varies with volume are important to the reduction of shock wave data, to the determination of the adiabatic temperature gradient in the Earth, and to the more general problem of the equation of state of solids, which was discussed in subsection 2.2. The uncertainty in the variation of γ with volume has been discussed recently by ANDERSON (1968) and by KNOPOFF and SHAPIRO (1969).
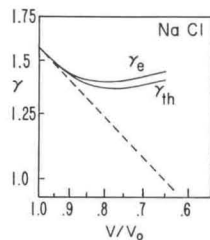

Fig. 5. Model calculation of Grüneisen parameter in NaCl as a function of volume. — – lattice theory (this paper); --- – finite strain theory (AHRENS and THOMSEN, 1972).
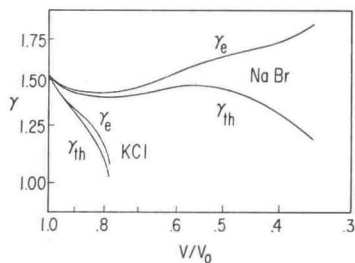

Fig. 6. Grüneisen parameter in NaBr and KCl calculated from lattice theory as a function of volume.

The predicted variation of γ with volume at 300 K is given in fig. 5 for NaCl and in fig. 6 for NaBr and KCl. Initially, γ decreases with compression, in accord with many simple theories. In KCl, the behavior is nearly linear up to the phase transition. In NaCl, NaBr and the other sodium halides, the model calculation for γ reaches a minimum and then increases with compression. This is consistent with ANDERSON's (1968) prediction that the behavior of $\gamma(V)$ would be different at high pressure than at low pressure.

The present prediction of $\gamma(V)$ and the prediction of finite strain theory begin to diverge at about $V/V_o = 0.8$, which is the limit of accuracy claimed for finite strain theory by AHRENS and THOMSEN (1972).

In earlier lattice model calculations, based only on the low-frequency acoustic modes, ANDERSON and DEMAREST (1971) showed that γ might sharply decrease shortly before the occurrence of a phase change which

resulted from the softening of certain vibrational modes. There is some indication of this effect for KCl in fig. 6, but my present calculation indicates that this effect is negligible in the 12 alkali halides which I have studied because the phase change invariably takes place before any of the modes become very weak, for example, when $C_{44}/K = 0.18$ instead of 0.

Because γ depends on the volume derivative of the frequencies, its accuracy is uncertain, but probably less than the accuracy of the elastic constants. A different assumed form of the interatomic potential might lead to different results. Since the same set of assumptions was used to calculate $\gamma(V)$ in KCl and NaBr, the conclusion that $\gamma(V)$ can have sharply dissimilar behavior for different compounds of the same crystal structure is probably valid, as is the conclusion that for some compounds the Grüneisen parameter may increase with pressure, after an initial decrease.

5. Accuracy of high-pressure extrapolations

Data on the elastic constants and their first pressure and temperature derivatives are available for a number of geologically important materials (for example, ANDERSON et al., 1968; KUMAZAWA and ANDERSON, 1969). Although geological materials have been treated within the framework of lattice dynamics (for example, SAMMIS, 1970, 1971; WEIDNER and SIMMONS, 1972; STRIEFLER and BARSCH, 1972), these calculations are not well suited to extrapolation to high pressure because they do not agree with the experimental pressure derivatives in some cases, or in other cases do not assume a functional form for the interatomic potential, and thus cannot be extrapolated to high pressure. Accurate versions of finite strain theory (THOMSEN, 1972) are presently inapplicable to most geological materials because the required second pressure derivative data are lacking. Geophysicists are therefore often forced to make use of relatively naive extrapolation formulas with little knowledge of what sort of accuracy can be expected.

I have attempted to make rather crude estimates of the type of errors to be expected from using simple approximations to the equation of state and for the determination of the elastic wave velocities at high pressure, by seeing at what pressures different theories begin to diverge. The density and elastic wave velocities have been calculated based on a linear extrapolation

of the elastic constants (as in the Murnaghan equation of state) and compared to the lattice theory calculations described in his paper and other calculations based on a nearest-neighbor repulsive force of the form b/r^n rather than be^{-r}/p. The first pressure derivatives of the elastic constants are assumed to be known.

The results of these comparisons are given schematically in figs. 7 and 8. Fig. 7 compares the density cal-
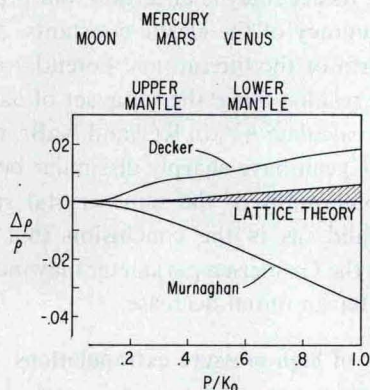

Fig. 7. Deviation of different equations of state calculations in NaCl from this paper, as a function of reduced pressure. For geological materials, the terrestrial planets or regions of the Earth corresponding to particular reduced pressures are represented by captions along the top axis.

culated from different equations of state for NaCl; fig. 8 compares the typical deviation of the calculated velocities from the present calculation for a linear extrapolation of the elastic constants, and for minor changes in the repulsive force, which represents for the present the inherent uncertainty of lattice theory.

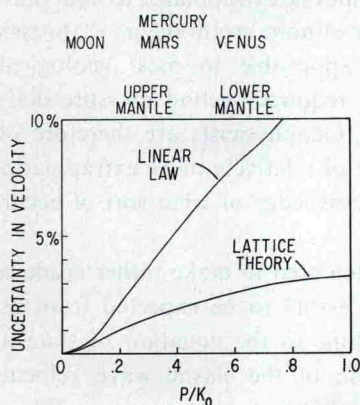If we assume a certain similarity between the high-

Fig. 8. Uncertainty in the estimated velocities in alkali halides as a function of reduced pressure. The captions on the top axis have the same meaning as in fig. 7.

pressure behavior of alkali halides and geological materials, we can estimate the accuracy of the application of simple formulas to problems of planetary interiors. Toward this end, captions above figs. 7 and 8 designate the regions of the Earth or deep interiors of the terrestrial planets which correspond to particular values of the reduced pressure for typical geological materials such as olivine or MgO.

This assumption implies that the density of geological materials under upper mantle conditions can probably be estimated to an accuracy of 1 % and to an accuracy of 2 % in the lower mantle.

There is a good chance that the sound velocities in olivine at a depth of 400 km ($P/K_0 = 0.1$) can be estimated to an accuracy of about 1 %, but at greater depths the accuracy of any extrapolation will be much worse. Even the uncertainty of lattice theory lies well above the uncertainty in seismic velocities ($\approx 1 \%$) through most of the Earth's interior. The full interpretation of presently available seismic data awaits significant improvement of theoretical methods of estimating elastic properties of geological materials at high pressure.

6. Conclusions

A very simple assumption about the nature of the interatomic potential in alkali halides, with only five arbitrary parameters, permits the calculation of the elastic constants and Grüneisen parameter at arbitrary pressure and temperature. The calculations are in excellent agreement with experiments at low pressure up to about half the melting temperature. The use of the pressure derivatives of the elastic constants in fitting the arbitrary model parameters is important if accuracy is to be obtained at high pressure.

The determination of a good interatomic potential for oxides and silicates would permit the application of this type of calculation to geologically important materials. Although this difficult problem has not yet been solved, several results of the application of the theory to alkali halides are of general interest.

Simple assumptions on the volume variation of the Grüneisen parameter may often be in serious error at volume compressions of greater than about 15%. The qualitative features of $\gamma(V)$ can vary, even among similar compounds, and may increase with pressure in some instances after an initial decrease.