ELASTICITY, CRYSTAL STRUCTURE AND PHASE TRANSITIONS

GEOFFREY F. DAVIES

Hoffman Laboratory, Harvard University, Cambridge, Mass. (USA)

It is demonstrated that in many cases the ratio of elastic velocities of polymorphs of a material depends primarily on the crystal structures involved, and only secondarily on the composition. Crucial to this demonstration is the use of estimates, from the Hashin-Shtrikman bounds, of the elastic properties of mixtures of simple oxides isochemical to particular compounds. Normalization to the oxide mixture properties displays the interrelationships between the densities and velocities of different crystal structures. A wide range of velocity–density trends through possible phase transitions is found. Transitions involving increases of Si coordination from 4 to 6 tend to have lower slopes. Velocity–density correlations are reasonably consistent with the average trends through phase transitions.

Comparison of models of the transition zone with the characteristics of the olivine–spinel–oxides transitions indicates that in some studies the lower mantle density may have been underestimated or the mean atomic weight of the lower mantle overestimated. The transition zone of Model B1 of Jordan and Anderson, which was derived entirely from seismic data, is consistent, overall, with the olivine–oxides transition and uniform composition, but the individual discontinuities are not consistent with the olivine–spinel and spinel–oxides transitions.

1. Introduction

The use of elastic velocity–density–mean atomic weight correlations (due originally to Birch [1]) to describe the effects of compression or phase change on the velocity depends on the assumption that the details of composition and crystal structure are not important [1, 2]. The subsequent success of such correlations is an indication that this assumption is a good first approximation, but exceptions have been evident from the beginning [1] – rutile (TiO_2) and calcium-rich rocks have exceptionally high velocities, and the α-quartz to β-quartz phase transition involves an increase in velocity, but a decrease in density. Such effects must ultimately limit such correlations, and further refinement will require that the details of composition and crystal structure be accounted for.

Shankland [3] has recently accounted for the exceptional behavior of Ti- and Ca-bearing materials in terms of the ionic size of the ions. These and other compositional effects can thus be more successfully described using ionic size as an additional parameter.

This paper presents an empirical method for isolating some of the details of crystal structure ef-

fects on elastic velocities. The ratio of velocities in polymorphs is, in many cases, found to depend mainly on the crystal structures involved, and less on the composition.

The number of polymorphic pairs for which elastic data are available is small, although rapidly increasing [4–9]. A crucial part of this paper is the observation that the elastic properties of mixtures of simple oxides, which can be accurately estimated from the bounds derived by Hashin and Shtrikman [10], are systematically related to the elastic properties of isochemical compounds. The mixtures can thus be regarded as "polymorphs", and the number of relevant data is thereby considerably increased. This, of course, does not assume that the mixture is the chemically stable form of a given composition.

2. Elasticity of mixtures

The elastic properties of mixtures can be fairly accurately estimated from the bounds derived by Hashin and Shtrikman [10]. They have used a variational method to derive bounds on the bulk modulus,

TABLE 1

Component elastic properties and elastic velocity bounds for the mixtures $MgO + Al_2O_3$ and $NiO + SiO_2$ (stishovite)

Oxide	K (Mb)	μ (Mb)	Velocity bounds (km/sec)		
			v_p	v_b	v_s
MgO	1.63	1.31	10.445	7.547	6.253
Al_2O_3	2.52	1.61	10.452	7.555	6.255
NiO	1.90	0.34	7.26	6.33	3.08
SiO_2	3.46	1.30	7.43	6.40	3.27

K, and shear modulus, μ, of a two-phase aggregate in terms of the moduli (K_1, μ_1), (K_2, μ_2) of the two component phases. One bound on each of K and μ is given by:

$$K_1^* = K_1 + \frac{V_2}{1/(K_2 - K_1) + V_1/(K_1 + 4\mu_1/3)} \quad (1)$$

$$\mu_1^* = \mu_1 + \frac{V_2}{1/(\mu_2 - \mu_1) + 2V_1(K_1 + 2\mu_1)/5\mu_1(K_1 + 4\mu_1/3)} \quad (2)$$

where V_i is the volume fraction of the ith phase. The other bounds are obtained by permuting the subscripts 1 and 2 in eqs. 1 and 2.

These bounds have been used here to compute bounds on the compressional velocity, $v_p = [(K + 4\mu/3)/\rho]^{1/2}$, the bulk sound velocity, $v_b = (K/\rho)^{1/2}$, and the shear velocity, $v_s = (\mu/\rho)^{1/2}$. For the cases considered here, the bounds on v_p are commonly separated by less than 1%, on v_b by less than 0.5% and on v_s by less than 2%. Almost always the bounds are separated by less than 2%, 1% and 5% for v_p, v_b and v_s, respectively. Table 1 gives the figures for one of the better cases, $MgO + Al_2O_3$, and for one of the worse cases, $NiO + SiO_2$ (stishovite).
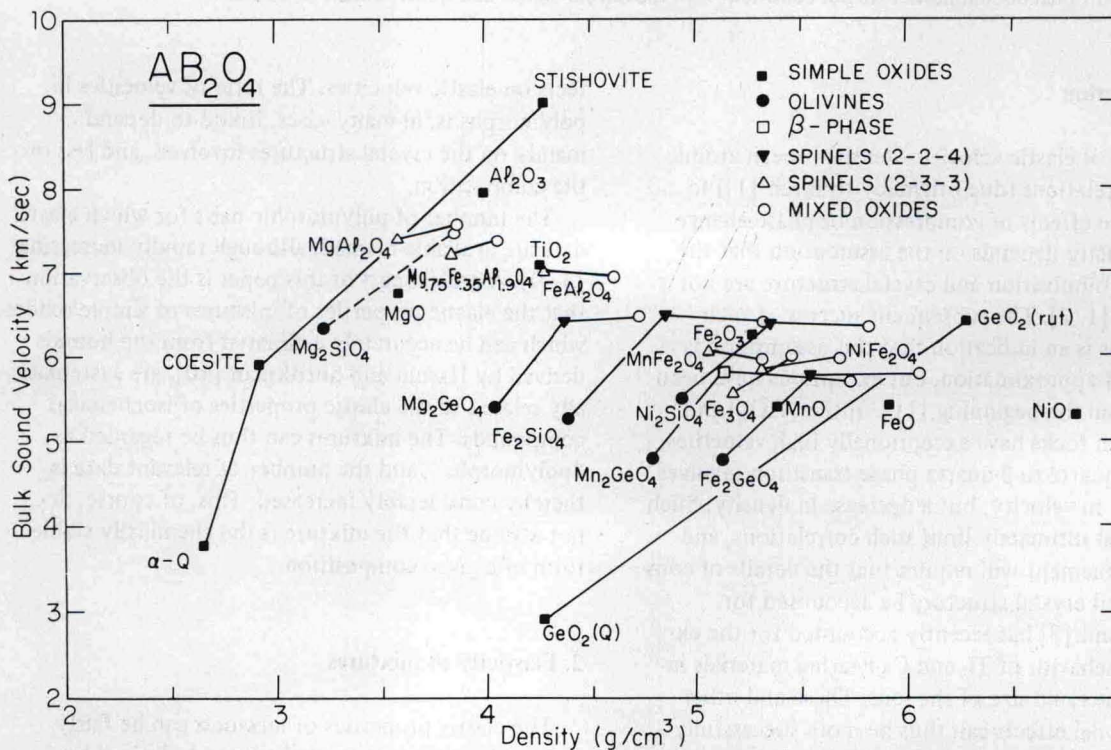

Fig. 1. Bulk sound velocity vs. density for some AB_2O_4-type compounds, their isochemical oxide mixtures and the relevant simple oxides. Polymorphs of SiO_2 and GeO_2 are included for reference (rutile-structure SiO_2 and GeO_2 were used for calculating oxide-mixture properties). Straight lines join compounds to their polymorphs and/or oxide mixtures. Data are from [4, 5, 9, 32–39].