Numerical results for m = 4, a common value, are listed in the appendix of this paper in normalized form. For a given value of  $(P/K_0)$ , the computed values of  $(V/V_0)$  and  $(\phi/\phi_0)$  from the Murnaghan and the Birch equations are tabulated. Note that because  $K_0$ and  $K_0$  are adiabatic, the values of  $(\phi/\phi_0)$  are also adiabatic. Differences between  $(\phi/\phi_0)_B$  and  $(\phi/\phi_0)_M$  are small at low values of  $P/K_0$  but are larger at high values of P/Ko; differences between  $(V/V_0)_B$  and  $(V/V_0)_M$  are small at all values of  $P/K_0$  less than one. Although the value of  $(V/V_0)_B$  differs from the corresponding (V/V<sub>o</sub>)<sub>M</sub> by less than 1% at a pressure corresponding to 0.5  $K_0$ , the value of  $(\phi/\phi_0)_B$  differs from  $(\phi/\phi_0)_M$  by 10%. At pressure in the vicinity of the bulk modulus of a solid, the difference between  $(V/V_0)_B$  and  $(V/V_0)_M$  is only 2½%, but the corresponding difference for  $(\phi/\phi_0)$  is at least 17%. For other values of m, these differences in  $(V/V_0)$  and  $(\phi/\phi_0)$  resulting from the Murnaghan and the Birch equations are tabulated in the appendix as a function of pressure.

The sensitivity of the seismic  $\phi(P)$  to the form of the equation of state is apparent. For an equation of state to provide as precise a formula for the seismic  $\phi$  as a function of pressure as it does for pressure as a function of density, the equation of state must not only fit the experimental pressure-density curves sufficiently well, but it must also have the correct functional form so that the derivatives match equally well. Comparison of an equation of state with experimental data on compression, as frequently seen in the literature, does not provide a good test of the validity of the expression for  $\phi(P)$  where  $\phi$  is derived from the equation of state.

The Murnaghan and Birch equations for  $\phi(P)$  may be illustrated with periclase (MgO). All the experimental data necessary to find  $K_0$  and m in equations 6 and 8 are well established [e.g., O. L. Anderson et al., 1968], and data on shock-wave compression to about 2.6 mb are available [Al'tshuler et al., 1965; McQueen and Marsh, 1966] to test the extrapolations. Periclase is interesting to geophysics because it is a rockforming mineral and also because it has been proposed as a separate phase in the lower mantle. Note that both the Murnaghan and the Birch equations for  $\phi(P)$  are completely speci-

fied by the values of  $K_0$  and m. Although these quantities are readily measurable with several different methods, the ultrasonic measurements of compressional and shear velocities as a function of pressure result in the most accurate values of  $K_0$  and m [e.g., Daniels and Smith, 1963; O. L. Anderson, 1965]. For the initial parameters we used  $K_s = 1623$  kb and  $(\partial K_s/\partial P)_s = 4.34$  (both evaluated at P = 0and  $T = 300^{\circ}K$ ) [Chang and Barsch, 1969; Chung and Simmons, 1969], with the result that the adiabatic  $\phi_0 = 45.3 \text{ km/sec}^2$ . Using these values in equations 6 and 8,  $(\phi/\phi_0)$  as a function of pressure was calculated; the results are shown in Figure 1. Although  $(\phi/\phi_0)_M$  is indistinguishable from  $(\phi/\phi_0)_B$  at pressures below  $0.05 K_0$ , the two parameters are very different at pressures greater than 0.05  $K_0$ . For example, at 1.4 mb (the pressure corresponding to the coremantle boundary), the value calculated from the Murnaghan equation is 18% larger than that calculated from the Birch equation, even though the density difference is only about 2%, as seen in Figure 2.2

Errors in  $K_0$  and m affect the precision of  $\phi(P)$ . Provided ultrasonic measurements are appropriately made, the value of  $K_0$  can be determined to an accuracy of a few parts in  $10^4$ , and the effects of this magnitude on  $\phi(P)$  is small. An error in m frequently amounts to as much as 3% in the usual ultrasonic measurements. The effects of a 3% error in m are

One of the earlier methods is an isothermal compression measurement of volume (or length) typified by work of Bridgman [1949]. An X-ray diffraction method, in which a change in dimension of the unit cell is measured as a function of pressure, has been used by a number of investigators [e.g., Drickamer et al., 1966; McWhan, 1967]. Shock-wave compression such as the work of McQueen and colleagues [McQueen et al., 1967] has been used to estimate  $K_0$  and m [see, for example, D. L. Anderson and Kanamori, 1968]. The ultrasonic methods pioneered by Lazarus [1949] have been improved to a degree that their data yield estimates of  $K_0$  to four significant figures and m to three.

<sup>&</sup>lt;sup>2</sup> The earlier correlation of the ultrasonic and shock-wave data established for periclase [O. L. Anderson, 1965, 1966] appears to be fortuitous since the ultrasonic  $K_0$  of this material was too high (compare the former value of 1717 kb with a revised value of 1622 kb) and ultrasonic m was too low (compare 3.96 against a new value 4.55; see O. L. Anderson et al. [1968]).

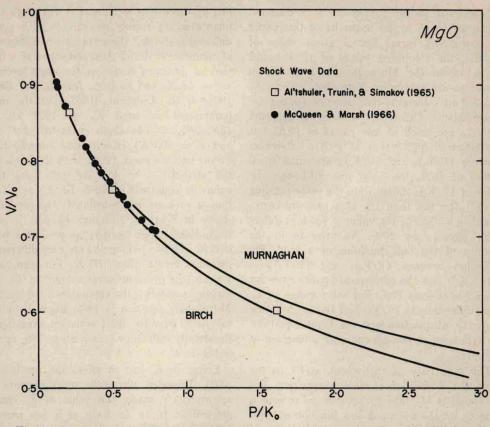


Fig. 2. Comparison of the calculated pressure-volume relations based on the Birch and the Murnaghan equations of state with shock-wave compression data for periclase. The equation-of-state parameters used are the adiabatic values evaluated at 298°K and zero pressure.

illustrated in Figure 1. Note that, at 1.4 mb, uncertainties seen in the seismic  $\phi$  values resulting from the Murnaghan and the Birch equations are about 4% each. It seems, then, that the accuracy of the calculation of  $\phi$  at high pressure is limited mainly by the accuracy with which m can be determined from ultrasonics.

## MURNAGHAN EQUATION VERSUS BIRCH EQUATION

The general superiority of the Birch equation of state over that of Murnaghan will be discussed elsewhere with respect to the pressure-volume relation of various solids. Use of the Murnaghan equation of state leads to overestimates of the volume at high pressure. The reason here is associated not only with the assumption of constant m but also with an inadequacy of the functional form of the equa-

tion itself. Analysis of Bridgman's data [Bridgman, 1964] on the compression of various solids reveals a nonlinear behavior of the bulk modulus. Chang and Barsch [1967] observed ultrasonically a nonlinear pressure dependence of all second-order elastic constants for single crystal CsCl, CsBr, and CsI at pressures as low as 3 to 4 kb. The significance of their experimental finding is that deviation from constant m may amount to as much as 40 to 50% at pressures in the vicinity of the bulk modulus of solids and raises a question as to the general validity of the Murnaghan equation of state and the Murnaghan assumption.

Bullen [1947, 1949] discussed the nonlinear dependence of the bulk modulus with pressure in connection with the compressibility of the earth's interior. More recently, Ruoff [1967] expressed the experimental bulk modulus in