the bulk modulus of the high-pressure phase would be about 10 per cent higher than that of the low-pressure olivine phase. However, as is seen in Table 6, values of the bulk modulus show about a 45 per cent increase for the Mg_2SiO_4 – spinel and a 60 per cent increase for the Fe_2SiO_4 – spinel from the respective bulk moduli in the olivine form.

There seems to be a relationship between the bulk modulus and the volume per atom at zero pressure for all solids. Birch (1961b), Anderson & Nafe (1965), D. L. Anderson (1969), and Knopoff (1967) have investigated such a relationship. The density of the solid depends upon the mean atomic weight ($\bar{m}$) and the mean atomic volume ($\bar{m}/\rho$). The oxygen ions account for most of the volume in olivine. Along a line of constant mean atomic weight (thus the composition remains constant), density changes only through changes of mean atomic volume caused by a change either in pressure or in temperature (or both in the case of the Earth's interior). Since the bulk modulus is related to the inverse of volume, and since by definition the density is proportional to the inverse of volume, there seems to be a definite relationship between the density and the rate of isothermal change of the bulk modulus with pressure (evaluated at zero pressure). Fig. 6 plots this rate of change of the bulk modulus with pressure termed (dK_0/dp) for olivine as a function of density and the $Fe/(Mg+Fe)$ ratio. Application of pressure to olivine will decrease the (dK/dp) value and this (dK/dp) after interpolation to the zero-pressure point will follow along the line of constant mean atomic weight. This trend is illustrated with an *arrow* in the diagram. As olivine becomes a spinel at high pressure, the corresponding value of (dK_0/dp) can be estimated by knowing the density value of the olivine-transformed spinel. These estimated values for (dK_0/dp) are identified by *open circles* in Fig. 6 and entered in the last column of Table 6. These estimated values, although subject to confirmation, provide a basis for specifying equations of state of the olivine-transformed spinels; the equations of state of these spinels are discussed in a subsequent paper (Chung 1971b).
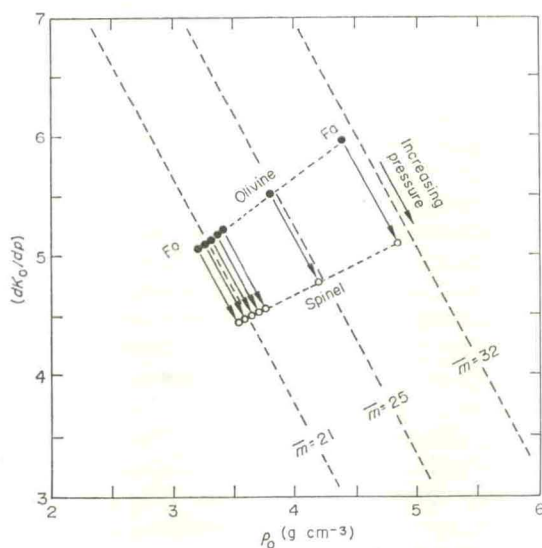

FIG. 6. An empirical relation for dK_0/dp) and density and mean atomic weight in olivine. The closed circles are the present experimental data on olivines; the open circles are estimated values for the olivine-transformed spinels.

5. Equations of state of olivine

5.1. *Variation with (Fe/Mg) Ratio*

The equations of state most widely used in geophysics are those of Murnaghan (1944, 1951) and Birch (1952). Chung, Wang & Simmons (1970), referred to below as CWS, discussed the general superiority of the Birch equation of state over that of Murnaghan with respect to calculation of the density and the seismic parameter from the low-pressure laboratory data. Use of the Murnaghan equation of state leads to overestimates of the density and seismic parameter at high pressures. The reasoning here is associated not only with the Murnaghan assumption of a linear variation of the bulk modulus with pressure but also with an inadequacy of the functional form of the equation itself. In his recent review, Macdonald (1969) presented several other limitations for the use of the Murnaghan equation of state at high pressure; he concluded from thermodynamics that the Murnaghan equation yields a finite negative pressure at which the density approaches a finite value, an unacceptable result. For these reasons, this paper uses the Birch equation in the discussion of equations of state for olivine.

The Birch equation of state is a phenomenological equation based on rapidly converging Taylor expansion of the interatomic potential. The equation was derived from the finite strain theory with cubic and quadratic terms of the Eulerian strain retained in the Helmholtz free energy:

$$p = (3K_0/2)\,(y^7 - y^5)\,[1 + \tfrac{3}{4}(m-4)\,(y^2-1)] \tag{10}$$

where $y = (\rho/\rho_0)^{\frac{1}{3}} = (V_0/V)^{\frac{1}{3}}$. K_0 and m are material parameters corresponding to the isothermal bulk modulus and its first pressure derivative evaluated at zero pressure. (If equation (10) is used in an adiabatic form, as in the calculation of the seismic parameter, K_0 and m are respectively the adiabatic bulk modulus and the adiabatic pressure derivative of the adiabatic bulk modulus).

Values of K_0 and m for olivine as a function of Fe/(Mg + Fe) ratio in the forsterite-fayalite series have been tabulated in Table 2 (under K_T and dK_T/dp). It was seen that K_0 decreases with increasing the Fe/(Mg + Fe) ratio, whereas m increases with an iron enrichment in olivine. Fig. 7 represents, in accordance with equation (10), the relative density-pressure trajectory for olivine by varying the Fe/(Mg + Fe) ratio. Effects of iron substitution in olivine on the olivine equation of state are seen here to be rather small. The iron enrichment in olivine yields a gradual reduction, though small, in the K_0 value, but increases the m value; apparently, in accordance with equation (10), these K_0 and m work in the opposite direction in such a way that the effect of the iron substitution for magnesium on the olivine equation of state is small.

In the following, the density–pressure trajectories calculated from equation (10) are compared with isothermal compression data as well as data on shock-wave compression. Data on the static compression of a fayalite-olivine were first reported by Adams (1931) to about 15 kb and of a peridot-olivine by Bridgman (1948) to about 40 kb. The volume compression of olivine has been determined recently from X-ray measurements of the lattice parameters to about 120 kb by Olinger & Duba (1970) and by Takahashi (1970) for a fayalite-olivine to about 150 kb. McQueen, Marsh & Fritz (1967) and Ahrens *et al.* (1971) presented the shock-compression data of various olivines to several hundreds of kilobars. Rigorously speaking, the shock-compression data cannot be directly compared with data on the isothermal compression resulting from the static volume measurements with pressure. Nor can they be directly compared with the density–pressure trajectories resulting from the isothermal form of equation (10). The shock-wave measurements result in adiabatic quantities, whereas the static compressions give the isothermal values; the proper comparison of these compression data with the density–pressure trajectories resulting from a particular equation of state must in principle include an adiabatic-isothermal correction.