



FIG. 6. Comparison of the bulk elastic properties of the isostructural oxides  $\text{TiO}_2$ ,  $\text{GeO}_2$ , and  $\text{SiO}_2$  in the rutile-structure with respect to volume per unit cell.

germania as a function of the volume per unit cell in Fig. 6. It is apparent that  $K^S$  and  $(\partial K^S / \partial T)_P$  systematically decrease with increasing unit cell volume for the three isostructural oxides, while  $(\partial K^S / \partial P)_S$  increases. The related behaviour between the ultrasonic and shock-wave results support, at least qualitatively, the accuracy of the latter.

On the basis of a lattice-theoretical model involving an interaction potential composed of Coulomb, van der Waals, and first and second nearest-neighbour repulsive forces, Barsch & Shull (1971) were able to explain semi-quantitatively that the first-pressure derivatives of the elastic constants of alkali halides depend almost exclusively on the ionic radius of the cation. Considering the analogous relation between the unit cell volume and  $(\partial K^S / \partial P)_S$  for the rutile-structure oxides, it is tempting to relate the present results to a simple lattice model formulation. As a first approximation, the expression for the potential energy of interaction between the  $i^{\text{th}}$  and  $j^{\text{th}}$  ions may be written

$$U_{ij} = -\frac{Z_i e_i Z_j e_j}{r_{ij}} + \frac{A}{r_{ij}^n} \quad (13)$$

where  $Z$  represents an 'effective charge parameter'. The first term represents the usual Coulomb attraction, and the second the repulsive interaction. If the non-centrosymmetric aspects of the rutile structure are neglected, and the cohesive energy is regarded in terms of a single structural parameter represented by the volume, the total binding energy may be written

$$U(V) = -\frac{1}{2}N \left[ \frac{\alpha_M Z e^2}{V^{1/3}} - \frac{B_n}{V^{n/3}} \right] \quad (14)$$

where  $\alpha_M$  is the Madelung constant (defined in terms of the cube root of the volume per unit cell). The repulsion constant  $B_n$ , neglecting thermal effects, may be determined in the usual manner with respect to the ambient equilibrium volume  $V_0$ . In addition, differentiating equation (14) with respect to volume up to order three and equating the results with the definition of the bulk modulus and its first pressure derivative yields the result

$$\left( \frac{dK^T}{dP} \right)_T = \frac{2}{3} \left[ \frac{9V_0^{4/3} K_0^T}{N\alpha_M Z e^2} + 4 \right] \quad (15)$$

Equation (15) may be used, as a first approximation, to predict  $dK/dP$  for any primarily ionic structure if the bulk modulus  $K_0^T$  and unit cell volume  $V_0$  are defined. A similar form has been used by Anderson & Anderson (1970) to predict  $dK/dP$  for pertinent mantle minerals.

Equation (15) has been used to predict values of  $(\partial K^S/\partial P)_T$  for stishovite, rutile, and germania from the appropriate elastic and crystallographic data. The results are indicated in Fig. 6. Values of  $(\partial K^S/\partial P)_T$ , as calculated by equation (15), are considerably lower than the experimental results; in addition, the theoretical prediction suggests a fairly constant value of  $(\partial K^S/\partial P)_T$  with respect to the various compounds, rather than the increase with increasing volume per unit cell as observed in the experimental data. The discrepancy between the experimental and theoretical results for  $(\partial K^S/\partial P)_T$  suggests that the elementary lattice model, assuming the interaction potential given by equation (13), is an inadequate representation for rutile-structure compounds. Approximation of the model in terms of a single structural parameter (unit cell volume) is not consistent with the non-centrosymmetric space group of the rutile structure. In an analysis of the lattice dynamics of rutile-structure  $\text{MgF}_2$ , Katiyar (1970) found it necessary to minimize the total potential energy of the crystal with respect to the three structural parameters,  $a$ ,  $c$ , and  $u$ , where the former represent the unit cell dimensions and  $u$  determines the positions of the anions. The importance of the non-centrosymmetric aspects of the rutile structure with respect to lattice dynamical models has also been pointed out by Gubanov & Shur (1966) and Sammis (1971). In addition, the inclusion of many-body forces and van der Waals and second nearest-neighbour interactions in the lattice model may be of importance for a more refined analysis. Lastly, meaningful values for the 'effective charge parameters' are not available; in the present formulation, values of  $Z$  for  $\text{SiO}_2$ ,  $\text{GeO}_2$ ,  $\text{TiO}_2$  were defined using electronegativity differences in conjunction with Pauling's (1960) relation for percentage ionic character of a bond.

#### Implications concerning the composition of the lower mantle

The composition of the lower mantle has been discussed frequently in terms of a mixture of the fundamental oxides  $\text{MgO}$ ,  $\text{FeO}$ , and  $\text{SiO}_2$  (e.g. Ringwood 1969; Anderson & Jordan 1970). Much of the attention concerning the prevailing mineral assemblage has focused on whether the lower mantle has transformed to a state somewhat denser than the isochemical mixed oxides, or alternatively, if the lower