ELASTIC PROPERTIES, CHEMICAL COMPOSITION, AND CRYSTAL STRUCTURE OF MINERALS

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Abstract. The observed systematic relations between velocities, density, and crystal structure in minerals are viewed as part of the general problem of the interactions of ions and electrons in solids. A complete explanation of these systematics would result from an adequate physical model of interactions between atoms in a crystal. For ionic models, understanding such interactions mainly requires knowledge of inter-ionic repulsive forces, which can be calculated from solutions for the electronic energy levels. The main forms of systematics developed in the last few years can be classed either as bulk modulus-molar volume (\(K\cdot V_M\)) or, equivalently, velocity-density (\(v-p\)) relations. Isostructural and isochemical (having constant mean atomic weight \(\bar{m}\)) trends exist, and for both classes of systematics it is possible to produce semi-empirical universal expressions with the ability to predict elastic properties to a few percent. The best estimates of composition of the Earth's interior come from comparisons of mineral elastic properties with seismic data. On the basis of current velocity profiles of the Earth, the mantle appears to be chemically homogeneous.

1. Introduction

In geophysics there is a broad class of problems associated with using measurements made on or above the surface of a planet to infer conditions at some depth through the use of theories for and laboratory measurements of properties like thermal and electrical conductivity, specific heat, density, velocities, thermal expansion, magnetism, and viscosity. The greater part of our information about temperature, pressure, fluid content, composition, and crystal structure in the inaccessible regions of the Earth's crust and deep interior comes almost routinely (if not always reliably) from such comparisons. This paper examines the relations between chemical composition, crystal structure, density, and elastic properties of minerals. It is from these relationships applied to the continuously improving seismic profiles of velocities and densities in the Earth that we obtain our most sensitive probes of the chemical composition and crystal structure of the materials composing the Earth's mantle and core.

The minerals within the Earth's mantle - 70% of the Earth's mass - have an apparent chemical simplicity. They are constituted principally of the oxides MgO, SiO\(_2\), FeO, CaO, and Al\(_2\)O\(_3\) as listed in the order of their molar abundances (Ringwood, 1975, Chs. 3 and 5). Thus, the problem of describing systematic relationships between velocities, densities, chemical composition, and crystal structure in mantle minerals is one of investigating the properties of simple and mixed oxides. This class of materials has in common the fact that the bulk of the crystal volume is composed of oxygen whose mainly ionic bonds dominate the interatomic forces and therefore the elastic properties. Birch (1961a) observed that a convenient measure of chemical composition is mean atomic weight \(\bar{m}\), determined by dividing...
the molecular weight of a compound by the number of atoms in a formula unit. The mean atomic weights in g/mole of some simple oxides are: Na₂O, 20.66; MgO, 20.16; Al₂O₃, 20.39; SiO₂, 20.03; CaO, 28.04; FeO, 35.45; and GeO₂, 34.86. As can be seen, the first four oxides all have \( \bar{n} \approx 20 \). Hence, mean atomic weights different from 20 result from oxides formed from different rows of the periodic table, most abundantly from FeO and CaO. While \( \bar{n} \) may be a good indicator of the presence of iron and calcium it also follows that it is an insensitive indicator of variations of Mg/Al/Si ratios because their oxides all have essentially the same \( \bar{n} \).

In its simplest form the premise of velocity-density systematics is that the sound speeds of a material can be specified when its density and chemical composition – as defined by mean atomic weight – are known. It is through the effect upon density that other variables should govern velocities: chemical variations, crystal structure, state of aggregation (e.g., whether a material of spinel composition exists as MgAl₂O₄ or as a mechanical mixture of the two phases MgO and Al₂O₃), and the intensive thermodynamic variables, temperature and pressure. If these variables entered only through their effect on density, then universal velocity-density relations would amount to equations of state. In fact, there are clear, qualitative trends in the effect of density upon velocities. However, ample experimental evidence demonstrates obvious distinctions between the separate effects of these variables (Liebermann, 1973; O. L. Anderson, 1973; and Davies and D. L. Anderson, 1971).

The apparent simplicities of the problem have led to lively interest in the solid state physics of oxides, and equally lively disagreements about the interpretation of seismic results have persisted. Nevertheless, more than two decades of elasticity measurements at pressures extending to beyond that at the Earth’s core, and of corresponding theoretical work on equations of state and on the properties of composite materials have resulted in some broad trends that describe the behavior of oxides under high temperature and pressure. The mantle may be terra obscura but it is no longer terra incognita, and many early hypotheses about its composition have disappeared. As an example, a core composed of the same oxides as the mantle is inconsistent with known properties of oxides (Birch, 1968).

In this paper we shall examine the background of velocity-density relations of minerals, indicate how such relations are founded in the theory of solids and how they are related to the same physical parameters that govern equations of state, test several forms of velocity-density relations, and demonstrate their application to determining chemical composition of the Earth. We know more about the Earth than any other planet so that our understanding of the Earth’s composition profoundly affects our thinking about chemical abundance in the whole solar system. Thus, for the case of a mantle having approximately olivine stoichiometry the lower mantle alone would contain at least \( \frac{3}{8} \) of the Earth’s iron if \( \bar{n} = 21 \) and \( \frac{1}{4} \) of the iron if \( \bar{n} = 22 \).

2. History

Geophysics, like astronomy, has a strong interest in regions that cannot be investigated directly and affords instances of two approaches to evaluating the conditions
and compositions in planetary interiors: (a) a forward or particular calculation that
presumes a hypothesis about the physical circumstances in the region under investi-
gation and then seeks to use this hypothesis to infer properties at depth, and (b) an
inverse inference that presumes general physical relationships and applies them
straightforwardly.

Birch (1952) presented an early example of the forward approach when he
demonstrated that only the densely-packed oxides like MgO or Al₂O₃ possess
sufficiently high values of seismic parameter \( \Phi = K/\rho \) to explain the values of \( \Phi \) in the
lower mantle. Thus, the lower mantle cannot contain the relatively open silicate
structures based on tetrahedrally coordinated silicon. Another instance of a forward
calculation would come from adopting the usually-accepted hypothesis that the
seismic discontinuity at 400 km depth is indeed caused by the transformation of
olivine to its \( \beta \)-phase having a structure similar to that of spinel. With this assumption
it is possible to calculate the temperature at 400 km using laboratory petrological
data on the transition. In a third example, the experimental verification (Ming and
Bassett, 1975) of the decomposition of olivine into its component oxides as suggested
for the lower mantle (Birch, 1952) makes it reasonable to calculate the velocities of
the mixed oxides under mantle pressures—from the theories of elasticity of aggregates
(Mao, 1974; and Davies, 1974a, 1974b).

However, it is the second approach with which we are concerned here. For
example, Birch (1961a, 1961b) on the basis of the data of Figure 1 formulated a
linear relation between compressional wave velocity \( v_p \) and density \( \rho \) that has since
become known as Birch’s law

\[
v_p = a_p (\bar{m}) + b \rho,
\]

where \( a_p \) and \( b \) are constants. Birch pointed out the essential features of velocity-
density systematics, notably the increase of velocity with density in materials having
differing composition and crystal structure but constant \( \bar{m} \), and the fact that materials
of constant crystal structure but varying \( \bar{m} \) have trajectories on a velocity-density
plot that are nearly perpendicular to the lines of constant \( \bar{m} \). The first set of trends can
be usually termed isochemical, with the reservation that all the chemical variations
that can be observed are subsumed in the parameter \( \bar{m} \), and the second group of
trends are termed isostructural. A velocity-density plot such as Figure 1 has
frequently been designated a Birchen plot.

Birch (1961b) added a term to explicitly allow for variations of mean atomic
weight, and Simmons (1964) introduced a correction term to allow for apparently
anomalous effects caused by the presence of calcium, giving

\[
v_p = 0.98 + 2.76 \rho - 0.7(\bar{m} - 21) + 4.6 \text{ (wt \% CaO)}, \text{ (km/s)}.
\]

Linear forms for other velocities have also been described, e.g., for shear velocity, \( v_s \),
in single crystals by Liebermann (1970) and for bulk velocity \( v_b \) by McQueen et al.
(1964). The bulk velocity is a calculated quantity related to the compressibility:

\[
v_b = [v_p^2 - \frac{4}{3} \cdot v_s^2]^{1/2}.
\]

C. Y. Wang (1968, 1969) gave a linear relation for \( v_b \).
The utility of such relations is the relative objectivity that they can give to inversion of seismically-measured velocities and densities to obtain $\bar{m}$. Birch (1961b) first used velocity-density plots to eliminate some proposed velocity profiles for the mantle on the grounds that these profiles implied an unacceptable decrease in iron content from the crust to the core, and they have been applied since then in a similar manner.

It is obvious that the direct approach, while capable of greater precision, permits observers with particular but not unique solutions to adjust the disposable parameters to prove a larger number of Earth models than are possible when the constraints of the second approach are included – provided that the velocity-density systematics can accurately describe elastic properties with a small number of variables.

3. Explanations of Velocity-Density-Composition Relations

The publication of Figure 1, with its implication that some useful simplicities exist in
the elastic properties of Earth materials, helped to stimulate both a substantial experimental effort to accurately measure velocities in rocks, minerals, and structurally, or chemically, related compounds and a corresponding effort to relate such properties to equations of state and to theories of solids. An explanation of velocity-density systematics is a physical explanation of elastic properties and can take two directions: first, it should ultimately be able to quantitatively describe elastic behavior in terms of fundamental physical constants like particle masses and charges, Planck's constant, and the Boltzmann constant, i.e., from first principles; and second, it should be able to predict the inter-relationships of elastic behavior when only a small number of variables are specified, most frequently density, molar volume, crystal structure, mean atomic weight, and Poisson's ratio. Both kinds of explanation require an atomic model of crystals. The utility of atomic models is that, even when oversimplified, they can indicate the important physical variables and suggest useful inter-relationships between them.

3.1. LAW OF CORRESPONDING STATES

Birch (1961b) suggested that for materials of constant \( \tilde{m} \) all changes of density, whether due to changes of temperature, pressure, phase change, or compositional substitution, would produce approximately the same change of velocity. The suggestion was later formalized and qualified (O. L. Anderson, 1966, and O. L. Anderson and Soga, 1967) as a law of corresponding states. There are now ample experimental data to demonstrate that this law is no more than approximately valid for any particular case (e.g., Liebermann and Ringwood, 1973; O. L. Anderson, 1973; and Davies, 1974a); however, it remains a useful hypothesis in a statistical sense. It may be best for the bulk sound speed \( v_b \). Wang (1970) showed that the changes of \( v_b \) with pressure and temperature in a material are nearly equal and opposite. Thus, for isothermal changes

\[
\left( \frac{\partial \ln v_b}{\partial \ln \rho} \right)_T = \frac{1}{2}(K_s' - 1)K_T/K_s \approx \frac{1}{2}(K_s' - 1),
\]

where \( K_s' = (\partial K_s/\partial P)_T \). For isobaric changes

\[
\left( \frac{\partial \ln v_b}{\partial \ln \rho} \right)_P = (\delta_s - 1)/2.
\]

An expression of velocity systematics can be put into a form (O. L. Anderson, 1973) that is parallel to (3) and (4)

\[
\left( \frac{\partial \ln v_b}{\partial \ln \rho} \right)_m = (x - 1)/2.
\]

Here \( K_T \) and \( K_S \) are the isothermal and adiabatic bulk moduli, respectively; the Anderson-Grüneisen parameter is \( \delta_s = -(K_s'\alpha)^{-1}(\partial K/\partial T)_P \), and \( \alpha \) is the volume coefficient of thermal expansion. The empirical parameter \( x \) as determined from
oxides of $\tilde{m} \approx 20$ is about 4 (O. L. Anderson and Nafe, 1965; O. L. Anderson and Soga, 1967), or 3.5 (Shankland and Chung, 1974) for a somewhat wider range of mean atomic weights. Since both $K'_s$ and the parameter $\delta_s$ are in the range 4–6 for most materials, almost constant, then the change of $v_b$ for a given density change is nearly the same regardless of the cause of the density change.

Equations (3), (4) and (5) illustrate an approach that has been particularly useful in explaining systematic relationships between elastic properties, namely, the effort to construct equations in a form such that they contain dimensionless parameters like $K'$, $\delta$, $x$, or the Grüneisen parameter $\gamma$ that have been demonstrated to have little variation in different materials, and to be almost independent of crystal structure, type of chemical bonding, and chemical composition. Thus, a physical accounting for the reasons for velocity-density systematics is in some measure equivalent to explaining why the parameters $K'$, $\delta$, and $x$ are so nearly equal. The question can only be resolved by adequate models of the interatomic forces that give rise to chemical bonding and cohesion in crystals.

### 3.2. General approaches to atomic interactions in crystals

To see how the various explanations of elastic properties arise, it is useful to look at a general expression for the interactions of atoms or ions in crystals. Apart from magnetic interactions the total energy (Hamiltonian) is given by

\begin{equation}
H = \frac{1}{2} \sum_i \frac{p_i^2}{M_i} + \frac{1}{2} \sum_{ij} (Z_i e) / |R_i - R_j| - \frac{1}{2} \sum_{i,k} (Z_i e) e / |R_i - r_k| \\
+ \frac{1}{2} \sum_k p_k^2 / m_k + \frac{1}{2} \sum_{k,l} e^2 / |r_k - r_l|.
\end{equation}

Here $P_i$, $R_i$, $M_i$, and $Z_i e$ are the momenta, positional coordinates, masses, and absolute charges of the nuclei; and $p_k$, $r_k$, $m$, and $e$ (treated as a positive number) are the corresponding quantities for electrons. It is common to treat the nuclei plus a closed shell of inner electrons as a unit so that $Z_i e$ is either the charge remaining after removing the outer (valence) electrons, or it is the charge of an ion in the ionic approximation. Thus, the first term is the nuclear (or ionic) kinetic energy, the second is the Coulomb potential energy of interaction of ion cores, the third is electron-ion potential energy, the fourth is electron kinetic energy, and the fifth is the potential energy of the Coulomb interaction between electrons.

Equation (6), if it could be solved, would unify electronic and elastic properties of crystals and thereby explain velocity-density systematics. Since the solution by either classical or quantum mechanical methods is not a present possibility, it is usually treated in a number of approximations. For example, in most of technological solid state physics interest is in electronic properties; the first two terms are separated and not treated. Schrödinger's or Dirac's equation for the last three terms is solved for electronic energies with the initial assumption that the electron-lattice interaction, mainly the third term of (6), is perfectly periodic with the periodicity of the lattice.
Solutions of the electronic problem are important because they give the electronic contribution to cohesive energy and the electron density distribution; it is the deformation of the electron clouds that gives rise to inter-ionic repulsion.

In the phonon treatment of ionic motions, the last four terms of (6) are lumped into a potential that is seen by the ion cores and that has the periodicity of the lattice. Solution of the dynamic equations of motion with respect to small displacements \( \Delta R \) yields the vibrational normal modes of the crystal, a finite spectrum of traveling waves (phonons). The vibrational spectrum, when thermally excited, contains virtually all of the heat content of the crystal. Ziman (1960) has treated the separate electron, phonon, and electron-phonon contributions to crystal energies.

A useful starting point for equations of state in ionic crystals is the second term of (6). The Coulombic ion-ion interaction is long-range and results in the Madelung attractive potential when summed over the lattice. Within the ionic treatment only the outer or valence electrons of the closed shell configuration of an ion contribute to the third term, and the remaining interaction is repulsive due to the last two terms of (6). The repulsion arises because the net kinetic and inter-electron potential energies of the electrons within an ion are raised when the electrons become confined by coming into contact with the outer shells of an adjacent ion. In the classical Born-Mayer treatment the third, fourth, and fifth terms of (6) are combined in a repulsive potential \( v(R) \) that is assumed to have the form \( Ce^{-R/a} \) or \( C/R^n \). Here \( R \) is the anion-cation separation; \( C, a, \) and \( n \) are constants that are usually determined from experiment, but it should be borne in mind that they arise from simplifying the electronic contributions. It may appear that the exponential form has more physical significance because it has the functional form of the hydrogen atom radial density distribution, but the interaction of outer electrons between adjacent ions is sufficiently complex that there is no reason to prefer one of these simple forms over the other beyond the criterion of which best describes the behavior of solids.

The use of the Born-Mayer model as an ionic equation of state should strictly apply only at absolute zero temperature. However, it is usually adequate at higher temperatures because the only remaining unconsidered term of (6) is mostly the first one and it is relatively small. The ionic kinetic energy is contained in the vibrational motions, and it is easy to show that the heat content \( U_{ih} \) of the crystal is only a few percent of the other terms that comprise the cohesive energy. The Mie-Grüneisen equation of state (Slater, 1939, Ch. 13) presumes the internal energy \( U(V, T) \) of a crystal to consist of a volume dependent term \( U(V) \) and a term incorporating the thermal energy contained in all the vibrational modes of frequency \( \nu_i \),

\[
U(V, T) = U(V) + U_{ih}(V, T) = U(V) + \sum_i h\nu_i/[\exp(h\nu_i/kT) - 1].
\] (7)

The Helmholtz free energy \( F \) can be derived from (7) and the pressure is \(-\partial F/\partial V\). If all the vibrational modes had the same variation with volume, then it would be possible to write

\[
P = -dU(V)/dV + \gamma_{ih}U_{ih}/V.
\] (8)
This is the Mie-Grüneisen equation of state. As a simplification of (6) it relates the vibrational spectrum and the interatomic potential to pressure. The thermal Grüneisen parameter $\gamma_m$ can be related to the other thermodynamic parameters by differentiating (8) with respect to temperature,

$$\gamma_m = \alpha K_T/\rho c_{V_m} = \alpha K_S/\rho c_{P_m}. \quad (9)$$

The volume coefficient of thermal expansion is $\alpha$; $c_{V_m}$ and $c_{P_m}$ are the specific heats per unit mass at constant volume and pressure, respectively.

An order-of-magnitude calculation demonstrates that $U_{\theta h} \ll U(V)$, which permits neglect of $U_{\theta h}$ in first-order calculations or at 0 K. $U(V)$ is discussed below.

Because of their almost purely ionic bonding the alkali halides are particularly susceptible of simple treatment, and because they afford solutions in closed form, they have frequently been a starting point for geophysical models of minerals. The fundamental interaction between two ions (terms 2–5 in Equation (6)) is represented by a Coulomb attractive potential and a repulsive potential which, because of its short-range nature, is ordinarily summed only for nearest (or occasionally next-nearest) neighbors:

$$\phi_{ij} = Z_i Z_j e^2 / R_{ij} + C_{ij} / R_{ij}^{12}. \quad (10)$$

The charges $Z_i e$ are here given their algebraic values. The cohesive energy results from the sum of all interionic potentials in the crystal,

$$U(R) = \frac{1}{2} \sum_{i,j} \phi_{ij}. \quad (11)$$

The factor $\frac{1}{2}$ prevents each interaction from being counted twice. In complex crystals there is a separate $C_{ij}$ and $n_{ij}$ for each kind of ion pair, e.g., Mg–O or Al–O, leading to a separate $\phi_k$ for each ion at the $k$th non-equivalent site in a unit cell.

$\phi_k$ is given by

$$\phi_k = Z_k e \sum_i Z_i e / R_{ki} + \sum_i C_{ki} / R_{ki}^{12}. \quad (12a)$$

The cohesive energy per mole is then

$$U(R) = N_0 / N_1 \sum_k \phi_k, \quad (12b)$$

where $N_0$ is Avogadro’s number and $N_1$ the number of formula units in a unit cell. Examples of Madelung sums and lattice energies in silicates, chosen for illustration but not completeness, are in the work of Raymond (1971), Sammis (1970, 1972), and Ohashi and Burnham (1972).

Apart from the mere complexity of computing Madelung sums like (10)–(12) in minerals, there is the multiplicity of unknown repulsive parameters and the inconvenient fact that the $\phi_k$ depend on the many internal coordinates of ions within a unit cell. Hence, a large number of investigators have retreated with relief to the diatomic
alkali halide model as a convenient method to indicate the fundamental ionic crystal physics with minimum complexity. In diatomic, high-symmetry crystals the ionic charges can easily be removed from the sums (12a, b) to leave a summation over the reciprocal ionic separations in terms of a structural constant, the Madelung constant $A$, and a characteristic distance $R_0$ usually given as the nearest neighbor separation at equilibrium. In this case,

$$U(V) = U(R) = -(AZ_1Z_2e^2/R_0)[R_0/R - (R_0/R)^n/n], \tag{13}$$

where the constant $C$ has been eliminated by the condition that $dV/dR = 0$ when $R = R_0$, and $Z_1$ and $Z_2$ are treated as positive numbers according to convention. Anderson and Liebermann (1970) supplied detailed calculations in a form similar to (13) for all the elastic constants of the NaCl, CsCl, and ZnS crystal structures on the assumption of centrally-directed forces. Weidner and Simmons (1972), Sammis (1970, 1972), and Cohen and Gordon (1975) included next-nearest-neighbor terms in the repulsive potential.

At 0 K, and to a good approximation at room temperature, we can equate pressure to the isothermal volume derivative of $U(V)$ instead of $F(V, T)$.

We have the result from (13) that

$$P = (\frac{1}{3} V_M)(AZ_1Z_2e^2/R_0)[(R_0/R)^n+3 - (R_0/R)^4], \tag{14}$$

Since the bulk modulus $K_T$ is $-V(\partial P/\partial V)_T$

$$K_0 = [AZ_1Z_2e^2/9V_M](n-1)/R_0, \tag{15}$$

where the subscript 0 indicates conditions at zero pressure. $V_M$ is given in terms of the inter-ionic distance $R_0$ by

$$V_M = N_0pR_0^3, \tag{16}$$

where $p = 2$ for NaCl structure, $8/3\sqrt{3}$ for CsCl structure, and $16/3\sqrt{3}$ for ZnS structure, e.g., O. L. Anderson and Liebermann (1970). D. L. Anderson (1967) extensively discussed equations of state of the form

$$P = 3K_0/(n-m)[(V_0/V)^{(n+3)/3} - (V_0/V)^{(m+3)/3}], \tag{17}$$

of which (14) is a special case having the index $m = 1$. For temperatures greater than zero (17) is the first term in (8).

It should be mentioned that the actual functional form of the interatomic potentials has significant consequences for inferred properties at high pressures. For example, the calculated Grüneisen parameter varies with volume in drastically different ways if an equation of state different than (17) is chosen (Irvine and Stacey, 1975).

In this section we have given an example of how an equation of state (8), (14), or (17) can be developed from a general expression (6) in terms of a small number of parameters $n$ and $R_0$ and can be related to an elastic modulus $K_0$. In the following
sections we shall see that the same parameters evaluated in materials of differing chemical composition are responsible for the systematics of elastic properties.

3.3 **Bulk modulus-molar volume relationships**

Within a given structural sequence, i.e., where there is no change of crystal structure (denoted by \(X\)) or of valence, then both \(A\) and \(Z_1Z_2\) should be approximately constant. One of the striking forms of systematics (O. L. Anderson and Nafe, 1965; O. L. Anderson and Soga, 1967; and D. L. Anderson and O. L. Anderson, 1970) is the observation that \(K_0 \sim V_M^{-1}\) as in Figure 2, that is,

\[
K_0 V_M|_X = \text{const.,} \tag{18}
\]
as would be inferred from (15) provided that the ratio \((n - 1)/R_0\) is constant within a sequence having constant crystal structure \(X\).

A physical explanation of (18) thus comes to the basic problem of explaining the value of the index of repulsion \(n\) and the equilibrium separation \(R_0\) -- or alternatively the coefficient of repulsion \(C\) -- in terms of the fundamental electronic interactions contained in the last two terms of (6). While there is no elementary way to understand the reason for \((K-V_M)_X\) systematics (18), the forces of repulsion can be numerically calculated for alkali halides starting with Hartree-Fock wavefunctions (Kim and Gordon, 1974; Cohen and Gordon, 1975). It is possible to calculate \(K, R_0,\) thermodynamic functions, and even transition pressures for phase changes in terms of calculated numbers and the fundamental physical constants. Thomsen (1975) has reported on similar methods in crystals of higher covalency. Thus, it is indeed possible to obtain a result like (15) or (18) from theory. Although computational complexity and the intercession of a computer obscure an easy explanation, nevertheless, any approach that permits an improved equation of state based on fewer empirical parameters is a clear advance.

The simplest way to gain a physical appreciation of the reasons for systematic velocity-density relations and for the law of corresponding states comes from Birch's (1961a) recognition that the atomic packing density \(1/V_A = \rho/\tilde{m} \sim 1/V_M\) determines elastic properties to the first order. D. L. Anderson (1967) showed that for small compressions equations of the form (17) lead to the result that

\[
(\frac{\partial}{\partial \ln \rho})_{\Phi} \approx 1/3(m+n+3), \tag{19}
\]
where \(\Phi = v_b^2 = K_s/\rho\). The changes of \(\Phi\) with pressure or temperature are of comparable order, as can be seen in Equations (3) to (5). To the extent that \(m\) and \(n\) are the same for materials of the same chemical composition \(\tilde{m}\), we have

\[
\Phi|_{\tilde{m}} \sim \rho^{1/3(m+n+3)}. \tag{20}
\]
Replacing density by packing density permits (20) to be generalized to the seismic equation of state applicable to a wide range of chemical compositions (D. L. Anderson, 1967)

\[
\rho/\tilde{m} \approx \Phi^w, w = 1/3(m+n+3). \tag{21}
\]
Fig. 2. Bulk modulus versus molecular volume for halides and oxides in the rocksalt, calcium difluoride, rutile, corundum, and spinel structures (Anderson and Anderson, 1970).
Empirical fits of (21) to materials of widely-varying composition (D. L. Anderson, 1967, 1969) yield values of $\omega$ of about $\frac{1}{3}$ as in Figure 3. Equations (18) and (21) are two of the main forms of bulk modulus systematics. The third results from (21) in the case of constant $\bar{m}$ (O. L. Anderson and Nafe, 1965; and O. L. Anderson and Soga, 1967),

$$KV_A^x|_{\bar{m}} = \text{const.}, \quad x = 4.$$  \hspace{1cm} (22)

Equation (22) is sometimes illustrated by using the molar volume per ion pair $2V_A$ instead of the mean molar volume $V_A$. While $2V_A$ is of use in diatomic crystals, where it equals the molar volume $V_M$, it has little physical significance in complex crystals.

Fig. 3. Relations between seismic parameter, density, and mean atomic weight in the seismic equation of state (D. L. Anderson, 1967).

Recently Davies (1976) observed that the rigidity modulus $\mu$ obeys a law similar to (18) in alkali halides of constant crystal structure, namely that $\mu V_M^{4/3}$ is constant.

In complex crystals the volume dependence of $\mu$ has more scatter. The physical reasons for Davies' relationship are less clear than is (18) because $\mu$ depends highly on crystal structure and non-central forces. However, lattice calculations can describe the behavior of $\mu$; for instance, electrostatic lattice sums (O. L. Anderson and Liebermann, 1970) can produce the negative pressure coefficient of $\mu$ for NaCl...
structure that appears to be an exception to the law of corresponding states. It is seen that for \( \mu \) the effect of pressure and chemical substitution on packing density can produce different, even opposite effects, depending on the details of crystal structure.

In conclusion, for \( K-V \) systematics we observe an isostructural form (18), an isochemical form (22), and a universal form (21) that relates the bulk modulus or the seismic parameter to packing density in a variety of crystal structures and oxide compositions. An adequate physical calculation of these relations entails calculation of the electronic energies that give rise to interionic repulsion. It will be seen that parallel forms can be developed for \( v-\rho \) systematics, although an additional parameter must be added to incorporate the effects of ionic size.

### 3.4. VELLOCITY-DENSITY RELATIONS AND VIBRATIONAL SPECTRA

Once we assume the validity of (18), it is easy to derive the useful relationship relating a bulk sound speed to mean atomic weight. The mean molar volume is defined as

\[
V_A = \bar{m}/\rho.
\]

Dividing Equation (18) by the mean molar volume and taking the square root produces the simple result

\[
v_b \bar{m}^{1/2} = \text{const.}
\]

The two expressions of isostructural systematics, Equations (18) and (24), are illustrated in Figures 4 and 5 for the same group of materials. It can be said that these two expressions are equivalent; however, Equation (24) has the feature that it explicitly connects composition with a velocity. Further, there is a greater percentage variation of \( \bar{m} \) than of \( V_A \) so that there is less clustering of the data in Figure 5 than in Figure 4.

The balance of repulsive and attractive sources results in a potential well in which the atoms of the crystal vibrate, hence it is not surprising that there should be some connection between the vibrational spectrum of the crystal and the elastic properties. For the purposes of illustration any relation between a velocity and a frequency will demonstrate this point; for example, it is possible to get a restoring force, therefore a representative vibrational frequency \( \nu_r \) from the second derivative with respect to \( R \) of Equation (13) or of Equation (17) (Shankland, 1972a). It is sufficient to use the requirement of a maximum cut-off frequency in the vibrational spectrum, i.e., from the Debye frequency

\[
\nu_D = \nu_D(4\pi/3 \cdot V_A/N_0)^{1/3} = \nu_D(4\pi/3 \cdot p/q \cdot R_0^3)^{1/3},
\]

where \( p \) is the structural factor in (16) and \( q \) gives the number of atoms in a formula unit. Chung (1972) used the requirement that the minimum wavelength be approximately equal to a mean inter-atomic distance \( (V_A/N_0)^{1/3} \). Shankland (1972a) derived a representative frequency \( \nu_s \) by calculating the restoring force from the second derivative of the potential (13) and used \( \nu_s \) in (25) to obtain a relation.
Fig. 4. Log-log plot of bulk modulus versus molar volume for compounds with olivine, spinel and beta phase structures. $K_V = \text{const.}$, lines represent isostructural series (Liebermann, 1975).

Fig. 5. Log-log plot of bulk sound velocity versus mean atomic weight for compounds with olivine, spinel, and beta phase structures. The $V_pM^{1/2} = \text{const.}$ lines represent isostructural series (Liebermann, 1975).
between bulk velocity $v_b$ and $m$. However, it is simpler to take the logarithmic derivative of (24) to obtain the isostructural slope

$$\frac{\partial \ln v_b}{\partial \ln m} = -1/2,$$  

(26)

$$\frac{\partial \ln v_b}{\partial \ln \rho} = -(1-c)^{-1/2},$$  

(27)

Here the ionic substitution parameter $c$ is given by

$$c = \left( \frac{\partial \ln V_M}{\partial \ln \rho} \right)_T,$$  

(28)

as obtained independently from crystallographic data (Shankland, 1972a). Chung (1972) illustrated Equations (24) and (26) for several structures as shown in Figure 6.

The isochemical derivative can also be obtained from (25) by using (23) and the appropriate mode Grüneisen parameter $\gamma_i = (\partial \ln v_i / \partial \ln \rho)_T$

$$\frac{\partial \ln v_b}{\partial \ln \rho} = \gamma_b - 1/3 = \lambda_b,$$  

(29)

Some difficulties with $v$-$\rho$ systematics occur in calcium-rich minerals (Birch, 1961a; and Simmons, 1964); calcium-bearing minerals do not behave irregularly on $K$-$V_M$ diagrams, however. Shankland (1971, 1972a) quantitatively showed this apparent anomaly to be an ionic size effect which can be corrected through the use of the parameter $c$. The ionic substitution parameter is of the order 0.14 for Fe-Mg and for Ge-Si substitutions, approximately 1.3 for Ca-Mg substitutions (Shankland, 1972a). The integrated form of Equation (27) is

$$\frac{v_{b1}}{v_{b2}} = \left( \frac{\rho_1}{\rho_2} \right)^{-1/2(1-c)}.$$  

(30)

which is tested in Figure 7. An important effect of ionic size is that the isostructural trajectories are not precisely parallel on a $v$-$\rho$ plot, a fact that is seen in both experiment and theory.

Equation (29) or similar expressions of isochemical systematics are implicit or expressed in much work. For a few examples see: O. L. Anderson (1967); D. L. Anderson (1967); or Knopoff (1967). These results have been summarized by O. L. Anderson (1973), who showed that the compression curve incorporates a change of $\gamma$ with $\rho$ that is almost linear. This represents an extension of (29) to higher orders, although the validity still depends on assumptions like a law of corresponding states. Nevertheless Equations (27) and (29) supply the means to physically understand the isostructural and isochemical trends on a Birch plot because the slopes are given in terms of quantities like the Grüneisen $\gamma$ that vary relatively little in different materials. As in illustration of isochemical systematics Figure 8 shows both the qualitative agreement with equations like (1) in the case of polymorphic phase transitions (see also Wang, 1970) and some notable exceptions. Other exceptions are given later.
Of course it is possible to improve upon the concept of a single representative vibrational frequency as given in (25). Plendl (1960) and Plendl et al. (1965) were able to show that a wavelength- or energy-weighted mean of the vibrational absorption spectrum of a large number of materials, mostly ionic, could be used to
Fig. 7. Calculated trajectories on a velocity-density plot together with calculated and measured hydrodynamic velocities, $v_h = v_b$ (Shankland, 1972a).
calculate the bulk modulus. However, he found it necessary to make a small correction for the mean atomic weight of the materials that he considered.

It is worthwhile to consider other details of the optical vibrational spectrum because the shift with pressure of the infrared- and Raman-active modes of the optical spectrum can be measured in diamond cells to quite high pressures, and this affords a way to infer elastic properties of transparent materials at these pressures, providing a suitable model relating optical bands to interatomic forces and therefore to elastic properties exists. Such models have been calculated, and some examples are: alpha quartz (Striefler and Barsch, 1975), stishovite (Striefler and Barsch, 1976), and several alkali halides and MgO (Achar and Barsch, 1971). It has been possible to obtain reasonable agreement with experiments with these methods.

The analogs in \( v - \rho \) systematics to the seismic equation of state for \( K - V_M \) systematics are a variety of relationships, including the linear forms like (2). A power-law relationship was developed by Shankland (1972b) to simultaneously...
satisfy isostructural (27) and isochemical (29) systematics:

\[ v_b = B \rho^\lambda \left( \frac{\rho_0}{\bar{\rho}} \right)^{1/2+\lambda(1-c)} \] 

(31)

Here \( \lambda \) is the parameter \( \gamma = \frac{1}{3} \approx 1.25 \) and \( \rho_0 = 20.2 \text{ g/mole} \). The constant \( B \) was determined empirically to be 1.42 from the observed velocities in 26 minerals, although the methods of Anderson and Anderson (1970) and Templeton (1953) could have been used to determine it. Simple sound speed systematics, Equation (31), permitted a quasi-theoretical explanation of several problems in velocity-density relations (Shankland and Chung, 1974): (a) Birch's Law (1) in its various forms for \( v_p \) and for \( v_b \) could be derived from a linearization of (31) analogous to previous results (e.g., Soga, 1971 or Chung, 1972); (b) the linearization of (31) with the inclusion of the appropriate value \( c \approx 1.3 \) for Ca-Mg substitution results in a quantitative derivation of Simmons' (1964) correction (2) to Birch's Law for calcium-bearing rocks and minerals; (c) a similar inclusion of ionic size effects quantitatively explains D. L. Anderson's (1969) corrections to the seismic equation of state (21), which can be put into the form of the law of Equation (22) to show that \( x \) in (5) and (22) is equal to \( 1 + 2\lambda \).

Equations (21) and (31) provided a fairly high predictive ability (to within a few percent) in a formula with some physical justification and general applicability. However, Mao (1974) pointed out that the materials of \( \bar{\rho} \approx 20 \) having velocities above a line described by (31) had relatively high values of Poisson's ratio, and those below the line – most conspicuously \( \alpha \)-quartz – had lower values of \( \sigma \). He defined a corrected velocity,

\[ v_b^* = 1.84 + 7.51\sigma + 1.98\rho, \] 

(32)

that was fitted to materials of \( \bar{\rho} \approx 20 \) and assumed to hold for any oxide or silicate. Equation (32) predicts bulk sound velocities in materials of \( \bar{\rho} \approx 20 \) with less than half the variance of previous formulas. His empirical equation for relating \( v_b \) to \( v_b^* \) was

\[ \frac{(v_b^* - v_b)}{(\bar{\rho} - \rho_0)} = 0.058 + 2.62(\rho - \rho_0)/(\bar{\rho} - \rho_0), \] 

(33)

which he showed to have considerably less variation than velocity formulas lacking a Poisson's ratio correction as shown in Figure 9. In (33) \( \rho_0 \) is the density of the material of \( \bar{\rho} \approx \rho_0 = 20.2 \) for any isostructural sequence. He evaluated the ratio on the right side of (33), essentially an improved linearization of (27) with \( c = 0.13 \), and obtained a form of (33),

\[ \frac{(v_b^* - v_b)}{(\bar{\rho} - \rho_0)} = 0.058 + 2.28\rho/\bar{\rho}, \] 

(34)

which is quadratic in \( \bar{\rho} \).

Equation (34) can be used to calculate \( v_b \), or \( \bar{\rho} \) can be calculated from the positive root of the quadratic. While only tested for Fe\(^{2+}\)-Mg\(^{2+}\) substitutions – for which it is presently the most successful method of relating velocity to composition regardless
Fig. 9. Plot of $(V'_o - V_o)/(\bar{m} - 20.2)$ versus $(\rho - \rho_0)/(\bar{m} - 20.2)$, illustrating the projection of lines of constant mean atomic weight onto a single line appropriate to $\bar{m} = 20.2$. Improved linearity results from the Poisson's ratio correction (Mao, 1974).
Fig. 10. Comparison of measured bulk sound speeds $v_b$ with those calculated from Equation (34). Calculated values for $\alpha$-$SiO_2$ and $\alpha$-$GeO_2$, usually difficult to predict, fit the measured values with little scatter.

of crystal structure – (34) should apply to any chemical substitution having $c \approx 0.13$ to 0.14.

A test of (34) for the prediction of bulk sound speed is given in Figure 10, where predicted velocities are compared with the measured ones. Figure 11 compares the success of (34) in predicting $\tilde{m}$ with a method having an elastic parameter as input, in this case (31). It is clear that the $v_b-\sigma$ systematics afford a more successful result; there is presently no way to reduce the scatter in the important region near $\tilde{m} = 20$ in Figure 11a without including the Poisson ratio or a similar correction. Equation (34)
is useful even in the difficult case of the phase change from spinel structure to mixed oxides. Simpler formulas that use only one elastic constant give an apparent composition change $\Delta \bar{n} \approx 1$, whereas (34) using two elastic constants $v_b$ and $\sigma$ gives

![Graph](image)

Fig. 11a. Comparison of actual $\bar{n}$ with that calculated from (31).

$\Delta \bar{n} = 0.1$ (Mao, 1974). In applications to the Earth, where two elastic properties $v_p$ and $v_s$ commonly result from seismic profiles, the requirement for both $v_b$ and $\sigma$ makes full use of available information in a consistent way, and produces good results over a wide range of packing densities in oxides and silicates. Even in the case of stishovite, where experimental velocities differ by 10%, the predicted $\bar{n}$ is in a reasonable range, indicating that effects of cracks in sintered sample aggregates are also accommodated.

In conclusion, it is not surprising that velocity-density systematics exhibit forms parallel to bulk modulus-volume systematics, namely an isostructural form (24) or
Fig. 11b. Comparison of actual $\bar{m}$ with that calculated from (34). The greater scatter in (a) as compared to (b) is a feature of any present form of systematics that uses a single velocity in its prediction. While there is tight clustering for most of the points in (a), there exist some obvious discrepancies that are better accommodated in (b).

(26), an isochemical form (29), and universal forms like (31) and (34). In contrast to $K-V_M$ systematics, many irregularities appear in $v-\rho$ systematics that demand compensation for ionic size effects. The corrections fall naturally from relationships connecting velocities to some measure of the vibrational spectrum. The physical reason for the importance of utilizing $\sigma$ in velocity systematics is not clear, but might appear in considerations of lattice sums, and of non-central forces.

3.5. BULK MODULUS-DENSITY SYSTEMATICS

Recently D. L. Anderson (1976) plotted bulk modulus against density as illustrated in Figure 12. He noted that there is little dependence of $K$ upon density as iron
content increases, and that such a plot is very useful in displaying the effect of differing crystal structures. In terms of $K-V_M$ systematics the small density effect is a consequence of the small change of $V_M$ with iron substitution, as can be seen in the fact that the parameter $c$ is small for $\text{Fe}^{2+}\text{Mg}^{2+}$ substitutions.

Fig. 12. Bulk modulus, $K$, versus density, $\rho$, for various crystal structures, illustrating the way in which different crystal structures are separated on a $K-\rho$ plot (D. L. Anderson, 1976).

3.6. Some exceptions

There are several reasons to expect considerable departure from the rules outlined here. It is, in fact, the extent of agreement within such a multiplicity of compounds that is remarkable. Now that single-crystal X-ray refinements are available for olivine (Hazen, 1975a,b) at high pressure and temperature, it is seen that virtually all the internal deformation takes place as changes of length and angle of the Mg-O and Fe-O bonds; the $\text{SiO}_4$ tetrahedra are virtually unaltered. However useful alkali halides may be as tests of equations of state, the complex silicates possess clear, qualitative differences. Huggins (1974) has discussed the contributions of cation site compressibilities to the compressibility of the entire crystal.
Another reason for exceptions is the neglect of non-central forces, a problem of increasing severity with decreasing ionicity; the more covalent bonds such as Si–O have electron densities that deviate considerably from spherical symmetry. All of the models discussed here, including the quantum mechanical ones, presume centrally-directed forces except for models that include bond-bending vibrational modes explicitly. The fact that bulk modulus $K$ or the bulk sound speed $(K/p)^{1/2}$ depends relatively little upon non-central forces makes it more appropriate for simple physical models. The shear modulus that is included in the definition of $v_p = [(K + 4\mu/3)p]^{1/2}$ or $v_s = (\mu/p)^{1/2}$ is more sensitive to non-central and next-nearest neighbor bonds, as elaborated by Weidner and Simmons (1972). Hence, the $\mu V_M^{4/3}$ rule that obtains in alkali halides breaks down in more complex oxides (Davies, 1976), whereas the $KV_M^{-1}$ rule, being less dependent on ionicity and complexity of structure, shows fewer fluctuations.

Other complications arise in isostructural substitutions. As has been indicated (Shankland, 1972a), the ionic size parameter $c$ actually varies from one structural sequence to another and differs for different cation substitution pairs. Thus, it is obvious that $c_{ca}$ for Ca$^{2+}$–Mg$^{2+}$ trends differs markedly from $c_{Fe}$ for Fe$^{2+}$–Mg$^{2+}$ trends, but it should also be noted that a still slightly different $c$ results for Fe$^{3+}$–Al$^{3+}$ trends, and the different slopes of FeO–MgO lines from the Al$_2$O$_3$–Fe$_2$O$_3$ line on a $v$–$p$ plot (Figure 7) is a predictable deviation. Further, a substitution may not be simple in a complex structure, as may happen along the MgAl$_2$O$_4$–FeAl$_2$O$_4$–FeFe$_2$O$_4$ sequence if there happens to be also a change from normal to inverse spinel. In such instances some of the divalent cations change from 6- to 4-coordination and the reverse occurs for trivalent cations. Davies (1976) demonstrated that coordination changes produce discrepancies in systematic trends, and Jackson (Figure 7.5, 1976) illustrates that the $KV_M$ products are different for normal and inverse spinels of several germanates and stannates.

Within isostructural systematics a consequence of the breakdown of relation (18) is the breakdown of the nearly equivalent relation (24). Chrysoberyl, Al$_2$BeO$_4$, (H. Wang et al., 1975) exemplifies this problem, because $KV_M$ of chrysoberyl is unequal to $KV_M$ of olivines even though both minerals have olivine structure; the $v_b\bar{m}^{1/2}$ products also differ. The consequence is that the universal forms (21), (31), and (33) that depend on (18) or (24) cannot be useful either. The difficulty may simply be that Be–O bonds are quite different from Si–O bonds, but another reason could be that chrysoberyl is not so obviously structurally similar to olivine; it has a trivalent instead of divalent ion at the 6-coordinated sites, and a divalent instead of quadrivalent ion at the 4-coordinated cation site. Hence, it is likely that both the Madelung constant $A$ and the valence products $(Z_1e) (Z_2e)$ to which $KV_M$ and $v_b\bar{m}^{1/2}$ are proportional will be different in the two materials, as they should also be for normal and inverse spinels. Garnets may also exhibit discrepancies due to having a multiplicity of cation sites of different coordination (Weaver et al., 1976; Isaak and Graham, 1976).

Hazen's previously-mentioned evidence for differential compressibility of the cation sites in olivine – and by inference, in other complex oxides – is consistent with...
volume-averaging schemes. For olivine and chrysoberyl, Wang et al. (1975) observed that the data can be reconciled by computing the incompressibility of the complex oxides from the molar volume average of the incompressibilities of the component oxides. (A still better prediction of $K_0$ for chrysoberyl results from the molar volume average of the compressibilities, as Hazen's results apparently indicate.) A similar approach to complex oxides was earlier advocated by D. L. Anderson (1969), who used a molar average of the seismic parameter $\Phi$ of each of the component oxides to obtain $\Phi$ for the complex oxide.

England (1970) and Simmons and England (1969) presented a case for substantial variations from the predictions of velocity systematics. However, much of the variation would probably be diminished by taking into account the effects of ionic size and of corrections based upon Poisson's ratio.

Davies (1974a) discussed the isochemical variations of structure: olivine–spinel–mixed oxides (Figure 13), where particularly strong departures from Birch's Law (or any other form of single-velocity systematics) take place. The effects of changing the state of aggregation from complex crystal to mixed oxides and changing Si coordination from 4 to 6 shown here are far worse than the irregularities associated with other phase changes (Liebermann and Ringwood, 1973; Liebermann, 1973; and Shaw,

![Figure 13](image-url)

Fig. 13. Bulk sound velocity versus 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 (Davies, 1974a).
1974). The change to mixed oxides appears to mimic the effect of an increase of $m\bar{\rho}$ on a $v-\rho$ plot. Only in the two-elastic-parameter systematics of Mao (1974) does this false $\Delta m\bar{\rho}$ appear to be negligible. Therefore, the petrofabric of rocks does have an influence. The systematics developed for separate mineral phases may still not be wholly appropriate for minerals aggregated into rocks of the same mean atomic weight.

Finally, it must be remarked that the consistencies in elastic properties are just that, and not equations of state. Well-documented statistical fluctuations exist, and it is known that pressure and temperature have different effects than inferences from unqualified use of the law of corresponding states would suggest. Hence, any inverse calculations of mantle properties must eventually be verified by more precise forward calculations.

4. Applications to the Earth

In this section are outlined a few elementary applications of velocity-density systematics. The inverse calculation of iron content in the mantle is exemplified in Figure 14 where two forms of systematics (31) and (34) are used to calculate $m\bar{\rho}$ directly from some recent seismic profiles. We note the following points: (a) the first set of $m\bar{\rho}$-profiles shows wide variations. In particular, there are apparent jumps or discontinuities in $m\bar{\rho}$ at the principal seismic boundaries at 400 and 670 km. Such jumps appear whenever systematics using only one elastic parameter are used. On the other hand Mao's (1974) systematics that use $\sigma$ as a second parameter imply virtually no change of $m\bar{\rho}$ at the places where it would be most expected. The simplest deduction from this inverse approach is that the mantle is chemically uniform with respect to iron content on the spherically averaged scale of present seismic profiles. Chemical uniformity with respect to iron content is consistent with a mantle that is well-stirred over geologic time on the large scale of spherically averaged models (O'Connell, 1977; Tozer, 1972). While these calculations cannot reveal anything about Mg:Si:Al ratios, there is every reason to believe that these ratios are sensibly constant in a convecting mantle on the same large scale as is $m\bar{\rho}$. On the basis of velocity changes in germanate analogs of silicate structures, Liebermann and Ringwood (1973) found no basis for inferring $m\bar{\rho}$ changes at structural phase changes. (b) Variations in $m\bar{\rho}$ between different profiles are as significant as uncertainties in the systematics in determining composition. If the upper mantle has a composition given by peridotite xenoliths, or by the pyrolite model (Ringwood, 1975, Ch. 3) that is, 21+, and we see no $m\bar{\rho}$-discontinuities at the most conspicuous places, then a constant $m\bar{\rho} \approx 21.1 \pm 0.4$ (Watt et al., 1975) is a reasonable value for virtually the entire mantle as suggested by a number of sources: 21.7 (McQueen et al., 1967); 21.3 (Ringwood, 1975, p. 501).

Systematic $v-\rho$ relations are not equations of state, and their naive application in Figure 14 is not justifiable on a quantitative basis, especially in regions of strong thermal gradients, i.e., in the outer mantle. A better procedure is to reduce the material from in situ conditions of temperature and pressure to room conditions to
which present systematics apply by means of a finite strain calculation (Birch, 1952; Davies, 1974b; Mao, 1974; Burdick and D. L. Anderson, 1975; and Davies and Dziewonski, 1975). The inferred values of \( m \) are still of the order 21+. Lower mantle densities are somewhat higher than the mixed oxides should be (Davies and Dziewonski, 1975; Burdick and D. L. Anderson, 1975). The former authors prefer this to be an effect of collapsing of the mixed oxides into a still denser phase, e.g. of perovskite structure, while the latter favor a slightly more complicated phenomenon, enrichment in the \( \text{SiO}_2 : \text{MgO} \) ratio and a consequent composition change in the region at 700–1000 km depth.

D. L. Anderson used \( K \)–\( \rho \) systematics as means to discriminate between possible changes of crystal structure at the principal seismic discontinuity. On the basis of Figure 12 he has argued that the phase change at 650 km depth is probably a change of material in garnet structure to mixed oxides rather than the more usual belief that it represents the breakdown of \( \gamma \)-olivine (spinel structure) to mixed oxides.

The work of Davies (1974a, b) affords an example of the use of elastic properties in a forward calculation. He presumed that the 670 km discontinuity is indeed a breakdown of the principal silicate phase to mixed oxides and shows that the calculated velocity changes are to be expected in this phase change (Figure 13), rather than a change of composition.
The fact that the lower mantle independently satisfies the Adams-Williamson Equation is also consistent with its being chemically homogeneous (Davies and Dziewonski, 1975).

5. Further Work

There are two main ways in which improvements in understanding and applying systematics will come about, apart from continued improvements in quantity and quality of elastic data. First is the recognition, through (6), that problems of crystal physics involve all the particles in the crystal. Thus, knowledge of, say, ionic motions depends on knowledge of the electronic levels that give rise to forces of repulsion and to the vibrational spectrum. The utility of physical models of crystals is that they help correlate apparently different properties, for example, velocities and refractive indices (O. L. Anderson, 1976). Other optical methods are only beginning to be used. Measurements of infrared and Raman spectra can be related to ionic motions and interatomic forces, e.g., vacuum ultraviolet measurements (Nitsan and Shankland, 1976) that reveal something of the energies of outer electron configuration and may prove helpful in calculations of repulsive interactions involving those electrons. Poole et al. (1975) have related the photoelectron spectra of alkaline-earth fluorides to the crystal binding energies and interionic distances. Further work in \textit{a priori} calculation of lattice energies can be expected. A field that has been only touched on so far is the systematics of dense and molten metals applied to investigation of the core composition.

Second, there is also considerable need for improvement in application of theories of elasticity of heterogeneous media to mineral aggregates (rocks) to refine the systematics of single phases to more complex situations.

6. Summary

The total energy of all interactions between ions and electrons in a crystal demonstrates that a true physical explanation of the reasons for the existence of systematic relations between elastic properties density, chemical composition, and crystal structure as well as of the law of corresponding states would come from a detailed knowledge of the electronic and ionic energies that are also necessary to an adequate equation of state. In the ionic crystals, the \textit{a priori} calculation of the ionic repulsion parameters represents the biggest step toward such a comprehension, but the details of computer calculation partially mask an understanding that presently exists in principle.

Even physical models having parameters to be determined empirically are useful because they suggest helpful interrelationships and because they permit the problems to be formulated in terms of relatively invariant quantities like the Grüneisen parameter. In the 15 years since the publication of Birch's law relating velocities to density and composition a number of new relations have developed. These have been
divided into $K - V_M$ and $v - \rho$ relations; in each kind of relation there exist isostructural and isochemical trends, and some universal equations embodying both trends. The most successful to date of these universal equations is one due to Mao that relates two elastic properties $v_b$ and $\sigma$ to $\rho$ and $n$ for a variety of silicates and oxides in different crystal structures and achieves the ability to predict $v_b$ to within a few percent at zero pressure.

The best estimates of bulk chemical composition and crystal structures within the mantle come from comparison of seismic velocity and density profiles with measured and extrapolated elastic properties of possible mantle materials. Applications of velocity-density relationships to seismic profiles show no apparent charges of mean atomic weight and therefore of iron content at the major seismic discontinuities where such changes would seem most likely to take place. It is inferred that chemical homogeneity with respect to iron content and probably of other major elements exists on the spherically symmetric scale of the seismic profiles, compatible with convectively-mixed mantle.

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