated thermal corrections than the quasiharmonic approximation will be necessary above about 600 K. The explicit inclusion of fourth-order vibrational effects begins to differ from the quasiharmonic approximation at about 300 K. Its inclusion in the present model calculations

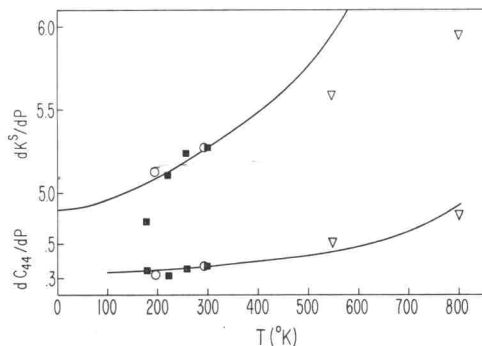


Fig. 3. Pressure derivative of  $K_s$  and  $C_{44}$  versus temperature in NaCl. Symbols as in fig. 2.

would be straightforward (COWLEY, 1971; GLYDE and KLEIN, 1971).

The second pressure derivatives of the elastic constants have been reported for NaCl by SPETZLER *et al.* (1972), and for five other alkali halides by CHANG and BARSCH (1971) and BARSCH and SHULL (1971). Predictions of my model are in fair agreement with the results of Barsch and his coworkers; however, neither my model nor that of SAMMIS (1971) can explain the unusually large values reported for NaCl. The measurement of the second pressure derivatives is a difficult task, and while this disagreement is cause for concern, a full evaluation cannot be made until the experimental results on a single compound are agreed upon by more than one laboratory.

#### 4. Extrapolation to high pressure

##### 4.1. The elastic constants

The procedures discussed in the preceding two sections permit the calculation of the elastic constants to high pressure at arbitrary temperature. The shear elastic constant  $C_{44}$  in NaCl is of particular interest for two reasons. First, a relatively low value of  $C_{44}$  at high pressure may be associated with the phase transition to the CsCl structure discovered by BASSETT *et al.* (1968) at 300 kbar. Second, a number of theorists have speculated about the variation of  $C_{44}$  with pressure, and it is useful to compare their predictions to this theory. A comparison of several theoretical extrapolations of  $C_{44}$  versus pressure is given in fig. 4. SAMMIS's (1971) lower curve results from a potential similar to this paper, but neglecting the anion-anion interaction. This results in a value of  $C_{44}$  which decreases much too rapidly with

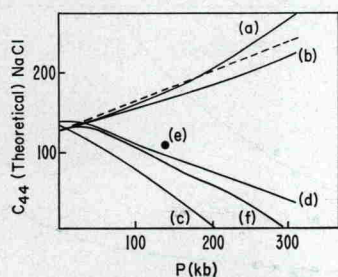


Fig. 4. Comparison of different theoretical extrapolations of shear constant  $C_{44}$  in NaCl to high pressure. (a) this paper; (b) DEMAREST (1972); (c) SAMMIS (1971), no anion interaction; (d) SAMMIS (1971), anion interaction; (e) WEIDNER and SIMMONS (1972); (f) THOMSEN (1972); --- linear extrapolation.

pressure and reaches zero before the observed phase transition. Similar results were achieved by ANDERSON and DEMAREST (1971) using a similar model. By including an anion interaction of the same strength as measured between inert gas ions, he obtained the higher curve, which still does not fit the experimental pressure derivative at zero pressure. A much stronger anion-anion force is needed to explain the pressure derivative of  $C_{44}$ . WEIDNER and SIMMONS (1972) predict  $C_{44}$  at only one pressure, assuming that the anion and coulombic forces are the same as in LiCl at the same volume. THOMSEN (1972) used finite strain theory to predict  $C_{44}$  at high pressure, using a model prediction of  $d^2C_{44}/dP^2$  as an input parameter, and predicting that  $C_{44}$  will vanish right at the observed transition.

My own predictions differ markedly from the others. My predicted curve for  $C_{44}$  is at first slightly concave downward, then upward, and stays close to the linear extrapolation (dashed line). The change in sign of  $d^2C_{44}/dP^2$  which may be an explanation for the disagreement with the finite strain theory result, which does not permit such a possibility.

There is unfortunately little experimental data to determine which of the curves in fig. 4 is most nearly correct. However, we may ask whether or not it is reasonable for  $C_{44}$  to become as weak as is predicted by SAMMIS (1971) or THOMSEN (1972). My calculations on eight alkali halides in which phase transitions to the CsCl structure are well known showed that the predicted value of  $C_{44}/K$  at the transition was about the same for all eight compounds (DEMAREST, 1972). The present calculations suggest that the value is  $0.185 \pm 0.035$ . This result cannot be disputed in RbCl, RbBr and RbI, which undergo transitions at pressures within the range of acoustical experiments, and cannot be seriously in error for the potassium halides which undergo transitions at a low enough pressure that linear extrapolation of the elastic constants is still fairly accurate. I believe that it is unlikely that NaCl is so different from the other alkali halides that  $C_{44}/K$  will decrease to 0 as predicted by THOMSEN or to 0.03 as predicted by SAMMIS. I therefore believe that my own prediction that  $C_{44}/K = 0.17$  at the transition is the most accurate.

##### 4.2. The Grüneisen parameter

Assumptions of how the Grüneisen parameter  $\gamma$