

which indicates that  $dK/dP$ , calculated along the adiabats and the Hugoniot, decreases with compression (see also Table 2). The hpp's of the silicates demonstrate a similarity (Figure 12) in the variation of the  $K_{0s}'$  parameter with compression. This is, of course, a consequence of employing the Birch-Murnaghan equation for an equation of state. We note that they all have  $(dK_{0s}'/d\rho)_s$  values of  $-0.5$  to  $-0.7$  cm<sup>3</sup>/g. Furthermore, the variation of  $K_{0s}'$  with density seems to have a similar value of  $(dK_{0s}'/d\rho)_s$  when the density is changed on substitution of iron. When going from MgO to FeO, a slope of  $-0.3$  cm<sup>3</sup>/g is obtained, whereas, when going from the hpp's of Twin Sisters dunite to Hortonolite dunite to Rockport fayalite,  $(dK_{0s}'/d\rho)_s$  values of  $-0.4$  and  $-1.6$  cm<sup>3</sup>/g are obtained. (The value of  $K_{0s}'$  for the Rockport fayalite should be viewed with some suspicion, since it is based on only 5 Hugoniot points in the high-pressure regime.) We note that the theoretical lower limit of  $5/3$  for  $K_{0s}'$  is obtained from the Thomas-Fermi theory [see, for example. Knopoff, 1965]. The reduced data for some

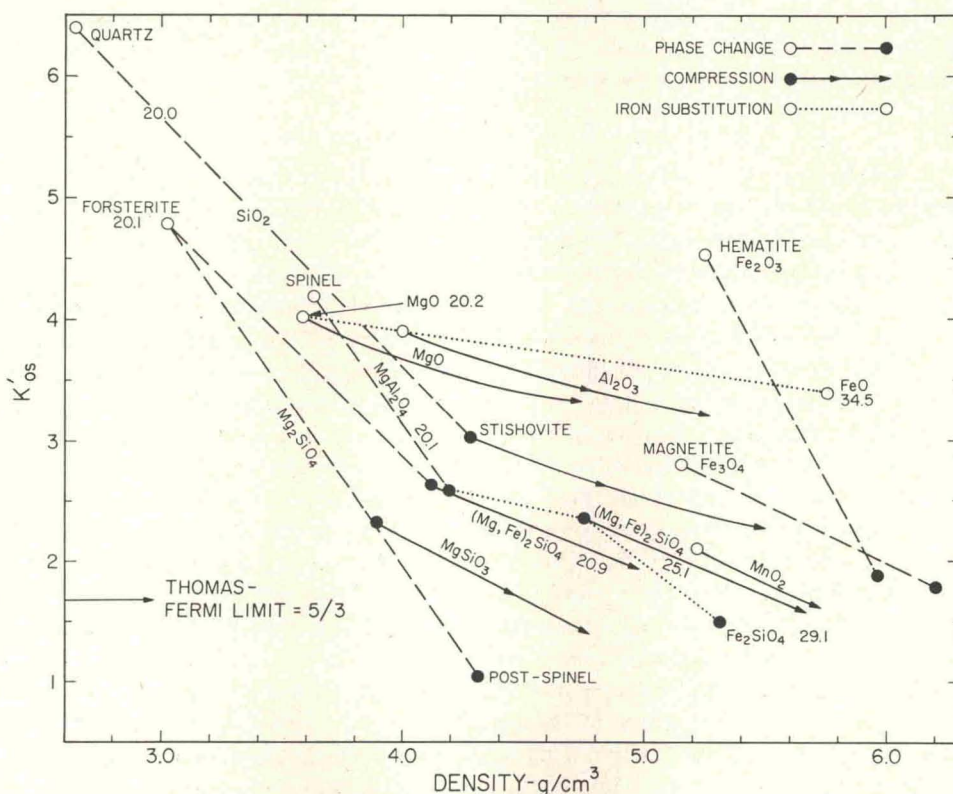


Fig. 12. Pressure derivative of adiabatic bulk modulus at zero pressure ( $K_{0s}'$ ) versus density for low-pressure phases (open circles) and high-pressure phases (closed circles). Note the general tendency of  $K_{0s}'$  to decrease with density for both iron substitution and phase changes. The solid lines with arrows indicate the trajectories of  $K_{0s}'$  versus  $\rho$  for compression implied by Birch-Murnaghan equation. Low-pressure data from Anderson *et al.* [1968] [quartz, forsterite, spinel, MgO,  $\text{Al}_2\text{O}_3$ ], England and Simmons (personal communication) [ $\text{Fe}_3\text{O}_4$ ] and Clendenen and Drickamer [1966] [ $\text{FeO}$ ].



of the higher-density compounds, such as  $\text{MnO}_2$  and the high-pressure phases of the olivines, suggest that  $K_{0s}'$  values lower than  $5/3$  may occur, although uncertainties both in the data and in the analysis make this point unclear. On passing through a phase transition, the values of  $K_{0s}'$  also decrease with increasing density. The value of the ratio  $\Delta K_{0s}'/\Delta\rho$  through a phase transition varies from  $-2.1$ , for quartz to stishovite, to  $-3.7 \text{ cm}^3/\text{g}$ , for normal  $\text{Fe}_3\text{O}_4$  to hpp  $\text{Fe}_3\text{O}_4$ .

Since the Grüneisen ratio is related to  $K_{0t}'$  by

$$\gamma_{\text{DM}} = (K_{0t}'/2) - \frac{1}{2}$$

and

$$\gamma_s = (K_{0s}'/2) - \frac{1}{6}$$

the systematics that apply to  $K_{0s}'$  or  $K_{0t}'$  should also apply to  $\gamma_{\text{DM}}$  or  $\gamma_s$ . Hence, if the Slater or Dugdale-MacDonald theory is valid, the Grüneisen ratio of the high-pressure phase will generally be lower than the value for the zero-pressure phase material. We also note (Table 3) that the Grüneisen ratio of the hpp decreases with increasing iron content.

#### NATURE OF HIGH-PRESSURE PHASES

In most of the cases previously discussed, there was clear evidence that major phase changes occurred at shock pressures of a few hundred kilobars. We now consider evidence relating to the nature of the high-pressure phases.

The maximum pressure obtainable by current static high-pressure temperature apparatus is in the vicinity of 200 kb, which is lower than the pressures observed for most shock transformations in oxides and silicates. Consequently, only in rare cases (e.g., stishovite) is it possible to identify the shock high-pressure phase with reasonable certainty by comparison with the known properties of a phase that has been synthesized under static conditions. Accordingly, identifications must be based on indirect evidence: for example, comparative crystal chemistry and static high-pressure studies of analog systems such as germanates. The classical rules of crystal chemistry explain the relative stabilities of ionic structures largely in terms of radius ratios and packing of constituent ions and from valence-bond and charge neutralization requirements. There are no grounds to suppose that these fundamental rules change at high pressure. Numerous static experiments show that there is a strong probability that a high-pressure phase will possess a structure that is already known to be adopted by many related compounds at atmosphere pressure (particularly for transformations involving large ( $>5\%$ ) volume changes). Thermodynamic considerations dictate that the new structure be denser, and it will usually be found to be characterized by a different set of ionic radius ratios than those of the low-pressure structure. Specifically, the high-pressure structure tends to be characterized by a higher cation/oxygen radius ratio, which may be simply explained if it is assumed that the effective radius of the large oxygen anion (1.32 Å) decreases relatively more with pressure than do the smaller cation radii. By means of crystal chemical systematics the relative densities of compounds in