

ELASTICITY, CRYSTAL STRUCTURE AND PHASE TRANSITIONS

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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,

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TABLE 1

Component elastic properties and elastic velocity bounds for the mixtures MgO + Al₂O₃ and NiO + SiO₂ (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 ₂ O 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 i th 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 + Al₂O₃, and for one of the worse cases, NiO + SiO₂ (stishovite).

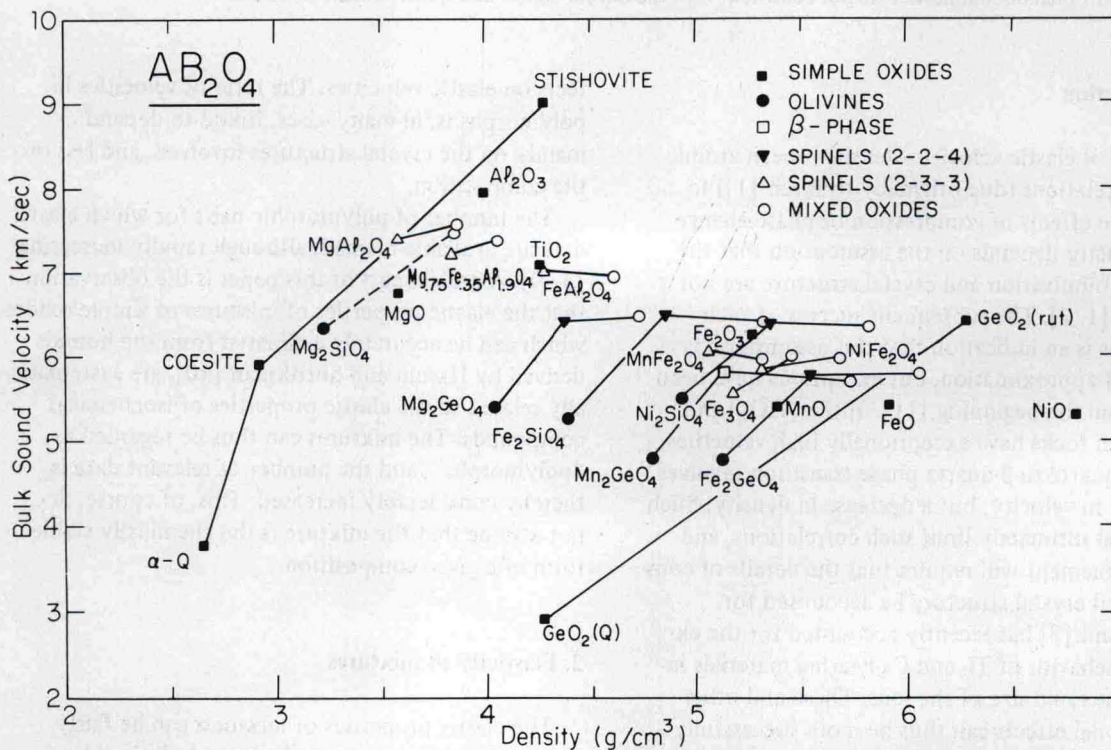


Fig. 1. Bulk sound velocity vs. density for some AB₂O₄-type compounds, their isochemical oxide mixtures and the relevant simple oxides. Polymorphs of SiO₂ and GeO₂ are included for reference (rutile-structure SiO₂ and GeO₂ were used for calculating oxide-mixture properties). Straight lines join compounds to their polymorphs and/or oxide mixtures. Data are from [4, 5, 9, 32-39].

For aggregates of more than two components, the Hashin-Shtrikman bounds can be generalized, but here the two-phase bounds were simply applied successively, using the arithmetic mean of the bounds for the two-phase aggregates. In these cases, the results are not strict bounds, but they should still be good estimates of the elastic velocities, with uncertainties of no more than a few percent. Anisotropies within individual components have not been considered, since in most cases the variations in moduli due to anisotropies are much less than the contrast in moduli between phases.

Fig. 1 shows some calculated oxide-mixture properties in relation to the isochemical phases — specifically, some olivine (α -), β - and spinel (γ -) phases. The relevant simple oxides and the polymorphs of SiO_2 and GeO_2 are included for reference. In all cases discussed in this paper, the rutile-structure phases of SiO_2 and GeO_2 were used in the oxide-mixture calculations. Compounds and polymorphs and/or their oxide mixtures are joined by the straight lines. Fig. 1 includes the data compiled by Liebermann and Ringwood [9] for these AB_2O_4 phases. It is evident from Fig. 1 that the oxide-mixture properties are quite systematically related to the properties of the other phases. If the oxide mixtures are considered as polymorphs, then the observation by Liebermann and Ringwood [9] of considerable variation in the velocity-density trends joining polymorphs is even more noticeable here, most notably in the nearly horizontal spinel-oxides trends. D. Anderson [11] has previously noted that spinels commonly have v_b 's comparable to their isochemical oxide mixtures. It was also noted by Liebermann and Ringwood [9] that the v - ρ slopes decreased with increasing mean atomic weight. This trend is also evident in Fig. 1.

3. Elasticity and crystal structure

In Figs. 2 and 3, the velocity ratios v_p/v_p^0 , v_b/v_b^0 and v_s/v_s^0 , where superscript "o" denotes the oxide-mixture property, are plotted against the density ratio ρ/ρ^0 for some AB_2O_4 - and ABO_3 -type compounds (the latter including some garnets). The straight lines join polymorphs. The cases in Fig. 1 are included in Fig. 2. It can be seen in Figs. 2 and 3 that in many cases compounds with the same crys-

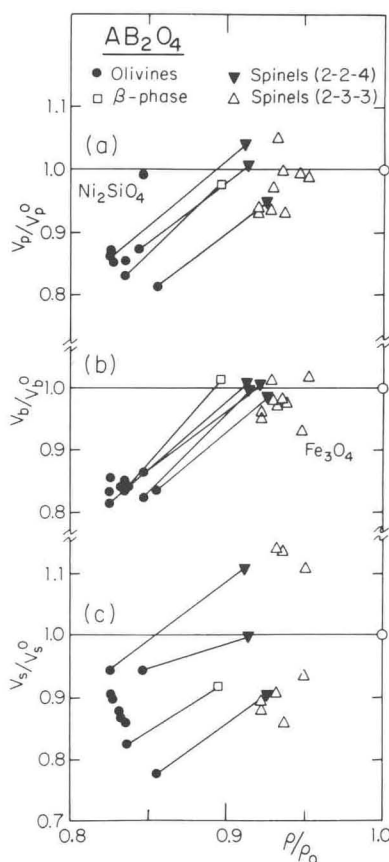


Fig. 2. Relative velocity vs. relative density for AB_2O_4 -type compounds. Compressional velocity, v_p , bulk velocity, v_b , shear velocity, v_s , and density, ρ , are normalized to those of the isochemical oxide mixtures, denoted by superscript "o". Straight lines join polymorphs. Data are those of Fig. 1, with additions from [32, 33, 40, 41].

tal structure cluster into a narrow range of the velocity and density ratios. The tendency is stronger for v_b than for v_p or v_s . The most notable exceptions are the shear velocities (and hence the v_p 's, to a lesser extent) of the spinels and olivines relative to the oxides. Note, however, that there is more regularity between the olivine-spinel pairs than between either of these and the oxides.

In Fig. 4, the polymorphs of SiO_2 and GeO_2 are plotted, in this case with the properties normalized to those of the rutile structure phase. For the α -quartz phases, the v_b ratios are similar, but the densities are quite discordant — note the change in scale from Figs. 2 and 3. The data in parentheses are the velocities for stishovite measured by Chung [12] relative to those of Mizutani et al. [5].

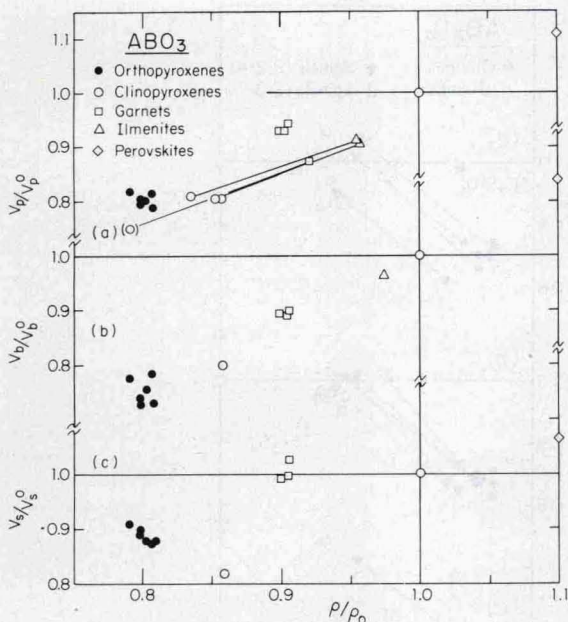


Fig. 3. Relative velocity vs. relative density for some ABO_3 -type compounds (including some garnets), analogous to Fig. 2. Data are from [9, 32, 33, 42–44].

The normalization to the oxide-mixture properties has evidently not removed compositional effects from the shear velocities of the olivines, spinels and α -quartz's. On the other hand, no compositional effects are evident in the v_s ratios for the orthopyroxenes and garnets, whereas crystal structural effects are quite evident (Fig. 3c). The commonly remarked irregularity of shear properties (e.g., [13]) thus seems to arise from both compositional and structural effects. Compositional effects on the v_b ratios cannot be resolved, except possibly for one or two spinels (e.g., Fe_3O_4 , Fig. 2b). Since v_p is not independent of v_b and v_s , it reflects the variations of v_s .

On the basis of the data for the olivine, spinel, orthopyroxene and garnet structures shown in Figs. 2 and 3, one would expect to be able to predict ρ , v_b and, for the ABO_3 compounds, v_s for an unmeasured phase to within 2–3% relative to the properties of a measured phase. The availability of data for many simple oxides makes the oxide mixture a convenient reference "phase" for this purpose, although spinel phases would probably be better referred to olivine phases. (The oxide mixture density as a reference for estimating the density of unmeasured phases has of

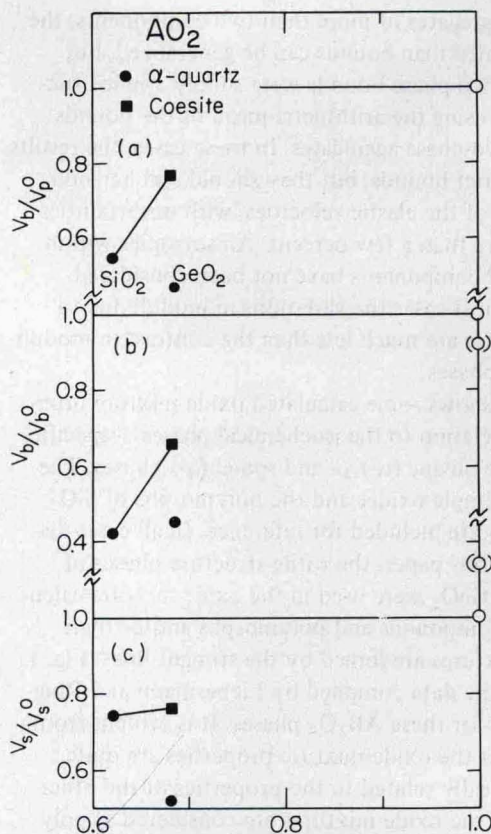


Fig. 4. Relative velocity vs. relative density for AO_2 -type compounds, normalized to the properties of the rutile-structure polymorph. Circles in parentheses are v_b and v_s of stishovite (SiO_2 -rutile) from Chung [12] relative to those of Mizutani et al. [5]. Data are from [4, 5, 12, 32, 33, 45].

course been frequently used before: e.g. [14].) In addition, the normalization to the oxide mixtures has defined relationships between structure pairs which are not represented, such as garnet–perovskite or ilmenite–perovskite.

A wide range of slopes is defined in Figs. 2–4 by the possible transitions between the structures represented. It is interesting that the slopes tend to be lower for transitions in which the silicon (or its analogue in non-silicates) changes from 4- to 6-coordination. Silicon is in 4-coordination in olivine, spinel, pyroxene, α -quartz and coesite structures, and in 6-coordination in the ilmenite, perovskite and rutile structures (note that rutile-structure phases were assumed in the oxide mixtures). The garnet structure is intermediate – for example, the high-pressure garnet form of $MnSiO_3$ has one-quarter of the silicon ions in 6-coordination [14].

4. Velocity–density trends

Although the data shown in Figs. 2–4 reveal compositional and crystal structural effects explicitly, they also provide a better test than has been possible hitherto of the applicability of general velocity–density correlations to the effects of phase changes. That is, they test Birch's [1, 2] conjecture that a phase change would move a substance, on average, parallel to his lines of constant mean atomic weight on a velocity–density plot. Liebermann and Ringwood [9] have discussed this question on the basis of their more limited data set, and concluded that the deviations from the trend of the velocity–density correlations can be large for specific transitions, such as the olivine–spinel transition. This conclusion is clearly supported by the present data. Nevertheless, we are concerned here with average trends, in so far as they can be defined by the still limited data set.

In Fig. 3b, for instance, most of the data lie close to a line of slope about 1.3. Thus, a transition between any two of the structures represented would move a material approximately along a line of slope 1.3. In Fig. 2b, the average trend is roughly defined by the olivine–oxides trend, giving a slope of about 1.0. The spinels deviate from this trend, but this is compensated when the olivine–spinel and spinel–oxides trends are averaged. In Fig. 4b, the main trend (excluding α -quartz–coesite) is between about 1.1 (coesite–stishovite) and 1.7 (GeO_2 α -quartz–rutile). Thus the average trend over all of the above cases is probably between slopes of about 1.0 and 1.5, with 1.3 being perhaps the most likely value.

The average trends for v_p and v_s are not so well defined. In Figs. 2a, 3a and 4a, the slopes are about 0.9, 1.1 and 0.7–1.7, respectively, so a representative value would be about 1.1 for v_p . For v_s , a slope between 0.5 and 1.0 might be representative, but there are wide variations. These results are summarized in Table 2.

The slopes in Figs. 2–4 are:

$$C = \frac{\rho^0(v^0 - v)}{v^0(\rho^0 - \rho)} = \frac{\rho^0 \Delta v}{v^0 \Delta \rho} \approx \frac{\Delta \ln v}{\Delta \ln \rho} \quad (3)$$

Thus C is approximately comparable to the parameter λ defined by Shankland and Chung [3, 15, 16] as:

TABLE 2

Slopes $C = \rho^0 \Delta v / v^0 \Delta \rho$ through selected phase transitions

| Transition | C_p | C_b | C_s |
|--------------------------|-------|-------|---------|
| Average, all transitions | 1.1 | 1.3 | 0.5–1.0 |
| Olivine–spinel | 1.9 | 2.0 | 1.4 |
| Spinel–oxides | 0.4 | 0.1 | (0) |
| Olivine–oxides | 0.9 | 1.0 | (0.9) |

$$\lambda = \left(\frac{\partial \ln v}{\partial \ln \rho} \right)_A \quad (4)$$

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where A is the mean atomic weight. Shankland and Chung determined λ by fitting the power-law analogue of Birch's [1] originally linear velocity–density correlation to a set of minerals with $A \approx 20$. They found $\lambda_p = 1.25$ and $\lambda_b = 1.25$, approximately [16]. These values are quite comparable to those for C found for phase transitions, above.

Comparisons can also be made with parameters derived from other proposed velocity–density relations. Thus D. Anderson's "seismic equation of state" [17] involved the parameter $n = (\partial \ln \rho / \partial \ln \phi)_A = 1/2 \lambda_b$. Anderson found $n = 0.323$ [17] and $n = 1/3$ [11], giving $\lambda_b = 1.55$ and 1.5. O. Anderson and Soga [18] suggested that λ_p should have a value of about 1.5. All of these values are slightly higher than the values of C_p and C_b found for phase transitions.

Parameters found from the linear velocity–density correlations [1, 2, 19] can also be compared, with suitable normalization; the quantity found is the derivative $(\partial v / \partial \rho)_A$, and this can be converted to the logarithmic derivative using suitable values of ρ and v . For discussions of the mantle, suitable values are the properties of the oxide mixture (0.9 MgO + 0.1 FeO) + SiO₂ (stishovite): $\rho = 4.0 \text{ g/cm}^3$, $v_p = 10 \text{ km/sec}$, $v_s = 7.5 \text{ km/sec}$. Thus, Birch [1] found, for two selections of rocks and oxides, $(\partial v_p / \partial \rho)_A = 3.05$ and 3.31, giving $\lambda_p = 1.2$ and 1.3, approximately. Wang [19] found $(\partial v_b / \partial \rho)_A = 2.4$ for $A \approx 20$, giving $\lambda_b = 1.3$. These values are all comparable to those for C_p and C_b found for phase changes.

In summary, the various velocity–density correlations for mean atomic weights near 20 have yielded slopes which are comparable to, and in some cases slightly greater than, the trends found here for phase

changes. However, trends through specific phase transitions can deviate widely from these average values.

5. Geophysical implications

Liebermann and Ringwood [9] have pointed out that the wide range of velocity–density trends through phase transitions which they observed may require that some previous interpretations of the mantle transition zone be revised. The present results indicate that the velocity–density relations which have been used are probably reasonable representations of the average effects of phase changes, but not of specific phase changes which may be important in the mantle. The point made by Liebermann and Ringwood is thus reinforced.

In particular, the spinel–oxides transition involves only a small increase in v_p , and possibly also of v_s (Fig. 2). Bassett and Ming [20] have reported evidence from static compression X-ray experiments that fayalite (Fe_2SiO_4) breaks down to the oxides FeO and SiO_2 above about 200 kilobars pressure. This suggests that the post-spinel phase of magnesium-rich olivines, $(\text{Mg, Fe})_2\text{SiO}_4$ might be the mixture $2(\text{Mg, Fe})\text{O}$ (rocksalt) + SiO_2 (rutile). If the major component of the mantle is olivine, the present results suggest that in the sequence of transformations olivine– β -phase–spinel–oxides most of the total increase of velocities would be accounted for by the olivine–spinel part of the sequence, and hence that this behavior should be reflected in the seismic velocity profiles of the mantle. In this connection, it is interesting to note that some recent v_p models of Helmberger and Wiggins [21, 22] show this tendency – the sharp velocity increase near 650 km depth is only about 4% in their models, whereas in some other models [23, 24] the increase is about 8–11%.

If the mantle is composed mainly of olivine, then the mean trend from olivine to oxides is the relevant quantity with which to compare velocity–density relations which have been used to interpret the transition zone as a whole. Thus the effect of the intermediate β - and spinel phases, which lie above the average trends defined by the other structures in Figs. 2–4, can be neglected in this comparison. For olivine–oxides, C_p is about 0.9 and C_b is about 1.0 (Table 2). Birch [2, 25] and D. Anderson [26], for instance, used

values of $(\partial v_p/\partial \rho)_A$ of 3.31 and 3.05, corresponding to values of λ_p of about 1.3 and 1.2, respectively. Thus Birch's [25] solution I for the mantle density may have underestimated the density increase through the transition zone, while Anderson [26] may have overestimated the velocity increase to be expected for a pure olivine model – it thus may not be necessary to invoke an increasing iron content through the transition zone to match the observed compressional velocity below the transition zone. In Birch's [25] solution II, $(\partial v_p/\partial \rho)_A$ was determined to be 2.64 km/sec, corresponding to a λ_p of about 1.05. This may be more consistent with an olivine model of the mantle. D. Anderson and Jordan [27] and D. Anderson et al. [28] used $\lambda_b = 1.5$ and 1.55, in effect, in the seismic equation of state to determine the mean atomic weight of the lower mantle from extrapolated zero-pressure values of the velocities and density. These high values may have caused the mean atomic weight to be overestimated.

In some recent earth models [29, 30] both the density and velocities have been determined entirely from seismic data. The velocity–density trends through the transition zones of these models may therefore be compared directly with the present results. Liebermann [31] examined some characteristics of the "400-km" discontinuity in these models, and concluded that none of them were compatible with experimentally observed characteristics of the olivine–spinel or olivine– β -phase transitions. The seismic (free oscillation) data did not give very good resolution of the details of the transition zone for any of these models. Since Model B1 of Jordan and Anderson [30] seems to employ the most reasonable assumptions about the transition zone, it will be examined further here. The parameters C_p , C_b and C_s for the discontinuities at 420 km and 670 km depth in Model B1 are listed in Table 3. The corresponding parameters for the olivine–spinel, spinel–

TABLE 3

Values of $C = \rho^0 \Delta v/v^0 \Delta \rho$ through the transition zone of Model B1 [30]

| Depth (km) | C_p | C_b | C_s |
|------------|-------|-------|-------|
| 420 | 1.2 | 0.6 | 1.8 |
| 670 | 1.0 | 0.3 | 1.8 |
| (420–670) | 1.1 | 0.9 | 1.3 |

oxides and olivine—oxides transitions are listed in Table 2. C_p and C_b for the 420-km discontinuity are much smaller than for the olivine—spinel transition. Corresponding results were found by Liebermann [31]. C_p and C_s for the 670-km discontinuity are much larger than for the spinel—oxides transition. Thus neither discontinuity is separately consistent with a predominantly olivine mantle. Also listed in Table 3, however, are the parameters of the entire transition zone of Model B1 (some compressional effects are thus included, but these should be small). These are quite reasonably compatible with the parameters of the olivine—oxides transition. The transition zone as a whole is reasonably consistent with a uniform composition olivine model. The mismatch with the individual transitions may be the result of the poor resolution of the details of the transition zone.

6. Conclusion

The demonstration here that in many cases the ratio of elastic velocities of polymorphs of a material depend primarily on the crystal structures involved, and only secondarily on the composition, promises to allow better estimates, perhaps with accuracies of 2–3%, of the elastic velocities of phases thought to be relevant to the earth's mantle. The use of the estimated properties of isochemical simple oxide mixtures not only increases the number of data immediately available, but renders relevant the properties of materials which are not necessarily close chemical analogues of silicates. Thus, for instance, considerable progress may be possible without recourse to the synthesis of high-pressure germanate analogues of silicate phases. The detailed effects of composition will, of course, have to be investigated further, especially for the olivines and spinels.

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