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ELASTICITY AND CONSTITUTION OF THE EARTH'S INTERIOR*

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ABSTRACT

The observed variation of the seismic velocities with depth, below the crust, is examined with reference to the variation to be expected in a homogeneous medium. A general equation is derived for the variation of the quantity, $\phi = V_P^2 - 4/3\, V_S^2$, in a homogeneous gravitating layer with an arbitrary gradient of temperature. The parameters of this equation are then discussed in terms of the experimental and theoretical relations for solids. The principal parameter is $(\partial K_T/\partial P)_T$, the rate of change of isothermal incompressibility with pressure, which can be found for large compressions from Bridgman's measurements. Comparison of observed and expected rates of variation of ϕ throughout the Earth's interior leads to conclusions regarding homogeneity and, with a larger uncertainty, to estimates of temperature.

A shadow zone at a depth of about 100 km, as suggested by Gutenberg, may be accounted for by a gradient of temperature of about 6°/km in a homogeneous layer of ultrabasic rock. Between depths of about 900 and 2,900 km, the mantle appears to be substantially uniform, and at a relatively uniform temperature of the order of several thousand degrees. Between about 200 and 900 km, the rate of rise of velocity is too great for a homogeneous layer, and indicates a gradual change of composition, or of phase, or both. New phases are required to account for the high elasticity of the deeper part of the mantle (below 900 km), and it is suggested that, beginning at about 200 to 300 km, there is a gradual shift toward high-pressure modifications of the ferro-magnesian silicates, probably close-packed oxides, with the transition complete at about 800 to 900 km. There may also be a concentration of alumina, lime, and alkalis toward the upper part of the mantle, in and above the transitional layer but below the crust, existing in minerals of high elasticity such as garnets and jadeites. The transitional layer appears to hold the key to a number of major geophysical problems.

The velocities in the core and inner core are also reviewed. The inner core is most simply interpreted as crystalline iron, the outer part as liquid iron, perhaps alloyed with a small fraction of lighter

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elements. The density and compressibility of iron at high pressures are estimated with the aid of the experimental compressions of the alkali metals; the central density is found to be about 15. Several other recent proposals regarding the crust are discussed.

NOTATION

v = specific volume
ρ = density; $\rho = 1/v$
T = absolute temperature
P = pressure
S = entropy
Ψ = Helmholtz free energy
α = volume thermal expansion; $\alpha = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_P$
β_T = isothermal compressibility; $\beta_T = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial P}\right)_T = 1/K_T$
β_S = adiabatic compressibility; $\beta_S = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_S = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial P}\right)_S = 1/K_S$
K_T = isothermal incompressibility; $K_T = 1/\beta_T$
K_S = adiabatic incompressibility; $K_S = 1/\beta_S$
ϕ = elastic ratio; $\phi = K_S/\rho$
γ = Grüneisen's ratio; $\gamma = \alpha/(\rho\beta_T C_v) = \alpha/(\rho\beta_S C_P) = \alpha\phi/C_P$
C_P = specific heat at constant pressure
C_v = specific heat at constant volume
G = gravitational constant
g = acceleration of gravity
V_P = velocity of waves of compression
V_S = velocity of waves of rotation or shear
σ = Poisson's ratio

INTRODUCTION

The interior of the Earth is a problem at once fascinating and baffling, as one may easily judge from the vast literature, and the few established facts, concerning it. There is no dearth of information—astronomical, geochemical, petrological, geological, geophysical—but the relationship of most of this material to the Earth's interior is vague. The only information about definite levels of the interior, derived from seismology, has an abstract character and requires deciphering. It is the intention of the following study to look for the physical significance of the seismic data, with the aid of such experimental and theoretical understanding of the condensed state of matter as can be brought to bear.

The following questions will be considered: What regions of the interior, if any, are homogeneous, and what can be said of the other regions? What materials may have the elastic properties demonstrated by the seismic waves under the conditions of the interior? What can be said, on this evidence, with regard to the temperature of the interior? The information furnished in the form of seismic velocities is, in principle, just what is needed for an approach to these questions; the answers arrived at below unavoidably reflect uncertainties still present in the seismological data, as well as in our knowledge of the materials. Little attention is given to the problems of the Earth's origin or development, which are hardly definable without reliable information concerning its present constitution.

Since the following discussion is largely an analysis of details of the variation with depth of the velocities of the two seismic body waves, we commence with some preliminary remarks upon the reliability of these velocities, and upon the likelihood of their drastic revision. The curves of velocity *versus* depth (or radius), with which we shall be chiefly concerned, are found by a process of integration of the travel-time curves, which embody the observations most directly. A considerable amount of interpretation is involved in the identification of the various phases of a seismogram, in the choice of material, and in the construction of travel-time curves, which fit more or less well the selected observations. The velocity-depth curves, in turn, are somewhat dependent upon the mathematical methods applied to the travel-time curves. The extent to which individual judgment and choice of material have affected the velocity-depth curves is illustrated by a figure given by Macelwane (Gutenberg, Editor, 1951, p. 276), in which a half-dozen different solutions are juxtaposed. It is clear that there is general agreement upon the major features of these curves, the differences pertaining, for the greater part, to minor inflections. In the latest work by Jeffreys (1939*a*) and Gutenberg (1948, 1951), nearly all of these inflections have disappeared, and it is the belief of Jeffreys that the velocities are unlikely to be further improved, except by introduction of regional differences. The depth to which regional differences may persist has been discussed by Dahm (1936) and by Macelwane (1937); it may well be some hundreds of kilometers, but the differences do not appear to be great. Disagreements among seismologists persist with respect to a number of features of the velocity-depth curves, and will be mentioned below. On the whole, however, the agreement with regard to the major characteristics of these curves is reassuring, and revision which would invalidate a serious portion of the following analysis seems unlikely.

The uppermost few tens of kilometers, below which high seismic velocities indicating some variety of "ultramafic" rock are first encountered, are commonly termed the "crust." This thin but complex layer comprises an insignificant fraction of the Earth's volume or mass, and it is sufficient for present purposes to adopt a conventional representation of the crust, with a uniform thickness and density, and to ignore such complexities as its variation with depth, with continentality, and the like.

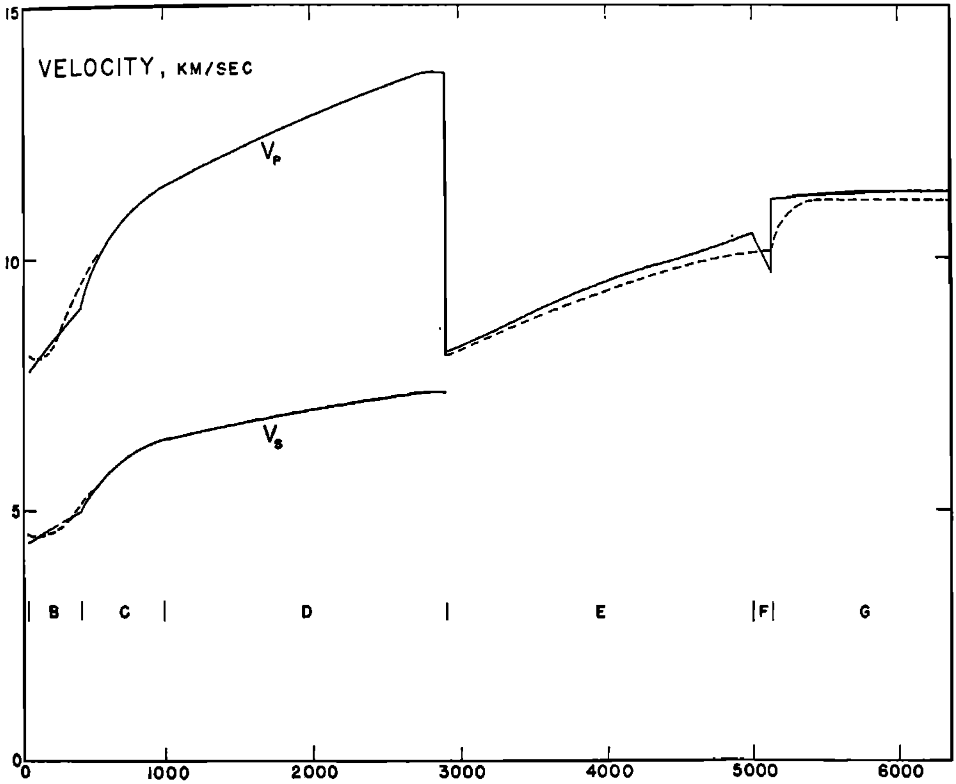
Seismologists now recognize some half-dozen subdivisions of the interior below the Mohorovicic discontinuity which marks the base of the crust. Although complete agreement as to the boundaries of these divisions, or even the existence of some of them, has not been reached, it is convenient to have designations for them, and at least rough indications of their positions and relative volumes and masses. The figures of Table 1 follow Bullen (1947), whose layers are based on Jeffreys' solution for the velocity-depth relations, with densities obtained by a method to be discussed below. The principal regions are evidently layers *B*, *C*, *D*, and *E*, which include over 97 per cent of the whole volume. The existence of layer *F* is in dispute, as are the nature and position of the division between *B* and *C*.

TABLE 1—*Dimensions and masses of the internal layers*
(After Bullen, 1947)

Layer	Depth to boundaries (km)	Radius (km)	Fraction of volume	Mass in 10^{25}gm	Fraction of total mass	Fraction of mass of mantle
	0	6371				
Crust *A*			0.0155	5	0.008	0.01
	33	6338				
B			0.1667	62	0.104	0.15
	413	5958				
Mantle *C*			0.2131	98	0.164	0.24
	984	5387				
D			0.4428	245	0.410	0.60
	2898	3473				
E			0.1516			
	4982	1389				
Core *F*			0.0028	188	0.315	....
	5121	1250				
G			0.0076			
Total				598		

The principal evidence for these subdivisions is shown in Figure 1, where the velocity-depth curves of both Jeffreys and Gutenberg are plotted. Two velocities are given throughout the mantle, corresponding to the two independent kinds of wave propagation which take place in the interior of an isotropic elastic solid. Few materials are isotropic on a fine scale; the highest symmetry for a crystal is cubic, with a minimum of three independent elastic constants. On a large scale, however, aggregates of crystals, even of low individual symmetry, often satisfy the requirements of the theory of isotropic elasticity to a good approximation; examples are the structural metals, such as steel and aluminum, and many igneous rocks, particularly at pressures high enough to eliminate porosity (Birch and Bancroft, 1938, 1940). At the present time, there seems to be no evidence of appreciable aeolotropy for the relatively long waves of seismology in the Earth's interior, and we shall assume that samples having dimensions of the order of kilometers are without preferred orientation of their crystalline components. Any vitreous phases present might be expected to be isotropic on a still finer scale.

The mere existence of two velocities throughout the mantle with a ratio corresponding to a value of Poisson's ratio of between 0.27 and 0.30 is highly significant, suggesting at once a "normal" type of elasticity. There appears, furthermore, to be no serious dependence upon frequency for periods between about one second and 24 hours (Takeuchi, 1950). The absence of the second velocity below layer *D* is the principal reason for characterizing at least layer E as "liquid," though there is support for this interpretation from calculations of tidal yielding (Jeffreys, 1929, p. 239; Takeuchi, 1950) and from the nature of the secular variation of the Earth's magnetic field (Bullard, 1950*b*; Elsasser, 1950*a*). The absence of the second velocity and the drastic decrease of the first are the outstanding seismic features which distinguish the "core" from the "mantle"; the surface of separation, which is considered to be sharp, to a fraction of a wave-length, has been fixed at a mean depth of 2,898 ± 2.5 km (Jeffreys, 1939*b*; see also Macelwane, Chapter 10, in Gutenberg, Editor, 1951) and is the best determined, as well as the major, discontinuity of the interior. An inner core (G of Table 1) is now recognized (Lehmann, 1936; Gutenberg and Richter, 1938, 1939; Jeffreys, 1939*c*; Gutenberg, 1951), but the velocity distribution is still in question.



DEPTH, KM

FIG. 1—SEISMIC VELOCITIES AS FUNCTION OF DEPTH

Much computation has been devoted to the distribution of density throughout the Earth's interior. The mean density is known with about the same precision as is the gravitational constant, to a few parts in five thousand; the moment of inertia, which depends upon the precessional constant, is nearly as well-determined. These two conditions alone, though of the greatest importance, do not suffice to determine the density distribution unless this is restricted to a form involving only two adjustable parameters; such forms are those suggested by Laplace, by Roche, or by Wiechert. In principle, Wiechert's subdivision of the interior into two parts, each of uniform density, bears a rough resemblance to the main structural feature, the division between mantle and core, and the two densities found on this assumption (with the modern value for the radius of the core), 4.3 and 12.2, may be taken as first approximations to the correct, more complicated, density variation.

It was first noticed by Adams and Williamson (1923) that the seismic velocities give information concerning the change of density with pressure which can be utilized to improve the crude results of Wiechert's hypothesis. If V_P and V_S are the velocities of the dilatational and rotational waves, respectively, then in an isotropic elastic medium

$$V_P^2 - 4/3\ V_S^2 = K_S/\rho = \phi = (\partial P/\partial \rho)_S \ldots\ldots\ldots\ldots\ldots (1)$$

(See "Notation," above)

where K_S is the adiabatic incompressibility, ρ is the density, ϕ a convenient notation for K_S/ρ introduced by Bullen. Results such as those of Figure 1 thus lead to ϕ as function of the radius r. We assume that the change of pressure is given by the hydrostatic relation, $\mathrm{d}P = -g\rho\ \mathrm{d}r$. Then, if the change of density is the result of adiabatic compression alone, we have the Williamson-Adams relation

$$\mathrm{d}\rho/\rho = -g(r)\ \mathrm{d}r/\phi(r) \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Numerical integration of this equation leads to the change of density within any layer satisfying the assumptions of homogeneity and adiabaticity; the absolute densities must be adjusted to satisfy conditions upon the mean density and the moment of inertia. This procedure, originally carried through by Williamson and Adams, has been repeated with more recent data by Bullen in a series of important papers.

The Adams-Williamson method does not, however, reduce the indeterminacy inherent in this problem as soon as more than two independent layers are recognized. At best, it gives the correct variation of density within certain layers. It is still necessary to introduce assumptions which cannot at present be verified. In Bullen's discussions, determinacy is secured with the assumption that the density at the top of layer B is 3.32, a plausible value suggested by the mean density of the Moon and of ultrabasic rocks and stony meteorites, but without observational support. Following an indication (Birch, 1939) that layer C is not homogeneous, Bullen (1940) has applied the Williamson-Adams relation throughout layers B, D, and E, and adopted a parabolic variation of density in layer C continuous with the adjoining layers. Layers F and G are so small and so near the center that they are unimportant with regard to the mean density and still less important for the moment of inertia; the density in these regions has consequently to be found by other methods, of which Bullen has suggested several, but in any case is without serious effect upon the values for the other zones. Bullen's densities have been useful for a variety of purposes, and while they are subject to revision on several counts, it is unlikely that the necessary changes will invalidate the general proportions of the various layers as shown in Table 1. One solution, with the accompanying pressure and gravity distributions, is shown in Figure 2.

It should be remembered, however, that these distributions and the accompanying density-pressure relations in no way represent direct determinations of density; they are affected by every substantial change of interpretation of the seismic data, as is evident from five successive recalculations by Bullen between 1936 and 1950, as well as by simplifying assumptions and special hypotheses concerning the relation of density or compressibility to pressure, which will be examined below. Bullen has adhered throughout to two basic assumptions: (1) That the density at 33 km is 3.32; and (2) that the density always increases with depth. Though plausible, these are still assumptions; and the relatively small differences among Bullen's recalculations show that the restrictions so imposed are in fact severe.

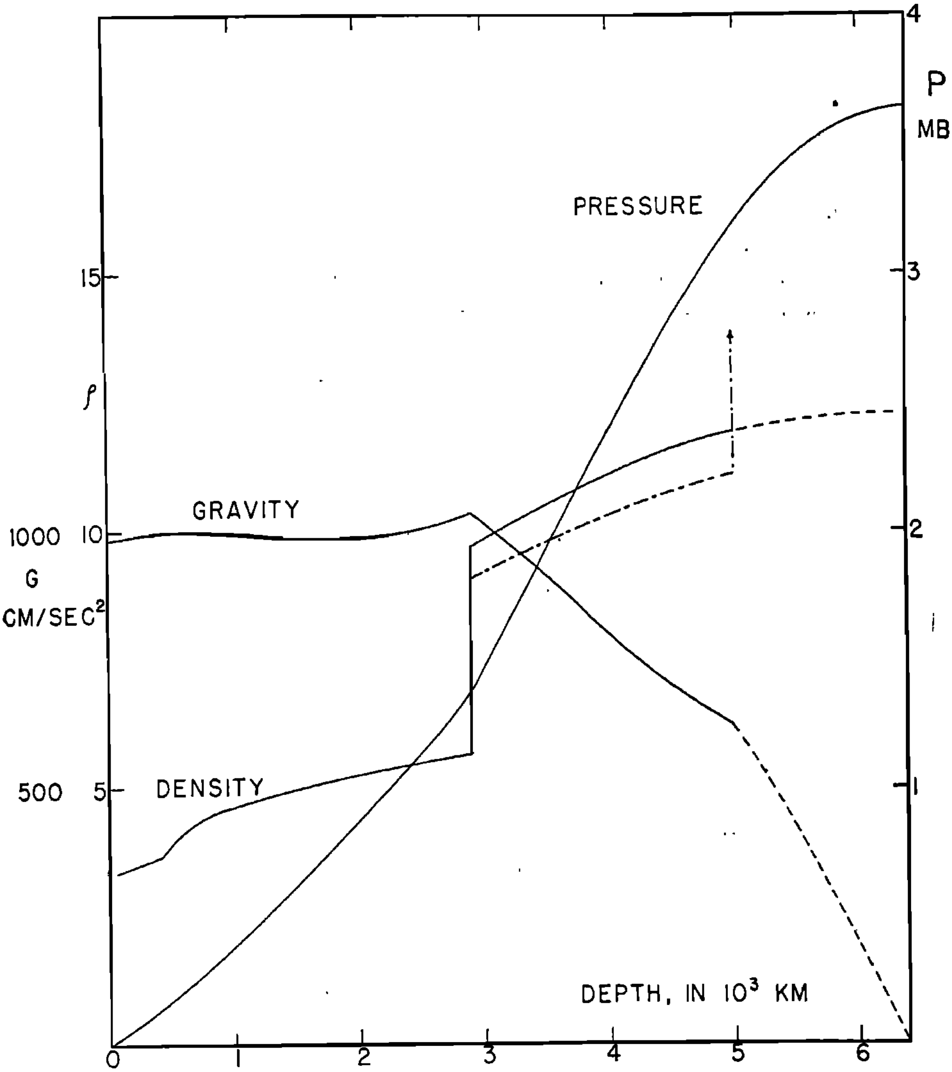


FIG. 2—DENSITY, PRESSURE, AND ACCELERATION WITHIN THE EARTH (AFTER BULLEN)

As these density distributions are derived with the aid of the Williamson-Adams relation, which is valid only for homogeneous layers, they can evidently not be used to investigate the question of homogeneity. It is necessary to return to the basic data, the seismic velocities. In an earlier paper (Birch, 1939), an effort was made to apply some approximate results of Murnaghan's theory of finite elastic strain as tests for homogeneity; in particular, to calculate the rates of change of the individual velocities with pressure and to compare these with the observed rates. There are now reasons for believing that this is not the most satisfactory approach; in addition, much new material, including Jeffreys' velocities, is now available for analysis. A more complete thermodynamic treatment is presented below, which shows what parameters are involved in the general case of a layer of uniform composition and phase, self-compressed, with an arbitrary gradient of temperature. The values of these parameters are then examined for a variety of materials, with the object of determining what general statements can be made without detailed knowledge of the composition and physical structure. Comparison of the theoretical changes for a homogeneous layer with the observed changes in the Earth then leads to certain tentative conclusions about the individual layers, with respect to homogeneity, gradient of temperature, and, finally, composition. Several abstracts of this work have already been published (Birch, 1950, 1951*b* and *c*).

A considerable number of papers concerning the Earth's interior have appeared within the last few years. Without attempting to give a complete bibliography, we may notice the reviews by Wildt (1942, 1947) and by Elsasser (1950); geochemical discussions by Kuhn and Rittmann (1941), Brown and Patterson (1948), Brown (1950), Urey (1951*a* and *b*), Latimer (1950); petrological-geophysical approaches by Buddington (1943) and by Daly (1943, 1946); several papers based on special hypotheses concerning behavior at high pressures by Ramsey (1948, 1949, 1950*a*) and Bullen (1949, 1950*a*); a new edition of "Internal Constitution of the Earth" (Gutenberg, Editor, 1951); Bullen's treatise (1947), which summarizes his earlier studies of density. Many others, including astronomical discussions of the origin of the solar system, have implications for the present problem. We shall have occasion to refer below to some of these studies, but it is not intended to discuss all of the numerous suggestions to be found in the literature.*

ACKNOWLEDGMENTS

The preparation of this paper has extended over several years, and I have had the advantage of many discussions. I owe the idea of a corundum-like structure for pyroxene and a rutile-like structure for silica to Dr. James B. Thompson. I am indebted to Professor Beno Gutenberg for an advance copy of his latest (now pub-

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*Unwary readers should take warning that ordinary language undergoes modification to a high-pressure form when applied to the interior of the Earth; a few examples of equivalents follow:

High-pressure form:	*Ordinary meaning*:
certain	dubious
undoubtedly	perhaps
positive proof	vague suggestion
unanswerable argument	trivial objection
pure iron	uncertain mixture of all the elements

lished) velocities for the core, and to Professor J. L. Rosenholtz for unpublished values of thermal expansion for several minerals. I am especially grateful to Dr. W. W. Rubey and to Professors P. W. Bridgman and Harvey Brooks for reading the manuscript in its nearly final form, and to Professors L. B. Slichter and Sidney Paige for opportunities to present various portions of it orally to critical audiences at Berkeley and New York.

EQUILIBRIUM OF A HOMOGENEOUS LAYER

Let us begin by considering the changes of density and compressibility which result from self-compression in a gravitational field and from variation of temperature. We suppose that there exists an equation of state, giving the density as function of pressure and temperature, and that there are no changes of phase or of composition. All quantities are taken as determined by the single variable r, the radius. The relation between pressure and radius is assumed to be the hydrostatic one*

$$dP = -g\rho\, dr \qquad (3)$$

In general the acceleration g is also a function of r; neglecting rotation, we have

$$g = -dU/dr$$

where U is the gravitational potential, given by Poisson's equation

$$\nabla^2 U = -4\pi G\rho$$

For spherical symmetry, the equation of equilibrium thus becomes

$$\frac{1}{r^2}\frac{d}{dr}\left(\frac{r^2}{\rho}\frac{dP}{dr}\right) + 4\pi G\rho = 0 \qquad (4)$$

With an equation of state giving a relation between P and ρ, this yields an equation for either P or ρ as function of r. Emden's book, "Gaskugeln," is largely devoted to developing solutions of equation (4) for the special case of the "polytropic" equation of state, $P = c\rho^k$, where c and k are constants. We need not, for the moment, introduce a particular equation of state.

The change of density with radius may be written in terms of coefficients of incompressibility K_T and thermal expansion α (see Notation):

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*The validity of treating the state of stress in the interior of the Earth as hydrostatic is sometimes questioned. The assumption of hydrostatic stress is, of course, an approximation, probably a poor approximation for the shallow crust, where the strength of the rocks is of the same order as the mean pressure. But the mean pressure steadily increases with the depth, while the strength, or maximum stress-difference, probably decreases; a depth is soon reached where the approximation is satisfactory. Suppose, for example, that the maximum stress difference at 300 km were comparable with that for surface rocks, say 10^3 bars; the mean pressure is about 10^5 bars. Thus the principal stresses would be equal to within one per cent. In fact, 10^3 bars is probably an overestimate of the strength below the crust, and from about 100 km down, the stress must be nearly hydrostatic, in the sense that the stress differences are always a small fraction of the mean pressure. A further consideration is that the density and compressibility depend only on the mean pressure, at least to the first order, and are independent of shearing stress. The assumption of hydrostatic pressure in this work is therefore to be understood as consistent with the presence of shearing stress even of large absolute value.

$$\frac{d\rho}{dr} = \left(\frac{\partial \rho}{\partial P}\right)_T \frac{dP}{dr} + \left(\frac{\partial \rho}{\partial T}\right)_P \frac{dT}{dr} = \frac{g\rho^2}{K_T} - \rho\alpha \frac{dT}{dr} \qquad (5)$$

For comparison with the Williamson-Adams equation (2), it is desirable to write (5) in such a way as to exhibit the effect of a departure from adiabatic conditions, by which we mean a relation between the changes of pressure and temperature with depth such that

$$dT/dP = (\partial T/\partial P)_S = T\alpha/\rho C_P$$

In general,

$$\frac{dT}{dr} = \frac{T\alpha}{\rho C_P}\frac{dP}{dr} - \tau = -\frac{T\alpha g}{C_P} - \tau \qquad (6)$$

the gradient of temperature τ merely denoting the difference between the actual gradient of temperature and the adiabatic gradient, $-T\alpha g/C_p$ (the negative sign arising from differentiation with respect to radius instead of depth). By virtue of the thermodynamic relations between isothermal and adiabatic incompressibility, $K_T/K_S = 1 - T\alpha^2 K_T/\rho C_P$, the equation for the density change may be written (see also Birch, 1939, p. 472)

$$\frac{d\rho}{dr} = -\frac{g\rho^2}{K_T}(1 - TK_T\alpha^2/\rho C_P) + \alpha\rho\tau = -g\rho^2/K_S + \alpha\rho\tau = -g\rho/\phi + \alpha\rho\tau \quad (7)$$

The term in τ is neglected in the Williamson-Adams method (see equation 2), but it may be appreciable. It is convenient to introduce a combination of quantities which we shall call "Grüneisen's ratio" and designate by $\gamma = \alpha K_S/\rho C_P$ (see below). Then we have

$$\frac{d\rho}{dr} = -\frac{g\rho}{\phi}(1 - \alpha\phi\tau/g) = -\frac{g\rho}{\phi}(1 - \gamma C_P\tau/g) \qquad (8)$$

Anticipating the results of a later section, we take γ as approximately 1 to 2, C_P as 10^7 ergs/gm.deg; g is about 10^3 cm/sec^2 throughout the mantle. Then for τ equal to 1°/km, we find $\gamma C_P\tau/g$ to be about 0.1–0.2, or 10 to 20 per cent of the main term. A departure from the adiabatic gradient by as much as 1°/km will thus sensibly affect the validity of the Williamson-Adams method, even for a homogeneous layer.

For an isothermal layer, $dT/dr = 0$, and $d\rho/dr = -g\rho^2/K_T$. This differs from (2) only by the appearance of K_T in place of K_S. The difference between these two quantities is proportional to $T\alpha\gamma$ and is estimated below (see Table 16).

Let us now consider what further evidence may be derived from the seismic velocities. Bullen (1949) has called attention to the quantity, $1 - g^{-1}\, d\phi/dr$, which may be formed from the $\phi - r$ tables. By definition of ϕ, $K_S = \phi\rho$, whence it follows that

$$1 - g^{-1}\, d\phi/dr = dK_S/dP + \alpha\phi\tau/g \qquad (9)$$

Bullen gives simply dK/dP for the right side of (9), in accordance with the assumption of an adiabatic gradient implicit in the Williamson-Adams method. In general, however, a temperature effect is also concealed in dK_S/dP, since we have

$$\begin{aligned}\frac{dK_S}{dP} &= \left(\frac{\partial K_S}{\partial P}\right)_T + \left(\frac{\partial K_S}{\partial T}\right)_P \cdot \frac{dT}{dP}\\ &= \left(\frac{\partial K_S}{\partial P}\right)_T + \left(\frac{\partial K_S}{\partial T}\right)_P \left[\frac{T\alpha}{\rho C_P} + \frac{\tau}{\rho g}\right]\\ &= \left(\frac{\partial K_S}{\partial P}\right)_S + \left(\frac{\partial K_S}{\partial T}\right)_P \cdot \frac{\tau}{\rho g}\end{aligned}$$

Consequently, we have

$$1 - g^{-1}\, d\phi/dr = \left(\frac{\partial K_S}{\partial P}\right)_S + \frac{\tau\alpha\phi}{g}\left[1 + \frac{1}{\alpha K_S}\left(\frac{\partial K_S}{\partial T}\right)_P\right] \ldots\ldots\ldots (10)$$

It is useful to have this result in terms of K_T, and we introduce the relation, $K_S = K_T(1 + T\alpha\gamma)$, equivalent to the expression given above. We then obtain the following exact relation, in which all quantities, including γ, have been treated as functions of P and T:

$$1 - g^{-1}\, d\phi/dr = (\partial K_T/\partial P)_T + T\alpha\gamma A + (T\alpha\gamma)^2 B + \alpha\phi\tau g^{-1} C \ldots\ldots (11)$$

where A, B, and C are functions of dimensionless parameters of the homogeneous material, as follows:

$$\left.\begin{aligned} A &= 2\left(\frac{\partial K_T}{\partial P}\right)_T - 1 + \gamma + \frac{3}{\alpha K_T}\left(\frac{\partial K_T}{\partial T}\right)_P\\ B &= \left(\frac{\partial K_T}{\partial P}\right)_T + \frac{3}{\alpha K_T}\left(\frac{\partial K_T}{\partial T}\right)_P + \frac{3}{\alpha^2}\left(\frac{\partial \alpha}{\partial T}\right)_P + 1 - \frac{1}{\alpha C_P}\left(\frac{\partial C_P}{\partial T}\right)_P\\ C &= 1 + \frac{1}{\alpha K_S}\left(\frac{\partial K_S}{\partial T}\right)_P = 1 + \gamma + \frac{1}{\alpha K_T}\left(\frac{\partial K_T}{\partial T}\right)_P\\ &\quad + T\alpha\gamma\left[1 + \frac{1}{\alpha K_T}\left(\frac{\partial K_T}{\partial T}\right)_P + \frac{2}{\alpha^2}\left(\frac{\partial \alpha}{\partial T}\right)_P - \frac{1}{\alpha C_P}\left(\frac{\partial C_P}{\partial T}\right)_P\right]\end{aligned}\right\} \quad (12)$$

The numerical values of these parameters will be considered in the next section, and we shall then attempt a comparison of the values of $1 - g^{-1}\, d\phi/dr$, as predicted by equation (11) for a homogeneous layer, with the values of this quantity as formed from the seismic velocities. Fortunately, the quantity $T\alpha\gamma$ is small enough so that its square may be neglected, with an appreciable simplification of the results.

EVALUATION OF THE PARAMETERS

In the preceding section, we have seen that a test for uniformity may be based on the comparison of the function, $1 - g^{-1}\, d\phi/dr$, which may be found from the seismic velocities, with a group of dimensionless parameters given in equations (11, 12), of which the most important is $(\partial K_T/\partial P)_T$. This formulation is useful only if these parameters can be shown to have relatively narrow ranges of variation for the conditions and materials likely to exist in the interior of the Earth. Since it is inherent in this problem that we do not know in advance exactly what materials we are dealing with, we are forced to rely only upon generalizations of the widest possible validity. Furthermore, since no experiments embrace the whole range of conditions, it is necessary to introduce theoretical considerations to show that experimentally-determined parameters may be applicable under the conditions of interest.

As the dominant physical variable in the deep interior of the Earth is the pressure, the extensive experimental work at high pressures is the most important body of information for this analysis. Bridgman's latest measurements of compression reach 100,000 bars, equivalent to a depth of some 300 km in the Earth, over twice the central pressure of the Moon, and about equal to the central pressure of Mercury. Even more important, in this experimental range the compressions of several relatively compressible materials exceed the compressions of any of the major components of the Earth. These measurements of large compressions enable us to apply severe tests to theoretical equations of state.

It is also part of our problem to appraise the effects of temperature. An important distinction between "high" and "low" temperatures, with reference to the properties of solids, depends upon recognition of a "characteristic temperature," which roughly marks the division between these two regions. Though certain properties, such as compressibility, which depend only in part upon the thermal energy, show little relation to the characteristic temperature, others, notably specific heat and thermal expansion, vary enormously in the neighborhood of this temperature. Both specific heat and thermal expansion are small at low temperatures, rise rapidly near the characteristic temperature, and approach high limiting values at high temperatures; their derivatives, such as $\alpha^{-1}(\partial\alpha/\partial T)_P$ or $C_P^{-1}(\partial C_P/\partial T)_P$, are very large at low temperatures, relatively small at high temperatures. The idea of the characteristic temperature originated in the theories of the specific heat of Einstein and of Debye, and has proved indispensable for the theory of the solid state. A number of excellent treatments of this subject are available, and we shall make use of some of the results without reproducing the derivations (see, for example, Grüneisen, 1926; Slater, 1939; Seitz, 1940).

It is thus necessary, in our attempt to decide upon the best *a priori* values for the parameters of equation (11), to commence by forming rough estimates of the characteristic temperatures at various depths in the Earth. These values, shown in Table 2, are obtained with the aid of Debye's relation (Slater, 1939, pp. 234, 235; see also equation 17 below), on substitution of the seismic velocities, the density as given by Bullen (1947, pp. 211, 218), and the assumption of a mean atomic weight of 20 gm (see Table 11). We find, approximately, $T_D = 100\rho^{1/3}V_S$, where V_S is in km/sec, and T_D in degrees absolute. As the temperature at 100 km is probably at least 900° (absolute), it seems likely that all parts of the mantle, below the crust, are above the Debye temperatures for the corresponding depths, and thus that we are interested in the properties at "high" temperatures, in spite of the important effects of pressure.

On the other hand, much of the experimental data refers to temperatures close to or below the characteristic temperatures. This is especially true of measurements on the oxides, silicates, and "harder" metals (hardness itself being a good indication of the distance below the characteristic temperature); the "softer" materials, such as the alkali metals and lead, are actually of more interest for the purpose of finding typical values for the "high" temperature coefficients.

TABLE 2—*Estimates of Debye temperatures at various depths*

Depth	V_S	ρ	T_D
km	*km/sec*	*gm/cm*^{3}	°*K*
100	4.45	3.4	670
600	5.66	4.1	900
1000	6.36	4.7	1060
2600	7.21	5.5	1280

EQUATIONS OF STATE

Equations of state for solids may be classified as follows: (1) Approximate quantum-mechanical treatments of elements and simple ionic lattices, at (absolute) zero temperature. The purpose of these calculations is usually to derive values of cohesive energy, equilibrium spacing, compressibility and other elastic constants in terms of atomic constants alone. (2) Equations derived by the Thomas-Fermi approximation, in which a solid is treated as an electron gas, subject to the Fermi-Dirac statistics. (3) Equations based on semi-empirical laws of cohesion, supplemented by approximate treatment of the temperature-dependent energy; for example, the theories of Grüneisen and of Born and his collaborators. These theories predict important relations among independently measured quantities, such as compressibility, thermal expansion, specific heats, and pressure and temperature coefficients of these parameters. (4) Equations based on thermodynamics, such as the theories of elasticity. Though of great generality, such equations do not in themselves supply values for the various parameters, which must be found by other means.

As yet, there are no complete quantum-mechanical studies for materials likely to be important in the interior of the Earth, though iron has received much attention, and the theory of simple ionic crystals such as the alkali halides is far advanced. Some of the simpler oxides might be amenable to this kind of treatment.

The Thomas-Fermi method has been applied by a number of writers to elements (Slater and Krutter, 1935; Jensen, 1938; Marshak and Bethe, 1940; Feynman, Metropolis and Teller, 1949; Elsasser, 1951), and might also be applied to compounds (Marshak and Bethe). The results are of interest principally for astrophysics, as the neglect of atomic structure can be justified only when the pressures are extremely high—probably greater than 10 megabars for the relatively incompressible materials. Jensen has constructed an interpolation curve for iron, connecting the experimental, low-pressure density with the Thomas-Fermi curve, with the aid of the seismic velocity in the Earth's core (see Fig. 8); this curve is now cited as support for the idea that the core is iron. This subject will be considered further below.

One of the outstanding successes of the classical theory of solids is the relation of Mie and Grüneisen, usually known as "Grüneisen's law," which connects the thermal expansion with the specific heat and compressibility in terms of a quantity γ, defined above. Although this quantity, a number usually between 1 and 3, changes remarkably little with temperature, it is not independent of volume, and it is proposed that it be called "Grüneisen's ratio," instead of the usual "Grüneisen's constant." In any case, γ is useful in condensing thermodynamic relations, and its variation will be considered with relation to the change of thermal expansion with pressure. The more rigorous theory of Born (1939) is developed only for temperatures above the Debye temperature, but it takes into account compressions of any magnitude, and furnishes theoretical values for Grüneisen's ratio; the conditions for which this theory is constructed are just those in which we are interested, and a vast amount of numerical calculation has been carried out by Born and his collaborators. The usefulness of this material is somewhat limited by special assumptions with regard to the laws of force between particles, and by the restriction to cubic lattices of a single kind of particle.

The theory of finite strain developed by Murnaghan (1937) is particularly useful in problems concerning elasticity at high pressures. This theory, thermodynamic in character, is a rigorous development of the theory of elasticity in which no restrictions are imposed on the magnitude of the strains. The theory is formally exact, but, in practice, limitations arise from ignorance of the coefficients of higher-order than the second which appear in the development of the strain-energy as a function of the strains. In the usual theory, only the coefficients of the second-order terms are retained in the strain-energy function; the strains are treated as small and their squares and products systematically discarded. It turns out, however, that even when only the known second-order coefficients in the strain-energy are retained, the theory of finite strain gives an excellent account of the compression of many materials, including those for which the greatest compressions have been observed—the alkali metals. It appears (Birch, 1947) that the third-order coefficient which occurs in the compressibility is in fact small in relation to the second-order term for a large number of materials, and to a good approximation may often be neglected. New experimental evidence on this point is reviewed below.

In an isotropic elastic medium, there are two independent groups of third-order terms which determine the wave-velocities at a given pressure; for cubic crystals, there are three independent groups, and so on. From the fact that one of these groups, which determines the change of compressibility with pressure, is small, it does not necessarily follow that the other groups are also small, although the assumption that all were negligible was made in earlier work (Birch, 1938, 1939) for lack of data to the contrary. There is now evidence that the group of third-order terms which determines the change of rigidity with pressure may be of the same magnitude as the second-order terms, and even of opposite sign. It seems that while the individual velocities at high compressions can probably not be predicted with confidence if third-order terms are unknown, the variation of density and even the variation of compressibility with pressure may still be found with remarkable success by use of the second-order elastic constant alone. The third-order term is retained in the results given below, but will usually be treated as negligible; the theory then gives a relation between pressure and volume for isothermal compression in terms of a single parameter, either the compressibility, or its reciprocal, the incompressibility, at zero pressure.

The complete form of Murnaghan's theory is required for the discussion of the effect of pressure upon individual elastic constants and velocities, but the relation between hydrostatic pressure and volume may be obtained directly from the thermodynamic relation, $P = -(\partial\Psi/\partial v)_T$, where Ψ is the Helmholtz free energy, and v the volume, per unit mass. In the ordinary theory of elasticity, the free energy is equated to the strain energy and expressed as a quadratic function of the strain components, higher powers being neglected. The coefficients of the second-order combinations of the strain components are the "elastic constants," which depend upon the temperature. These will be termed the "second-order elastic constants." In the theory of finite strain, the expressions for the strain components, referred to the strained state, are as follows, where (u, v, w) are the components of the displacement, (x, y, z) the Cartesian coordinates of a point after the displacement:

$$\epsilon_{xx} = \frac{\partial u}{\partial x} - \frac{1}{2}\left[\left(\frac{\partial u}{\partial x}\right)^2 + \left(\frac{\partial v}{\partial x}\right)^2 + \left(\frac{\partial w}{\partial x}\right)^2\right]$$

$$\epsilon_{yz} = \frac{1}{2}\left(\frac{\partial v}{\partial z} - \frac{\partial w}{\partial y}\right) - \frac{1}{2}\left[\frac{\partial u}{\partial y}\frac{\partial u}{\partial z} + \frac{\partial v}{\partial y}\frac{\partial v}{\partial z} + \frac{\partial w}{\partial y}\frac{\partial w}{\partial z}\right], \text{ etc.}$$

For the special case of hydrostatic strain of a medium of isotropic or cubic symmetry, the strain degenerates to a single component,

$$\epsilon = \frac{\partial u}{\partial x} - \frac{1}{2}\left(\frac{\partial u}{\partial x}\right)^2 = \frac{\partial v}{\partial y} - \frac{1}{2}\left(\frac{\partial v}{\partial y}\right)^2 = \frac{\partial w}{\partial z} - \frac{1}{2}\left(\frac{\partial w}{\partial z}\right)^2$$

The relation between strain ϵ and volume v or density ρ is

$$v_0/v = \rho/\rho_0 = (1 - 2\epsilon)^{3/2} = (1 + 2f)^{3/2}$$

where the subscript zero refers to zero pressure, and $f = -\epsilon$, a more convenient variable for compression, f being always positive. We suppose that for hydrostatic pressure alone, the strain energy may be expressed in the form

$$\Psi = af^2 + bf^3 + cf^4 + \cdots$$

where $a, b, c, \cdots$ are functions only of temperature. Then the pressure is

$$P = -(\mathrm{d}f/\mathrm{d}v)(\partial\Psi/\partial f)_T = (3v_0)^{-1}(1 + 2f)^{5/2}(2af + 3bf^2 + \cdots)$$

or, with the notation formerly used (Birch, 1947)

$$P = 3K_0 f(1 + 2f)^{5/2}(1 - fD_3/3K_0 + \cdots)$$

In terms of the density, and with $\xi = D_3/6K_0$, we have also

$$P = 3/2\, K_0[(\rho/\rho_0)^{7/3} - (\rho/\rho_0)^{5/3}]\{1 - \xi[(\rho/\rho_0)^{2/3} - 1] + \cdots\} \ldots\ldots (13)$$

K_0 and ξ are functions of the temperature alone; K_0 is the isothermal incompressibility at $P = 0$. The convergence of the series depends upon the amount of compression, given by f, or by ρ/ρ_0, and upon the magnitudes of the coefficients of higher powers of f. In the Earth, f does not exceed about 0.3, which corresponds to $\rho/\rho_0 = 2$; in the mantle f is less than 0.13 (see below, Table 3).

COMPARISON WITH MEASUREMENTS OF COMPRESSION

When ξ is so small that this and higher terms may be neglected, the pressure is given by

$$P = 3/2\,K_0[(\rho/\rho_0)^{7/3} - (\rho/\rho_0)^{5/3}] = 3/2\,K_0F, \text{ say} \ldots\ldots\ldots\ldots (14)$$

Then the ratio F/P, formed from the experimental data, should be a constant for a given material (and temperature). When this test was first applied to the measurements (Birch, 1947) for a number of elements and ionic compounds, it was found that the ratio F/P was in fact nearly constant, to an approximation usually comparable with the experimental uncertainty. The first measurements (Bridgman, 1941) on the alkali metals in the 100,000-bar range, however, deviated conspicuously from this relation at the higher pressures. Since this time, Bridgman has introduced a number of improvements of techniques, and the new measurements (Bridgman, 1948) are shown in Table 3, and Figure 3, as well as an older series, with different experimental arrangements, to 45,000 bars. It is clear that little improvement would result from taking a non-zero value for the ratio ξ, and that the agreement with (14) is well within the experimental uncertainty.

TABLE 3—*The ratio F/P for the alkali metals*
(Compressions from Bridgman, 1938, 1948; F/P in 10^{-6} cm²/kg)

P (in 10^3 kg/cm²)	Li		Na		K		Rb		Cs	
	v/v_0	F/P	v/v_0	F/P	v/v_0	F/P	v/v_0	F/P	v/v_0	F/P
5	0.957	6.41	0.929	11.3	0.884	21.0	0.826	37.4	0.818	40.1
10	0.926	5.99	0.883	10.7	0.817	20.2	0.767	30.1	0.729	39.7
15	0.899	5.84	0.852	9.8	0.770	19.6	0.721	28.0	0.674	38.7
20	0.875	5.81	0.818	10.0	0.732	19.4	0.684	27.1	0.628	39.5
25	0.855	5.73	0.791	10.0	0.699	19.6	0.655	26.4	0.586	41.7
30	0.835	5.77	0.767	10.0	0.671	19.7	0.629	26.1	0.568	39.2
35	0.816	5.81	0.746	10.0	0.647	19.9	0.607	25.9	0.542	40.0
40	0.798	5.91	0.727	10.1	0.627	19.9	0.587	25.9	0.519	40.9
45	0.782	5.97	0.710	10.1	0.604	20.6	0.569	26.0	0.499	41.7
30	0.833	5.84	0.770	9.81	0.668	20.2	0.652	22.4	0.571	38.4
40	0.801	5.76	0.737	9.38	0.628	19.7	0.612	22.0	0.521	40.3
50	0.773	5.76	0.708	9.21	0.595	19.7	0.578	22.0	transition	
60	0.748	5.78	0.683	9.11	0.568	19.6	0.551	22.0		
70	0.727	5.76	0.661	9.05	0.546	19.5	0.528	22.0		
80	0.707	5.79	0.641	9.05	0.528	19.2	0.507	22.2		
90	0.689	5.83	0.623	9.07	0.513	19.0	0.489	22.4		
100	0.672	5.88	0.606	9.13	0.500	18.7	0.473	22.6		

For relatively incompressible substances, another test may be applied. If the change of volume is expressed in the form, $-\Delta v/v_0 = aP - bP^2$, where Δv is the change of volume from the initial volume v_0 produced by the pressure P, then the equation of state (13) leads to the relation, $2b/a^2 = 5 - 4/3\,\xi$. For most elements and a large number of simple compounds, the experimental values of $2b/a^2$ are close to 5, with $|\xi| < \frac{1}{2}$ (Slater, 1940; Birch, 1938, 1947).

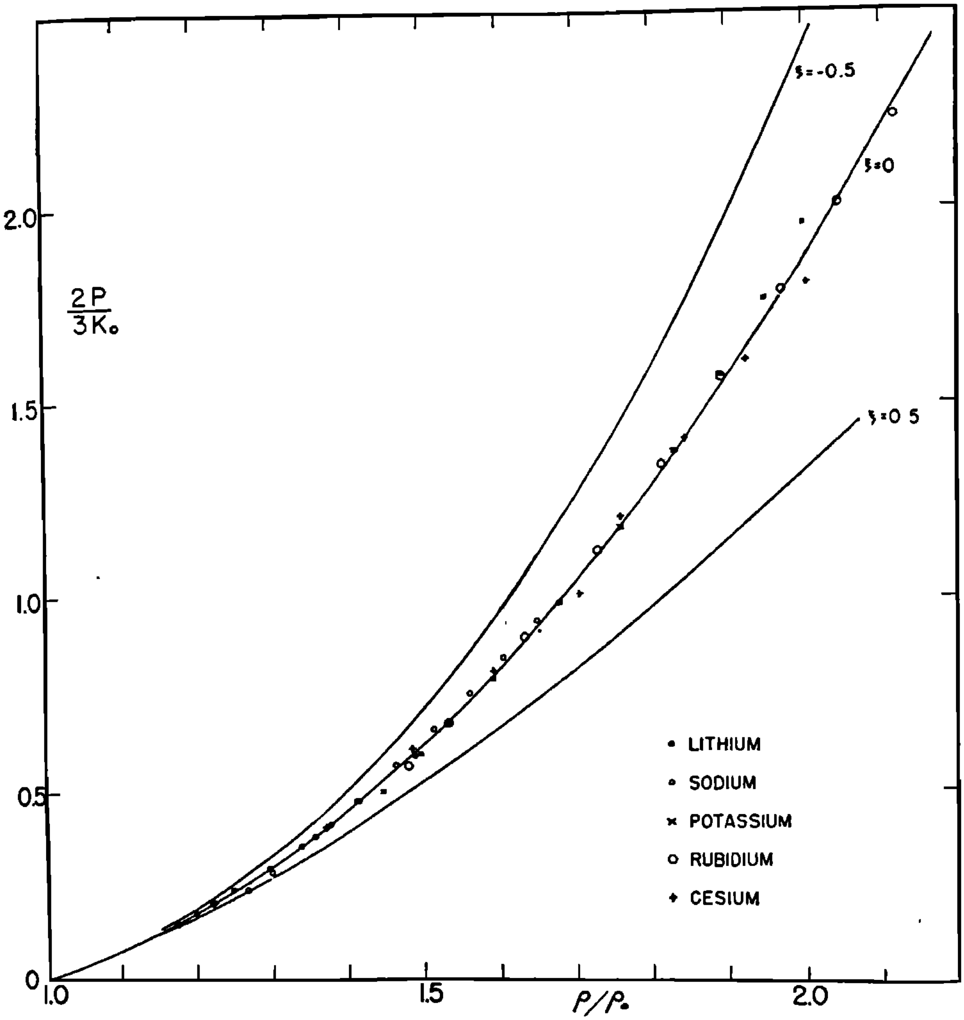


FIG. 3—COMPRESSION OF THE ALKALI METALS

New measurements to 30,000 kg/cm^2 (Bridgman, 1949) furnish still better tests of this relationship for materials of low compressibility, for which the former range of 12,000 kg/cm^2 was barely adequate to give reliable values of the initial curvature. When the relative change of volume is small, say less than 5 per cent, we may with an error of less than one per cent expand F in terms of $\Delta v/v_0$, the quantity given in Bridgman's tables (where Δv is taken positive for a decrease of volume), obtaining

$$\beta_0 = (\Delta v/v_0 P)(1 + 5/2\ \Delta v/v_0)(1 - 2/3\ \xi\Delta v/v_0)$$

If $\xi = 0$, then the quantity $(\Delta v/v_0 P)(1 + 5/2\ \Delta v/v_0)$ should be independent of pressure for each material. It is clear, however, that the last factor will remain close to 1 so long as $\Delta v/v_0$ is small; for example, if $\xi = 1$, the deviation from unity will reach 0.01 for $\Delta v/v_0 = 0.015$. An extraordinary precision is therefore required in order to set narrow limits on ξ for the incompressible materials. In Table 4 is tabulated the quantity $(\Delta v/v_0P)(1 + 2.5\Delta v/v_0)$ for six pressures; if $\xi = 0$, this should be constant and equal to β_0, the initial compressibility.

TABLE 4—*Data for materials of low compressibility*

[Initial compressibility, β_0, calculated from $(\Delta v/Pv_0)(1 + 2.5\Delta v/v_0)$, β_0 in units of 10^{-7} cm^2/kg; after Bridgman, 1949]

Material	P in kg/cm^2					
	$P = 5{,}000$	10,000	15,000	20,000	25,000	30,000
Iridium	2.74	2.74	2.75	2.76	2.78	2.78
Tungsten	3.12	3.15	3.24	3.25	3.26	3.33
Ruthenium	3.12	3.18	3.26	3.30	3.40	3.38
Platinum	3.57	3.60	3.68	3.58	3.59	3.59
Molybdenum	3.60	3.60	3.62	3.64	3.64	3.64
Rhodium	3.63	3.69	3.68	3.68	3.68	3.68
Tantalum	4.88	4.91	4.92	4.95	4.98	5.00
Cobalt	5.10	5.10	5.16	5.16	5.17	5.16
Nickel	5.58	4.85	5.10	5.13	5.21	5.24
Palladium	5.38	5.24	5.16	5.21	5.26	5.27
Gold	5.66	5.66	5.66	5.66	5.66	5.64
Iron	5.82	5.83	5.83	5.83	5.82	5.82
Copper	7.12	7.08	7.11	7.09	7.07	7.04
Titanium	9.08	9.20	9.17	9.46?	9.17	9.16
Silver	9.72	9.63	9.58	9.52	9.48	9.35
Silicon	10.02	9.90	9.84	9.90	9.92	9.86
Germanium	12.75	12.77	12.76	12.73	12.72	12.72
Aluminum	13.95	13.56	13.63	13.45	13.39	13.32
Zinc	16.26	16.41	16.23	16.01	15.88	15.77
Tin	18.2	18.1	17.9	17.8	17.7	17.7
Thorium	19.1	18.1	17.5	17.2	17.0	17.1
Antimony	25.8	25.7	25.6	25.0	24.7	24.5
35%Ni, 65%Fe	9.16	9.16	9.22	9.18	9.14	.....
Garnet	5.48	5.45	5.45	5.50	5.51	5.50
MgO	5.84	5.79	5.85	5.85	5.84	5.81
Fluorite	11.88	11.80	11.78	11.68	11.70	11.71
LiF	14.50	14.55	14.50	14.39	14.30	14.20
Al_2O_3	3.56	3.58	3.62	3.58	3.64	3.66
Beryl	5.19	5.20	5.33	5.30	5.37	5.38
Topaz	5.74	5.78	5.88	5.92	5.92	5.97

As Bridgman has pointed out, the three elements of lowest compressibility (*Ir*, *W*, *Ru*) are all "abnormal," in that the compressibility increases with the pressure, an effect perhaps arising from lack of homogeneity or from initial strain. For a number of materials, the best value for ξ is close to zero. The most common deviation is toward a small negative value of ξ. The deviations are larger for many of the intermetallic compounds, some of which exhibit surprising properties. For example, the alloy containing 35 per cent Ni, 65 per cent Fe is nearly twice as compressible as either pure nickel or pure iron.

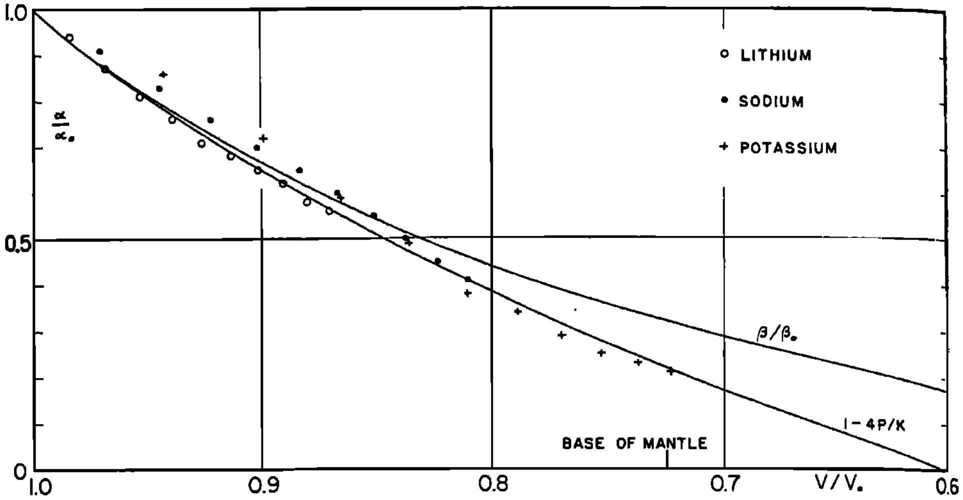
Extraordinarily consistent results are shown for Pt, Co, Au, Fe, and Ge, and the cubic compounds garnet, periclase, fluorite, and lithium fluoride; fairly constant values are found even for corundum, beryl, and topaz, to which the theory does not strictly apply because of their lower symmetry.

Lazarus (1949) gives the effect of pressure on all of the adiabatic elastic constants of KCl, NaCl, Al, and Cu, and has used these to compute the isothermal compressibility and change of compressibility. From these measurements, it is found that $2b/a^2$ is close to 5 except for KCl, for which it is equal to 4.5, and hence $\xi = 0.4$; ξ is negligible for Al and Cu, and equals -0.3 for NaCl. Slightly different values have been found by other experimenters (Birch, 1947). On the other hand, the effect of pressure on the individual elastic constants is in many instances decidedly different from the effect to be expected if all of the third-order constants were negligible. This is especially true of the shear modulus, C_{44} ; in NaCl and KCl, the third-order terms are approximately equal to the second-order terms, and, though relatively smaller for Al and Cu, they are still appreciable; furthermore, except for Al, the sign of the third-order terms is such as to reduce the effect of pressure on C_{44}, even reversing its direction for KCl. This is consistent with Bullen's observation (1940) that when the third-order terms are neglected the theory predicts too high a rate of variation of the velocity of shear waves with pressure. In order to calculate the individual velocities as function of pressure, we still require a way of finding the individual third-order terms, or what is equivalent for an isotropic medium, a way of calculating the change of Poisson's ratio with pressure.

For many purposes, it is convenient to write the equation of state (13) in terms of the strain f; we also require the compressibility β or its reciprocal K. At $P = 0$ these are β_0 and K_0 , functions only of the temperature. These and several other useful relations, all for isothermal compression, are as follows:

$$\left.\begin{aligned}
&P = 3K_0f(1 + 2f)^{5/2}(1 - 2\xi f)\\
&K = K_0(1 + 2f)^{5/2}[1 + 7f - 2\xi f(2 + 9f)]\\
&(\partial K/\partial P)_T = [12 + 49f - 2\xi(2 + 32f + 81f^2)]/3[1 + 7f - 2\xi f(2 + 9f)]\\
&K/\rho = K_0(1 + 2f)[1 + 7f - 2\xi f(2 + 9f)]/\rho_0\\
&\Psi = 9/2(K_0/\rho_0)f^2\,(1 - 4/3\,\xi f)\\
&\text{with } \rho/\rho_0 = (1 + 2f)^{3/2}
\end{aligned}\right\}\quad ..(15)$$

The agreement of equation (14) with the experimental compressions appears to be within the experimental errors for most materials, and the fact that this is achieved with a single adjustable parameter gives this equation very great utility. Any other equation which fits the experimental data as well must be practically indistinguishable from (14). The range of compression, if not of pressure, over which it has been tested, covers the range of compression of major components within the Earth. The principal question is whether a law which is evidently highly accurate for the alkali metals and halides is necessarily correct for the relatively incompressible materials of the interior. The available evidence for the incompressible materials supports a value in the neighborhood of zero for the parameter ξ, just as for the alkali metals, but with small experimental compressions the determination cannot be very exact. The dependence of ξ upon temperature is also a troublesome question which arises in connection with the thermal expansion.



THERMAL EXPANSION Versus VOLUME

FIG. 4—THERMAL EXPANSION OF THE ALKALI METALS AS FUNCTION OF COMPRESSION

CHANGE OF COMPRESSIBILITY WITH PRESSURE

With $\xi = 0$, its most probable, or most frequent, value, equation (15) gives an expression for $(\partial K_T/\partial P)_T$ as function of the (negative) strain f

$$\left(\frac{\partial K_T}{\partial P}\right)_T = \frac{12 + 49f}{3(1 + 7f)} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (16)$$

Thus its value is 4 at zero pressure,* and it diminishes toward about 3 for the greatest compressions of the mantle. Values for several strains, and for other values of ξ are shown in Table 5.

Table 5—$(\partial K_T/\partial P)_T$ *as function of compression*

f	ρ/ρ_0	$(\partial K_T/\partial P)_T$		
		$\xi = 1/2$	$\xi = 0$	$\xi = -1/2$
0	1.000	3.33	4.00	4.66
0.1	1.315	2.58	3.31	3.84
0.2	1.656	2.07	3.03	3.53
0.3	2.024	1.53	2.87	3.37

---

*Some confusion has resulted from carelessness in defining K. Thus, if we take $K' = \rho_0(\partial P/\partial \rho)_T$, where ρ_0 is the density at zero pressure, we find $(\partial K'/\partial P)_0 = 5$, instead of the value 4 given above. In the present paper, K is always $\rho(\partial P/\partial \rho)$, ρ being the density at pressure P.

These results may be compared with certain simplifying hypotheses introduced by Bullen (1950*a*) and by Ramsey (1950*a*). The latter supposes that the interior of the Earth consists essentially of a single material, that the density depends on

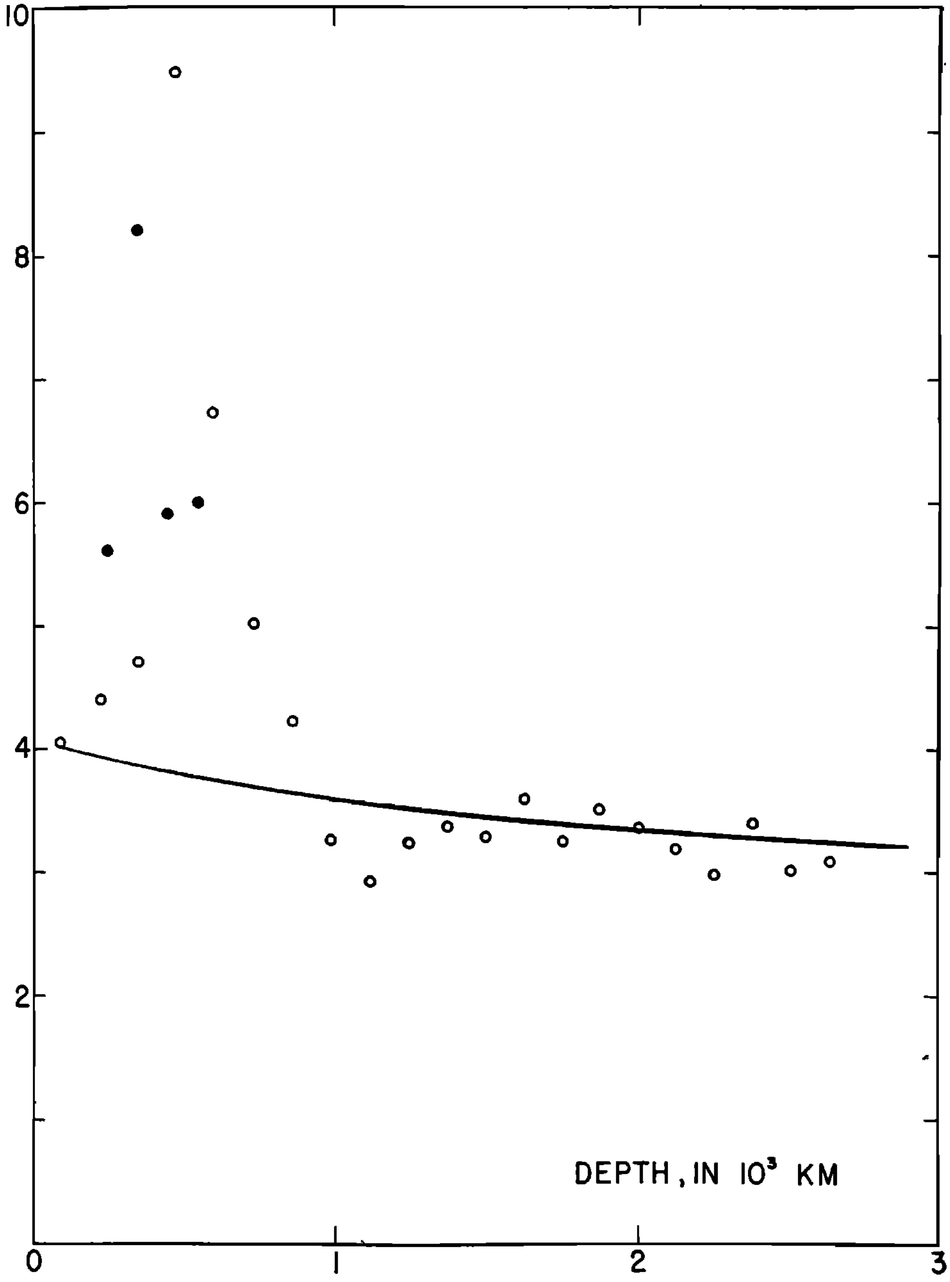


FIG. 5—THE FUNCTION, $1-g^{-1}\Delta\phi/\Delta r$, FOR THE MANTLE

the pressure alone, and that except at low pressures, dK/dP is a constant, equal to 3.7 for the mantle, 3.8 for the core (see also Murnaghan, 1944). Bullen supposes that at high pressures, all major components of the Earth have the same compressibility, expressed by a universal formula, $K = 2.25 + 2.86P + 0.16P^2$, with K and P in megabars. This leads to $dK/dP = 2.86 + 0.32\,P$. Both of these treatments fail at low pressures, so that they cannot be compared directly, as can (14), with experiment. They are evidently not in agreement with the measurements of large compressions, and it is unlikely that dK/dP increases with pressure, as Bullen's formula implies. In neither case has the variation of ϕ been used directly to find dK/dP according to (9); instead, the density distribution has been first calculated, with the aid of various assumptions, then K according to $K = \phi\rho$; and this is then found to be approximately linear in the pressure. Bullen's and Ramsey's expressions may be regarded as at best approximately valid over limited ranges of pressure for the particular materials of the Earth's interior. A better average value for dK/dP in layer D is about 3.3, rather than 3.7 (see Table 12 and Fig. 5).

It is true that as the pressure increases, compressibilities which are initially different tend to approach one another. As a numerical example, consider two materials characterized by initial incompressibilities $K_0(A)$ and $K_0(B)$, compressed to a common pressure at which the strains are, respectively, $f_A = 0.10$ and $f_B = 0.15$. With the aid of (15) we readily find, for $\xi = 0$, that the ratio of initial compressibilities is 1.83, while the ratio at the high pressure is only 1.24. The components of the Earth do not differ greatly with respect to initial compressibility (see Table 15) and it is not surprising that the difference at high pressures is relatively small. There is no reason to believe that it vanishes, or becomes independent of composition, except in this sense.

For the compressions of the core, equation (16) leads to a value of $(\partial K/\partial P)_T$ (see below, Table 17), insignificantly different from 3. This leads, approximately, to $K \propto \rho^3$, and $V_P \propto \rho$, relations which may prove useful in computing the density of layer E. It is also noteworthy that $dK/dP = 3$ is equivalent to the assumption, $n = \frac{1}{2}$, or $k = 3$, in the polytropic equation of state; the solution of equation (4) given in Emden's book for this case may be used in discussing the equilibrium of the core. The assumption, $dK/dP =$ constant, always leads to a form of Emden's equation; $dK/dP = 2$ yields Laplace's law of density.

THERMAL EXPANSION AND GRÜNEISEN'S RATIO

The theory of thermal expansion is closely related to the theory of specific heat. Grüneisen's ratio is very nearly independent of temperature and, consequently, except for the change of compressibility with temperature, thermal expansion is proportional to specific heat. By virtue of the relation $\alpha = \gamma C_P/\phi$, we can obtain estimates of the thermal expansion in the interior of the Earth, since ϕ is given by seismology, C_P may be assigned its high-temperature value (see below), and γ is usually in the neighborhood of 1 to 2. Values of γ for a few minerals are collected in Table 6, and it is noteworthy that they tend to be appreciably smaller than for metals or the alkali halides (Slater, p. 393, 451). There are few cases where the relation in the form, $\gamma = \alpha/\rho\beta_T C_v$ has been tested over a considerable range of temperature; Table 7 gives two examples, based on the measurements of the elastic

TABLE 6—*Grüneisen's ratio for a few minerals (ordinary temperature and pressure)*
(General reference: Birch, Schairer, and Spicer, 1942)

Mineral	$\alpha \times 10^6$	ρ	C_v	$\beta_T \times 10^{13}$	γ
	deg^{-1}	*gm/cm*^{3}	*j/gm*	*cm*^{2}*/dyne*	
Quartz	40	2.65	0.698	27	0.8
Rutile	24	4.2	0.70	4.8	1.7
Corundum	18	4.0	0.71	3.6	1.7
Periclase	30	3.58	0.87	6	1.6
Diamond	2.9	3.51	0.47	1.8	1.0*
Pyrite	27	5.0	0.50	6.8	1.6
Zircon	9	4—5	0.61	8.6	0.4
Beryl	5	2.7	0.84	5.4	0.4
Albite	17	2.6	0.71	19	0.5
Anorthite	15	2.76	0.7	11	0.7
Diopside	20	3.2	0.69	11	0.8
Olivine (Forsterite)	25	3.3	0.79	8	1.2

*See also Krishnan, 1946.

constants of NaCl by Hunter and Siegel (1942), which extend to the melting point (801°C), and of MgO by Durand (1936*a*) in an interval of temperature well below the Debye temperature. In both cases, the variation of γ with temperature is probably small enough to be attributed to experimental error, but exact constancy is hardly to be expected.

Relatively little attention has been given to the question of the change of α or of γ with pressure. The experimental data are scanty, and subject to relatively large uncertainties. The importance of the thermal expansion in a number of geophysical problems makes it desirable to attempt to estimate the probable pressure variation with some care.

Both theory and experiment suggest that γ depends upon the volume, and that appreciable changes are to be expected for the large compressions with which we are concerned. This is not inconsistent with its apparent constancy for changes of temperature at one atmosphere; the total change of volume by thermal expansion between absolute zero and the melting point is but a few per cent even for the alkali metals, as compared with changes of 20 or 30 per cent for the same materials for pressures of the order of 2×10^4 kg/cm^2. Thus a dependence of γ upon volume, which is insignificant under ordinary conditions, may become important at high pressures.

The thermal energy of a simple lattice is most readily, if only approximately, treated as the energy of a spectrum of elastic waves, having at any temperature a certain maximum frequency of vibration (Slater, 1939, p. 234). Grüneisen's ratio then depends upon the density or volume and the frequency ν according to the relation (Slater, p. 288)

$$\gamma = d \log \nu / d \log \rho$$

It is not necessary to suppose that there is a single frequency, so long as all frequencies depend upon the density in the same way, as in the Debye theory of specific

TABLE 7—*Grüneisen's ratio and other parameters for NaCl and MgO, as function of temperature (one atmosphere)*

T	$10^{13}\beta_S$	C_P	$10^6\alpha$	γ	$\frac{1}{\alpha C_P}\left(\frac{\partial C_P}{\partial T}\right)_{P=0}$	$\frac{1}{\alpha^2}\left(\frac{\partial \alpha}{\partial T}\right)_{P=0}$	$\frac{1}{\alpha\beta_S}\left(\frac{\partial \beta_S}{\partial T}\right)_{P=0}$
°K	cm²/dyne	j/gm	deg⁻¹				
NaCl (ρ_0 = 2.135; Debye temperature = 320°K)							
300	41.4	0.870	120	1.56			
					2.7	5.2	3.4
400	43.1	0.898	128	1.57			
					2.4	4.6	4.5
500	45.6	0.925	136	1.56			
					2.3	3.6	7.3
600	50.1	0.954	143	1.46			
					3.0	4.1	6.5
700	54.8	0.982	152	1.40			
					1.9	5.2	5.4
800	59.3	1.010	165	1.38			
					1.6	5.1	3.9
900	63.1	1.037	180	1.39			
					1.5	5.5	2.3
1000	65.7	1.065	201	1.50			
MgO (ρ_0 = 3.576; Debye temperature = 950°K)							
200	6.41	0.71	24	1.5			
					135	82	2.6
300	6.45	0.94	30	1.4			
					32	55	3.1
400	6.51	1.03	36	1.5			
					13	21	3.5
500	6.60	1.08	39	1.5			

References: C_P, Kelley, 1949; β_S, NaCl, Hunter and Siegel, 1942; MgO, Durand, 1936*a*; α, NaCl, Walther, *et al.*, 1937; MgO, Durand, 1936*b*.

heat. The Debye relation for the maximum frequency ν_m for an isotropic solid may be written

$$\nu_m = \left(\frac{3}{4\pi}\frac{N}{A}\rho\right)^{1/3} c, \qquad \text{with } 3/c^3 = 1/V_P^3 + 2/V_S^3 \quad \ldots\ldots\ldots\ldots (17)$$

V_P and V_S are the two velocities of elastic waves, N is Avogadro's number, 6.03×10^{23}; A the atomic weight, ρ the density. The "Debye temperature" is $h\nu_m/k$, h and k being Planck's constant and Boltzmann's constant, respectively. A considerable simplification results on introducing a numerical value for the ratio V_P/V_S; this is commonly about 1.7, and we find, approximately, ν_m^3 proportional to ρV_S^3. In terms of the elastic constants

$$V_S^2 = \frac{K_S}{\rho}\frac{3 - 6\sigma}{2 + 2\sigma}$$

and hence

$$\nu_m = \text{constant times} \left[\frac{K_S(3 - 6\sigma)}{\rho^{1/3}(2 + 2\sigma)}\right]^{1/2}$$

On differentiation, we obtain

$$\gamma = -1/6 + 1/2 \text{ d} \log K_S/\text{d} \log \rho - 3/2\ \rho\ (\text{d}\sigma/\text{d}\rho)[(1 - 2\sigma)(2 + 2\sigma)]^{-1} \quad (18)$$

For $\sigma = 0.25$, the factor of ρ dσ/dρ is 2.4, and the part of this factor omitted as a result of the simplifying assumption is 0.07. This result, without the last term, is given by Slater (p. 239), who has shown that fairly good values for γ can be obtained in this way, by using the experimental values of d log K_S/d log ρ, which is, nearly enough, $(\partial K_T/\partial P)_T$. Not much is known about the variation of σ with density, but anticipating a later result, we may suppose that the variation of σ with depth, found from the seismic velocities (Fig. 6), between about 1,000 km and 2,200 km, is an indication of the order of magnitude; in this range, σ increases by about 0.022,

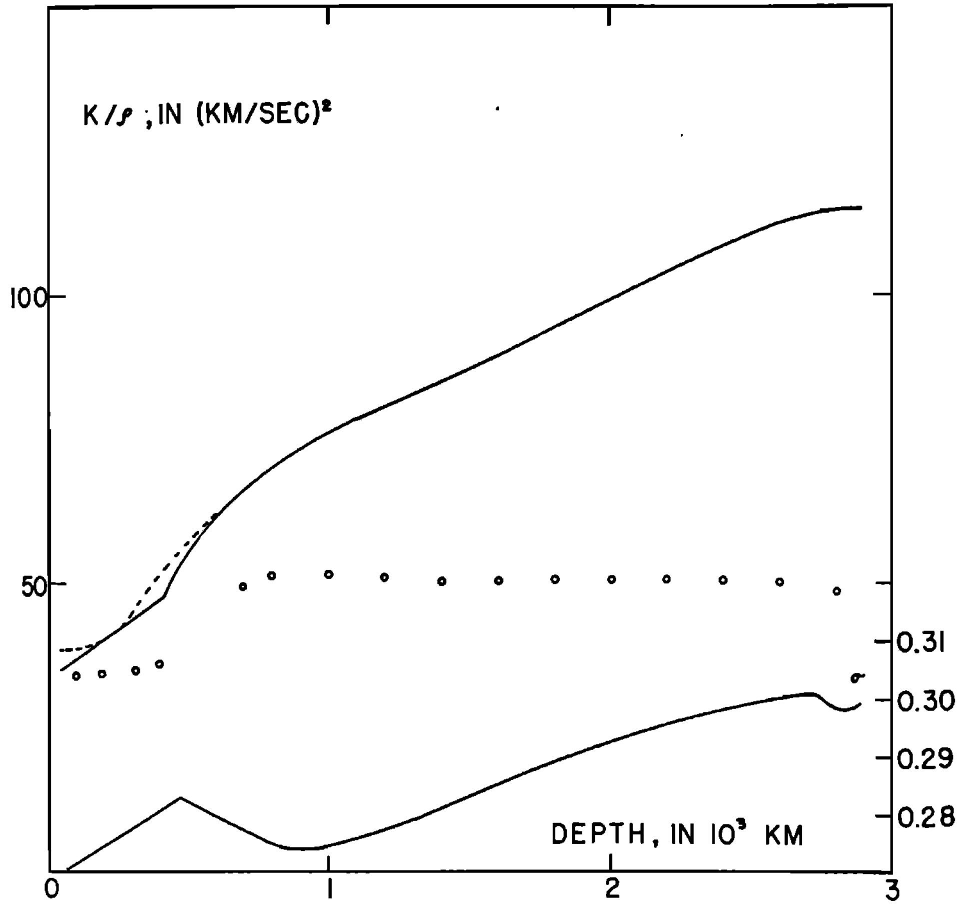


FIG. 6—VARIATION OF ϕ, ϕ_0, AND σ IN THE MANTLE

and ρ increases by about 0.7, according to Bullen. The quantity $\rho\ d\sigma/d\rho$ is thus about 0.15 and the contribution to γ is roughly -0.36. An unknown fraction of this may be the effect of temperature, but this correction is in the right direction to improve the agreement between Slater's calculated values and the values obtained from the basic relation, $\gamma = \alpha/(\rho C_v \beta_T)$.

The variation with volume of $(\partial K_T/\partial P)_T$ is given in Table 8 for $\xi = 0$; the value is 4, at zero pressure, and if the term in $d\sigma/d\rho$ is neglected, the initial value of γ is 1.83. Table 8 also gives the corresponding values of γ, and the thermal expansion relative to its value at zero pressure; this is calculated from $\alpha = \gamma\rho C_v \beta_T$, with the additional assumption that the change of C_v is negligible. This approach suggests that the thermal expansion changes somewhat less rapidly than compressibility.

TABLE 8—*Estimates of the change of Grüneisen's ratio, compressibility, and thermal expansion with compression*

f	v/v_0	$(\partial K_T/\partial P)_T$	γ	γ/γ_0	β/β_0	α/α_0
0	1	4	1.83	1	1	1
0.05	0.867	3.57	1.62	0.885	0.583	0.595
0.10	0.760	3.31	1.50	0.820	0.373	0.402
0.15	0.674	3.15	1.41	0.770	0.253	0.289
0.20	0.604	3.03	1.35	0.738	0.180	0.220
0.25	0.544	2.94	1.30	0.710	0.132	0.172
0.30	0.494	2.87	1.27	0.694	0.100	0.140

Any equation of state contains an implication about the effect of pressure upon thermal expansion, often conveniently found by application of the thermodynamic identity, $(\partial P/\partial T)_v = \alpha K_T$. For example, the work of Born and others leads to equations of the form, $P = f_1(v) + Tf_2(v)$, where f_1 and f_2 are functions of the volume alone, which have been calculated for the body-centered and face-centered cubic lattices for power-law potentials. Thus we have at once, $\alpha K_T = f_2(v)$, which is equivalent to Grüneisen's law if we identify $f_2(v)$ with $\gamma\rho C_v$. In Born's notation, this leads to a value of γ of $H_1/3$, for the body-centered cubic lattice, above the Debye temperature. Born uses the values, $m = 6$, $n = 12$ for which $H_1 \approx 13$, and hence $\gamma = 4.3$, which is too high; these exponents also lead to rates of change of compressibility with pressure which are considerably too high (Birch, 1947). On the other hand, the exponents which give the best fit with the compressions are $m = 2$, $n = 4$; these yield $H_1 = 4.5$, and thus $\gamma = 1.5$, a good value for the body-centered lattice (Slater, p. 451; Druyvesteyn, 1946; Grüneisen, 1926). The function H_1 and thus γ decrease as the volume decreases, though less rapidly than the values of Table 8. A number of the approximations of Born's theory may be expected to become increasingly unsatisfactory as the volume decreases; for example, only nearest neighbors are considered in forming the vibrational energy, which determines the effect of temperature on volume. In the more complete treatment by Miss Gow (1944) of the face-centered cubic lattice, the substitution of $m = 2$, $n = 4$, leads to divergent terms, but values in this neighborhood are still required to give the correct change of compressibility with pressure. Reasonably good values for γ, which is $-B_1/3$ in Miss Gow's notation, are found for $m = 4$, $n = 8$, and $m = 5$, $n = 10$.

Similarly, the equations (15) with $\xi = 0$ lead to the following relation for the change of thermal expansion (Birch, 1939):

$$\alpha/\alpha_0 = 1 + \frac{P}{K}\frac{1}{\alpha_0 K_T}\left(\frac{\partial K_T}{\partial T}\right)_{P=0} = 1 - \frac{P}{K}\frac{1}{\alpha_0 \beta_T}\left(\frac{\partial \beta_T}{\partial T}\right)_{P=0} \quad \ldots\ldots\ldots(19)$$

where the zeros refer to zero pressure. This is an integral form of the thermodynamic relation, $(\partial\alpha/\partial P)_T = -(\partial\beta_T/\partial T)_P$, which expresses the change of thermal expansion with pressure in terms of the change of compressibility with temperature. The coefficient $(\alpha\beta)^{-1}(\partial\beta/\partial T)_P$, as we shall see below, is a small positive number, between 3 and 8, and hence (19) predicts a definite pressure at which α vanishes, and then becomes negative. A negative thermal expansion is not thermodynamically impossible: it is shown by water between 0° and 4°C, and by ice at low temperatures, but it is at least unusual, and need not be inferred from this approximate result, which omits the unknown third-order term. On the other hand, the experiments, which will next be considered, do not extend to high enough compressions to rule out a change of sign, and equation (19) is in good agreement with the observations, so far as they go.

TABLE 9—*Measured effects of compression on thermal expansion*
(After Bridgman, 1935; 1940)

Pressure	Lithium		Sodium		Potassium	
	$-\Delta v/v_0$	α/α_0	$-\Delta v/v_0$	α/α_0	$-\Delta v/v_0$	α/α_0
kg/cm²						
2.10^3	0.0164	0.94	0.0295	0.91	0.0571	0.86
4	0.0320	0.87	0.0552	0.83	0.1002	0.72
6	0.0466	0.81	0.0779	0.76	0.1347	0.59
8	0.0606	0.76	0.0981	0.70	0.1640	0.49
10	0.0739	0.71	0.1165	0.65	0.1890	0.38
12	0.0866	0.68	0.1332	0.60	0.2108	0.34
14	0.0984	0.65	0.1488	0.55	0.2300	0.29
16	0.1094	0.62	0.1632	0.50	0.2472	0.25
18	0.1198	0.58	0.1767	0.45	0.2626	0.23
20	0.1296	0.56	0.1894	0.41	0.2767	0.21

$P = 50{,}000$ kg/cm², −80° to 20°C

	$-\Delta v/v_0$	α/α_0
NaCl	0.1309	0.52
NaBr	0.1464	0.92
CsCl	0.1596	0.70
CsBr	0.1748	0.71
CsI	0.2025	0.34

The measurements on lithium, sodium, and potassium were between 0 and 95°C. The tabulated values of α/α_0 are ratios of "true" thermal expansions, calculated with respect to the volumes at 0°C and at the indicated pressures; α_0 refers to zero pressure (one atmosphere).

The direct determination of thermal expansion at high pressure is extraordinarily difficult, but Bridgman (1935) has measured the mean expansion of three alkali metals between 0° and 95°C at pressures up to 20,000 kg/cm^2, and of a number of alkali halides between −80°C and 20°C at 50,000 kg/cm^2 (1940). These measurements are summarized in Table 9 and plotted in Figure 4. The thermal expansions of Bridgman's paper were computed with respect to the original volume, at one atmosphere; they have been corrected to "true" expansions with the aid of the compressions given in the same paper, and plotted against v/v_0 as suggested by theoretical considerations. Bearing in mind the likelihood of appreciable experimental errors, we may conclude that the observations for the alkali metals are fairly well represented by a single curve of α/α_0 *versus* v/v_0. The few points for the halides are widely scattered, a fact perhaps to be accounted for in part by the circumstance that the measurements for these materials, unlike those for the alkali metals, were at temperatures below or comparable with the Debye temperatures. For comparison, the theoretical curve of β/β_0 is also plotted, as is the curve given by (19), with $(\alpha\beta)^{-1}(\partial\beta/\partial T)_P$ taken as 4 (see below, Table 10). These measurements indicate a more rapid change of thermal expansion with compression than of compressibility, whereas the theoretical predictions, even with the allowance of Table 8 for a decrease of γ, are for a slower rate. The difference is perhaps not beyond the possible uncertainty, however, and the safest generalization for solids at high temperatures is probably that the thermal expansion changes with compression at approximately the same rate as the compressibility. The compressibility cannot become negative, however, while this interesting possibility for the thermal expansion cannot be definitely excluded.

ISOTHERMAL AND ADIABATIC COMPRESSIBILITIES

The difference between the isothermal and adiabatic compressibilities involves both α and γ; we have the thermodynamic relations

$$\frac{\beta_T}{\beta_S} = \frac{K_S}{K_T} = \frac{C_P}{C_v} = 1 + \frac{T\alpha^2 K_T}{\rho C_v} = 1 + T\alpha\gamma \qquad \text{(20)}$$

At ordinary temperatures and pressures, this difference is commonly of the order of a few per cent for materials of low compressibility. For example, for iron at 300°K, $\alpha = 33 \times 10^{-6}$, $\gamma = 1.6$, and the difference is about 1.6 per cent; for olivine, it is roughly the same. Since the difference is proportional to the absolute temperature, it might become serious in the interior of the Earth if it were not for the effect of pressure upon the thermal expansion. In the mantle, β_S decreases several fold (Bullen, 1947, p. 220), while T reaches perhaps several thousand degrees; it seems likely that the relative difference of the compressibilities will not exceed some 10 per cent.

The "adiabatic gradient" is also expressible in terms of γ; we have

$$-(\partial T/\partial r)_S = T\alpha g/C_P = Tg\gamma/\phi.$$

The quantities ϕ and g are known, γ may be estimated, as above; the principal uncertainty is with regard to T. Let $T = q \times 10^3$ degrees; the adiabatic gradient then becomes about $0.17q$ °/km at a depth of 800 km, $0.07q$ °/km at 2,800 km. If, as seems possible, q is between 2 and 5, the corresponding gradients become 0.3 – 0.9°/km at 800 km, 0.1 – 0.4°/km at 2,880 km. (see also Verhoogen, 1951).

CHANGE OF COMPRESSIBILITY WITH TEMPERATURE

Another important parameter is $(\partial K_T/\partial T)_P$, or the dimensionless quantity, $(\alpha K_T)^{-1}(\partial K_T/\partial T)_P$. By virtue of the thermodynamic identities

$$\frac{1}{K_T}\left(\frac{\partial K_T}{\partial T}\right)_P = -\frac{1}{\beta_T}\left(\frac{\partial \beta_T}{\partial T}\right)_P = \frac{1}{\beta_T}\left(\frac{\partial \alpha}{\partial P}\right)_T$$

This may be found either by measuring the change of compressibility β_T with temperature, or the change of thermal expansion α with pressure. Either way is experimentally difficult. The change of compressibility may also be computed from

TABLE 10—*Change of compressibility with temperature*

(All determinations at low pressure unless otherwise noted)

Material and method	Temperature	$\frac{1}{\beta_T}\left(\frac{\partial \beta_T}{\partial T}\right)_P \times 10^6$	$\frac{1}{\alpha\beta_T}\left(\frac{\partial \beta_T}{\partial T}\right)_P$	Authority
Li, β_T	30–75°C	720	4.3	Bridgman, 1931
$(\partial\alpha/\partial P)$	0–95°C	. . . .	4.9	Bridgman, 1935
$P = 18{,}000$–$20{,}000$	0–95°C	. . . .	4.7	Bridgman, 1935
Na, β_T	30–75°C	860	4.4	Bridgman, 1923
$(\partial\alpha/\partial P)$	0–95°C	. . . .	4.3	Bridgman, 1935
$P = 18{,}000$–$20{,}000$	0–95°C	. . . .	7.7	Bridgman, 1935
elastic constants	100–200°K	850	4.7	Quimby and Siegel, 1938
K, $(\partial\alpha/\partial P)$	0–95°C	800	3.2	Bridgman, 1935
$P = 18{,}000$–$20{,}000$	0–95°C	. . . .	4.9	Bridgman, 1935
Al, β_T	30–75°C	540	7.4	Bridgman, 1931
β_T	23–435°C	530	6.5	Birch and Law, 1935
elastic constants	0–100°C	550	7.6	Birch and Bancroft, 1940
Fe, β_T (Mallock's method)	−190–17°C	215	7.2	Grüneisen, 1926
	17–165°C	450	12.5?	Grüneisen, 1926
β_T	30–75°C	220	6.3	Bridgman, 1923
elastic constants	0–100°C	310	8.9	Birch and Bancroft (unpublished)
LiCl, β_T	30–75°C	650	5.3	Slater, 1924
NaCl, β_T	30–75°C	860	7.2	Bridgman, 1931
elastic constants	300–1000°K	(See Table 8)	2–7	Hunter and Siegel, 1942
KCl, β_T	30–75°C	510	5.1	Slater, 1924
elastic constants	180–280°K	820	8.2	Durand, 1936*a*
RbCl, β_T	30–75°C	800	8	Bridgman, 1932
MgO, β_T	30–75°C	300	10?	Bridgman, 1932
elastic constants	200–500°K	(See Table 8)	3	Durand, 1936*a*
α-quartz, β_T	30–75°C	400	10	Bridgman, 1928
elastic constants		350	9	Mason, 1940
Olivine, rigidity . . .	0–400°C	200	7	Birch, 1943

the changes of elastic constants. Theoretical values are furnished by equations of state, such as those of Grüneisen and Born, which include the effect of temperature. For example, Grüneisen gives the relation

$$(\alpha\beta_S)^{-1}(\partial\beta_S/\partial T)_P = -\gamma + (m + n + 6)/3$$

which by the aid of (12), is approximately equivalent to

$$(\alpha\beta_T)^{-1}(\partial\beta_T/\partial T)_P = (m + n + 6)/3.$$

A similar relation obtainable from Born's theory has been discussed by Fürth (1944). Since the sum $(m + n)$ of the exponents in the power-law approximation to the cohesive energy of a pair of particles is usually found to lie between 6 and 18, the parameter $(\alpha\beta_T)^{-1}(\partial\beta_T/\partial T)_P$ may be expected to lie between 4 and 8, at high temperatures.

Experimental values for a number of materials are collected in Table 10, where an effort has been made to include several independent determinations wherever possible (see also Grüneisen, 1926, p. 38; Bridgman, 1933, p. 219; Fürth, 1944, p. 100). These values fall in the anticipated range, and show little systematic variation with temperature (see also Table 7) or with pressure. The value 4, used in equation (19), leads to a satisfactory account of the change of thermal expansion with pressure of the alkali metals over the entire range; the corresponding curve is plotted in Figure 4.

The quantity $\alpha^{-2}(\partial\alpha/\partial T)_P$ is also given in Table 7 for NaCl and MgO. This evidently depends strongly upon temperature, being large below the Debye temperature, falling to the order of a few units above the Debye temperature (see also Fürth, 1944, p. 100).

SPECIFIC HEATS

Thanks especially to the measurements of White (1919), it has long been known that the specific heats of the silicates show a close approach to the "classical" values

TABLE 11—*Specific heats*
(After Kelley, 1949)

Material	M	z	M/z	C_P/z	C_v/z
	gm/mole	*No. of atoms*	*Mean atomic weight*	*At 1400°K cal/deg.gm.atom*	
Quartz, SiO_2	60.06	3	20.02	5.71	....
Albite, $NaAlSi_3O_8$	262.15	13	20.17	6.09	5.92
Anorthite, $CaAl_2Si_2O_8$	278.14	13	21.40	6.36	6.06
Diopside, $CaMgSi_2O_6$	216.52	10	21.65	6.31	5.95
$MgSiO_3$	100.38	5	20.08	6.37	6.10
Fayalite, Fe_2SiO_4	203.76	7	29.11	7.09	6.44
Periclase, MgO	40.32	2	20.16	6.27	5.70
Forsterite, Mg_2SiO_4	140.7	7	20.10	....	....
Rutile, TiO_2	79.90	3	26.63	6.05	....
Corundum, Al_2O_3	101.94	5	20.39	6.26	....

for ionic crystals at temperatures of the order of 1000°C, where each particle has acquired 3 degrees of freedom. Under these conditions, the specific heat at constant volume, C_v approaches 6 cal/deg.gm.atom for each particle of the chemical formula, and as the mean atomic weight is close to 20 gm for most of the rock-forming silicates, the specific heat at high temperatures is commonly close to 0.3 cal/deg.gm (see Table 11).

The variation of the specific heat with pressure is given by the thermodynamic relations (Bridgman, 1925)

$$\frac{1}{C_P}\left(\frac{\partial C_P}{\partial P}\right)_T = -\frac{T\alpha\gamma}{K_S}\left[1 + \frac{1}{\alpha^2}\left(\frac{\partial\alpha}{\partial T}\right)_P\right] \dots\dots\dots\dots (21)$$

$$\frac{1}{C_P}\left(\frac{\partial C_P}{\partial P}\right)_S = -\frac{T\alpha\gamma}{K_S}\left[1 + \frac{1}{\alpha^2}\left(\frac{\partial\alpha}{\partial T}\right)_P - \frac{1}{\alpha C_P}\left(\frac{\partial C_P}{\partial T}\right)_P\right] \dots\dots (22)$$

Along an isothermal, C_P will normally decrease as the pressure increases, since $(\partial\alpha/\partial T)_P$ is normally positive; along an adiabatic, the decrease with increasing pressure will be smaller. For a rough estimate of the rate of decrease of C_P along an isothermal, let us take $\alpha^{-2}(\partial\alpha/\partial T)_P = 4$, a mean value of $T\alpha\gamma$ of 0.10 (Table 16). We have $K_S = K_T(1 + T\alpha\gamma)$, and $K_T = \rho(\partial P/\partial\rho)_T$. On integration of (21), we obtain, approximately, $\log C_P/C_{P=0} = -0.5 \log (\rho/\rho_0)$; for the deeper part of the mantle, we have $\rho/\rho_0 = 1.4$, at most, and thus the maximum decrease of C_P, in the mantle, may be of the order of 20 per cent, if the temperature is uniform and of the assumed order, or about half of this if the temperature rise is adiabatic.

The special assumptions of Grüneisen's theory (Grüneisen, 1912, p. 277) lead to $(\partial C_v/\partial P)_S = 0$. This is also true, of course, if we suppose C_v to have exactly its classical high-temperature value at all depths. In either case, along an adiabatic we have C_P proportional to $(1 + T\alpha\gamma)$, and this leads to an estimate of maximum decrease of the order of 10 per cent in the mantle. It seems reasonably certain that the changes of C_P, and especially of C_v, will be small by comparison with the changes to be expected for compressibility and thermal expansion.

This review of thermodynamic parameters of solids shows that in spite of variations of some hundred fold in the absolute magnitude of the compressibility (as between iron and cesium, for example), in spite of differences in chemical binding (as between metals and ionic compounds), there are systematic relations which enable us to assign values to the parameters of equation (11) with a reasonable expectation that they will be correct; a law of "corresponding states" appears to hold, at least approximately, for a wide variety of substances. For the further use of these relations, we must suppose that we have correlated the observed variations with the correct variables, such as temperature and compression, and that the laws of correspondence which we have read from (or into) the experimental data also hold for the interior of the Earth.

DISCUSSION OF THE INDIVIDUAL LAYERS

The mantle: Layers B, C, and D

We now return, with numerical values for the various coefficients, to the equations for a homogeneous layer, in particular to equation (11), which we wish to

TABLE 12—*Variation of ϕ and in the mantle*
(After Jeffreys, 1939*a*)
$\Delta r = 0.02R' = 126.8$ km ($R' = 6{,}338$ km); $g = 10^3$ cm/sec^2

r/R'	ϕ	$\Delta\phi$	$1 - g^{-1}\Delta\phi/\Delta r$	Mean depth of interval (from surface)	σ
	(km/sec)^2			*km*	
1.00	34.75				0.269
		3.89	4.06	96	
0.98	38.64				0.273
		4.31	4.40	223	
0.96	42.95				0.277
		4.70	4.70	350	
0.94	47.65				0.280
		10.77	9.48	477	
0.92	58.42				0.282
		7.25	6.72	604	
0.90	65.67				0.278
		5.09	5.01	730	
0.88	70.76				0.275
		4.09	4.22	857	
0.86	74.85				0.274
		2.87	3.26	984	
0.84	77.72				0.276
		2.43	2.92	1111	
0.82	80.15				0.277
		2.83	3.23	1238	
0.80	82.98				0.279
		3.01	3.37	1364	
0.78	85.99				0.281
		2.89	3.28	1491	
0.76	88.88				0.283
		3.27	3.58	1618	
0.74	92.15				0.286
		2.85	3.25	1745	
0.72	95.00				0.289
		3.19	3.52	1872	
0.70	98.19				0.292
		2.99	3.36	1998	
0.68	101.18				0.294
		2.78	3.19	2125	
0.66	103.96				0.296
		2.51	2.98	2252	
0.64	106.47				0.297
		3.04	3.40	2379	
0.62	109.51				0.298
		2.56	3.02	2506	
0.60	112.07				0.300
		2.65	3.09	2632	
0.58	114.72				0.301
		0 ?	1	2759	
0.56	114.72				0.298

employ as a test for homogeneity. This equation may be simplified, without appreciable loss of generality, by the omission of terms in $(T\alpha\gamma)^2$. For T of the order of several thousand degrees, $T\alpha\gamma$ will be about 0.1 to 0.2; the term B is of the same order as A and C, and consequently the term $(T\alpha\gamma)^2B$ will be small compared with the terms in A and C; these in turn are essentially corrections to the main term, $(\partial K_T/\partial P)_T$. For the evaluation of A and C, let us assume that $(\partial K_T/\partial P)_T \approx 3.5$; $\gamma \approx 1.5$; $(\alpha K_T)^{-1}(\partial K_T/\partial T)_P = -4$; then $A \approx -5$, and $C \approx -2$. The quantity $\tau\alpha\phi/g$ lies between 0.2 and 0.1 for a supra-adiabatic gradient τ of 1°/km. Equation (11) becomes, nearly enough

$$1 - g^{-1}\, d\phi/dr = (\partial K_T/\partial P)_T - 5T\alpha\gamma - 2\tau\alpha\phi/g \quad \text{..........(23)}$$

Now the quantity on the left can be formed from the seismic velocities, and is plotted in Figure 5 for the mantle; g has been taken as 10^3 cm/sec^2 throughout, an assumption in error by no more than a few per cent. For this purpose, the original intervals of Jeffreys' and Gutenberg's tables have been used in forming the differences, $\Delta\phi$ and Δr, as shown in Tables 12 and 13. The conspicuous feature of these curves is the high value of $1 - g^{-1}\, d\phi/dr$ in the interval above about 800 to 900 km; this is, of course, the region of rapid rise of velocity, comprising layer C, and perhaps part of B. If the layer were homogeneous, we would expect to find values in the neighborhood of 4, according to equation (23) and the probable values of the coefficients, especially $(\partial K_T/\partial P)_T$. No reasonable adjustment of values can give so rapid a rise in a homogeneous layer; there must be changes of phase, of composition, or both. Thus the first conclusion, in agreement with the somewhat different earlier argument (Birch, 1939), is that this region cannot be homogeneous.

TABLE 13—*Variation of* ϕ
(After Gutenberg, 1948)

Depth	ϕ	$-\Delta\phi/\Delta r$	$1 - g^{-1}\Delta\phi/\Delta r$
km	*(km/sec)²*	*cm/sec²*	
200	40.2		
		4600	5.6
300	44.8		
		7200	8.2
400	52.0		
		4900	5.9
500	56.9		
		5000	6.0
600	61.9		

Jeffreys and Bullen place the boundary between layers B and C at a depth of 413 km (Jeffreys, 1939*a*), where Jeffreys' solution for the velocities shows a discontinuity of velocity-gradient, a discontinuity said to be of the "second order." Earlier, Jeffreys (1936, 1937*b*) had proposed a first-order discontinuity for about this depth (474 km), interpreted, after a suggestion by Bernal (1936), as a pressure transition from ordinary olivine to cubic olivine, a form unknown at ordinary pressure. Between about 30 and 413 km, Jeffreys' solution shows a nearly linear increase of velocity with depth, agreeing closely with the theoretical increase in a homogeneous, isothermal layer (see Fig. 5).

Gutenberg (1948), however, believes that the velocity remains nearly constant or even decreases slightly with increasing depth between about 50 and 100 km, and gives several solutions which show a reversal of the "normal" trend. At about 200 km, a rapid increase of velocity with depth sets in, and below 600 km, Gutenberg's velocities are in close accord with Jeffreys'. The division between layers B and C becomes indefinite with this velocity distribution, but might be put at about 200 km rather than 413 km. For the present, this considerable difference remains unresolved.

There are reasons for believing, however, that approximate constancy of velocity in the region between 50 and 150 km is physically reasonable. In this range, the pressures are still comparable with laboratory pressures, and use may be made of experimentally determined coefficients. In a *homogeneous* layer, the change of velocity, say C, with depth h, may be written $\mathrm{d}(\log C)/\mathrm{d}h = (\partial \log C/\partial T)_P(\mathrm{d}T/\mathrm{d}h) + (\partial \log C/\partial P)_T(\mathrm{d}P/\mathrm{d}h)$. The critical condition for a shadow zone at a radius R is (Gutenberg, 1948) $\mathrm{d}(\log C)/\mathrm{d}h = -1/R = -160 \times 10^{-6}\ \mathrm{km}^{-1}$ for $R = 6{,}270$ km. As typical values for ultrabasic rock, we may take $(\partial \log C/\partial T)_P \approx -100 \times 10^{-6}$/deg.;* $(\partial \log C/\partial P)_T = 1.5 \times 10^{-6}$/bar; $\mathrm{d}P/\mathrm{d}h = 330$ bars/km (Birch and Bancroft, 1938; Birch, 1943). On substitution, we find for the critical gradient of temperature, 6.6°/km; if the gradient exceeds this value, there will be a shadow zone; if it is less, normal upward refraction will occur. On the other hand, Jeffreys' solution gives $\mathrm{d}(\log C)/\mathrm{d}h$ equal to about $+400 \times 10^{-6}$/km, which, with the same coefficients, leads to a gradient of about 1°/km, consistent with the earlier finding (Birch, 1939) that Jeffreys' solution is almost identical with the isothermal one. Whether there is actually a shadow zone or not, a gradient higher than 1°/km seems probable for this shallow region, and the critical gradient required to produce a shadow zone is not unreasonably high. If this region is homogeneous, Gutenberg's velocities are consistent with Jeffreys' thermal theory, while Jeffreys' velocities are not. The thermal theory (Jeffreys, 1929, p. 151) gives a gradient in this neighborhood of about 5°/km, on the assumption that the radioactive elements are completely separated from the interior and concentrated in the crust; other assumptions remaining the same, this distribution gives the lowest possible gradient below the crust. If Jeffreys' velocities and thermal gradients are correct, then layer B must be characterized by a progressive change of composition.

It is a curious feature of Gutenberg's solution that the decrease of V_S at about 100 km is smaller than the decrease of V_P; this may be the result of poorer readings for S. But, if there were a close approach to melting, as suggested by Gutenberg, V_S would be more affected than V_P. An approach to melting is not required, however; a moderate gradient of temperature is sufficient. As the depth increases, the gradient required for a shadow zone increases for several reasons: $\mathrm{d}P/\mathrm{d}h$ increases, $1/R$ increases, and probably $|(\partial \log C/\partial T)_P|$ decreases. At the same time, the real gradient probably decreases. In a homogeneous layer, there is thus a limited region where a shadow zone may occur. Considerably higher gradients are

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*Mean for three different dunites; the experimental values for one eclogite are significantly smaller, about -50×10^{-6}/deg.

required to produce shadow zones within the crust because of the relatively low temperature coefficients of crustal rocks (Birch and Bancroft, 1938, p. 135; Birch, 1943).

Another point of interest is the ratio of the gradients of temperature and of pressure; with the critical gradient of 6.6°/km, this is 6.6/330, or 1°/50 bars. For constant volume, $(\partial T/\partial P)_v = \beta_T/\alpha$; with $\beta_T = 0.8 \times 10^{-6}$/bar and $\alpha = 40 \times 10^{-6}$/deg,* this is also 1°/50 bars. The critical gradient for a shadow zone would thus be accompanied by approximately uniform density, on the assumption of homogeneity. The Adams-Williamson equation is not applicable to this region, since either the gradient of temperature is too high to be neglected, or else the material is not homogeneous.

Between a depth of about 800 or 900 km and the core boundary, the values of $1 - g^{-1}\Delta\phi/\Delta r$, though somewhat ragged for the intervals Δr which have been selected, all fall between 3.6 and 2.9. This is close to the expected value of $(\partial K_T/\partial P)_T$ alone (for $\xi = 0$) for a homogeneous layer at uniform temperature, for which the theoretical curve is plotted in Figure 5. Below 1,100 km, the deviations from this theoretical curve rarely exceed 0.2; the standard deviation for the 12 values beginning with 1,238 km is 0.19; and for the 15 points beginning with 857 km, 0.29. The least-squares straight line, below and including the point at 857 km, for which the standard deviation is 0.27, lies roughly 0.1 below the theoretical curve. The most straightforward interpretation of this result, with reference to (23), is that this region is reasonably homogeneous and that the terms in $T\alpha\gamma$ and τ are small.

The conclusion as to uniformity does not depend upon the particular value of ξ which has been adopted as most representative; any other value, within the relatively narrow permissible range, say $| \xi | < 1/2$, would also lead to a smooth curve of $(\partial K_T/\partial P)_T$, merely displaced upward or downward from the curve of Figure 5 (see Table 5). The conclusions about the temperature and temperature gradient, however, depend upon the differences between the theoretical and observed values, and are consequently somewhat uncertain. These differences are easily reconciled with temperatures of the order of several thousand degrees; for example (see Table 16) for $T = 4{,}000°$, the term $5T\alpha\gamma$ is about 0.5 at 800 km, about 0.15 at 2,800 km; if τ were as great as 1°/km, the term in τ would equal 0.14 at 800 km, 0.09 at 2,800 km. Both of these terms are to be subtracted from $(\partial K_T/\partial P)_T$, and, in view of the various uncertainties, there is no serious discrepancy. A temperature as high as 10,000°, however, seems to be improbable (see below).

The roughness of the observed values of $\Delta\phi/\Delta r$ is perhaps surprising at first glance, since the tables of both V_P and V_S given by Jeffreys have been smoothed. This smoothing was carried out independently for each velocity, however, and does not guarantee smooth differences for ϕ. There is evidently a tendency for the differences $\Delta\phi$ to alternate between high and low values, and a somewhat smoother appearance would be found on taking intervals of Δr twice as great as those used for Table 12 and Figure 5.

Let us suppose that layer D is not only homogeneous, but nearly adiabatic as well ($\tau = 0$). The analysis of this layer may then be carried further. The acceleration

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*Olivine at 800°C, Kozu, *et al.*, in Birch, Schairer, and Spicer, 1942; also J. L. Rosenholtz, private communication.

g is nearly independent of depth throughout the mantle for all of the modern distributions of density, the greatest variation being of the order of one or two per cent. For g uniform, the equation of equilibrium becomes

$$\left.\begin{aligned} d\rho/dr &= -g\rho^2/K_T\text{, for uniform temperature}\\ d\rho/dr &= -g\rho^2/K_S\text{, for the adiabatic gradient}\end{aligned}\right\}\cdots\cdots\cdots\cdots(24)$$

Introducing the depth, h, in place of the radius, we have

$$g\,dh = K_S\,d\rho/\rho^2 = (3K_T/\rho)_0(1 + 7f)\,df\,(1 + T\alpha\gamma)$$

Now $(1 + T\alpha\gamma)$ is close to 1, the maximum difference amounting perhaps to 10 per cent (Table 16). Taking a mean value of this quantity and integrating, we obtain

$$\left.\begin{aligned} g(h - h_0) &= (3K_T/\rho)_0f(1 + 3.5f)\overline{(1 + T\alpha\gamma)}\\ &= 3\phi_0f(1 + 3.5f),\text{ approximately}\end{aligned}\right\}\cdots\cdots\cdots\cdots(25)$$

Again making use of (15), we find

$$\frac{g(h - h_0)}{3\phi} = \frac{f(1 + 3.5f)}{(1 + 2f)(1 + 7f)}\text{, approximately}\cdots\cdots\cdots\cdots(26)$$

Substitution of the mean value of $(1 + T\alpha\gamma)$ produces an error in the left-hand term, and approximately in f, of no more than a few per cent in layer D. If the temperature is uniform, a similar, but exact expression is obtained (Birch, 1939),

TABLE 14—*Calculation of strain and of ϕ_0 for the mantle*
(Values of ϕ after Jeffreys, 1939*a*)

Depth	ϕ	$g(h - h_0)/3\phi$	f	ϕ_0	
km	*(km/sec)*^{2}			*(km/sec)*^{2}	
100	36.8	0.0084	0.0090	34.0	h_0 = 6 km
200	40.1	0.0160	0.0175	34.6	
300	43.2	0.0224	0.0254	34.9	
400	47.0	0.0276	0.0323	36.0	
500	55.3	0.0293	0.0346	41.6	
600	61.6	0.0318	0.0382	45.1	
700	66.4	0.0298	0.0354	49.6	h_0 = 100 km
800	70.7	0.0327	0.0397	51.2	
1000	76.7	0.0387	0.0490	51.8	
1200	81.0	0.0448	0.0590	51.2	
1400	85.1	0.0504	0.0688	50.5	
1600	89.7	0.0552	0.0775	50.4	
1800	94.8	0.0592	0.0853	50.7	
2000	99.5	0.0630	0.0930	50.8	
2200	104.0	0.0666	0.1007	50.7	
2400	108.4	0.0701	0.1088	50.5	
2600	112.4	0.0734	0.1167	50.1	
2800	115.0	0.0775	0.1271	48.5	

except that ϕ is replaced by (K_T/ρ). Here h_0 is the depth at which $f = 0$. We can now employ the seismic values of ϕ in (26) for a calculation of the strain f, and thence from (25) find ϕ_0. If the assumption of homogeneity is correct, and the variation of temperature insignificantly different from adiabatic, the values of ϕ_0 so obtained should all be equal, and refer to the material at zero pressure, and at the mean temperature of the layer. On the assumption of homogeneity, a single value of ϕ_0 can also be found by simple extrapolation of the $\phi - h$ curve to zero pressure.

For a layer beginning at the surface, h_0 is zero, but for layers beginning at other depths it is necessary to allow for the fact that the pressure at the top of the layer may be different from what it would be in a layer of the same material extending to the surface; the correction requires assumptions about the relative densities of the overlying layers and the layer under consideration. Fortunately, h_0 is never a large fraction of h, and decreases in importance as h increases. Except close to the top of a layer, the error to be expected from incorrect assumptions about the densities cannot appreciably affect the results.

The results of this calculation for the region between depths of 33 and 2,900 km are shown in Table 14, where Jeffreys' values of the velocities have been replotted and read off for 100-km intervals. For depths down to 600 km, h_0 has been taken as 6 km; for greater depths, 100 km (see also Bullen, 1940).

Qualitatively, the values of $(K_T/\rho)_0$, plotted in Figure 6, simply support the conclusions already reached on examination of the function $1 - g^{-1}\, d\phi/dr$: a region of rapid change above 800 km, and a deep, substantially uniform, layer between 800 km and the core. We now have in addition the zero-pressure values of ϕ, and the strain f, which gives the amount of compression. The curve of $(\partial K_T/\partial P)_T$ of Figure 5 is plotted with the aid of these values of f, substituted in (16). With Gutenberg's velocities, slightly different values would be found in the uppermost few hundred kilometers.

Close to the core boundary, the variation with radius, $\Delta\phi/\Delta r$, in Jeffrey's tables becomes zero, or even changes sign. This feature has appeared in a number of solutions (Dahm, 1936; see also Macelwane, in Gutenberg, Editor, 1939, 1951), but like many other small inflections it may not be real. If the curves of velocity are instead continued to the core boundary with no change of slope, the difference of velocity is less than 0.2 km/sec, an amount insufficient to produce a significant change of travel time. Though the theoretical position of the ray that just grazes the core is appreciably affected (Jeffreys, 1939*b*, p. 542), the actual angle of emergence of this ray is probably uncertain by several degrees (Macelwane, in Gutenberg, Editor, 1951, p. 283).

The figures of Table 14 show that if layer *D* is a uniform layer, with a relatively low gradient of temperature, then the material is characterized by a value of ϕ_0 of about 51 $(\text{km/sec})^2$. Examination of the experimental values of this quantity [strictly $(K_T/\rho)_0$] for a number of materials (Table 15), shows at once that none of the familiar silicates satisfies the requirements for layer *D*. In particular, the values for the olivine series are far too low. With a conservative allowance for the effect of temperature, we require about 60 $(\text{km/sec})^2$ at room temperature, and of all the silicates, only the exceptional beryl shows so high a value (notice also metallic Be). The figures for periclase, corundum, and rutile, however, show that

Table 15—*Density, compressibility, and* $(K_T/\rho)_0$
(Room temperature, one atmosphere)

Substance	Formula	ρ_0	$10^{13}\beta_0$	$(K_T/\rho)_0$
		gm/cm^3	*cm*^{2}*/dyne*	*(km/sec)*^{2}
Elements:				
Lithium	....	0.53	89	21
Beryllium	....	1.8	8	70
Silicon	....	2.4	9.9	42
Diamond	....	3.5	1.8	160
Iron (α)	....	7.87	5.94	21
Molybdenum	....	10.2	3.63	27
Platinum	....	21.45	3.63	13
Oxides:				
Periclase	MgO	3.6	5.98	47
Corundum	Al_2O_3	4	3.6	69
Spinel	$MgO \cdot Al_2O_3$	3.5–4.1	....	..
Magnetite	$FeO \cdot Fe_2O_3$	5	5.5	37
Hematite	Fe_2O_3	5.24	6	32
Rutile	TiO_2	4.2	4.8	50
Quartz (α)	SiO_2	2.65	27	14
Silicates:				
Albite	$Na_2O \cdot Al_2O_3 \cdot 6SiO_2$	2.62	19	20
Orthoclase	$K_2O \cdot Al_2O_3 \cdot 6SiO_2$	2.6	21	18
Jadeite	$Na_2O \cdot Al_2O_3 \cdot 4SiO_2$	3.33	7.8	39
Spodumene	$Li_2O \cdot Al_2O_3 \cdot 4SiO_2$	3.19	7.0	45
Anorthite	$CaO \cdot Al_2O_3 \cdot 2SiO_2$	2.76	11	33
Diopside	$CaO \cdot MgO \cdot 2SiO_2$	3.26	11	28
Enstatite	$MgO \cdot SiO_2$	3.35	10.6	29
Hypersthene	$(Mg, Fe)O \cdot SiO_2$	3.42	10.4	28
Forsterite	$2MgO \cdot SiO_2$	3.29	8.4	36
Fayalite	$2FeO \cdot SiO_2$	4.07	9.6	26
Andradite	$3CaO \cdot Fe_2O_3 \cdot 3SiO_2$	3.48	6.7	43
Grossularite	$3CaO \cdot Al_2O_3 \cdot 3SiO_2$	3.54	6.3	45
Pyrope	$3MgO \cdot Al_2O_3 \cdot 3SiO_2$	4.12	5.5	44
Almandite	$3FeO \cdot Al_2O_3 \cdot 3SiO_2$	4.16	6.0	40
Beryl	$3BeO \cdot Al_2O_3 \cdot 6SiO_2$	2.75	5.4	67
Sulfides:				
Marcasite	FeS_2	4.9	8	26
Pyrite	FeS_2	5.0	6.9	29
Oldhamite	CaS	2.8	23	16
Sphalerite	ZnS	4.1	13	19
Galena	PbS	7.6	19	7

References: Nearly all of these measurements are reported in Birch, Schairer, and Spicer, 1942; see also Chapter 4 by Adams in Gutenberg, Editor, 1939, or 1951.

oxide structures can possess the required tightness of binding, combined with a suitable density. Thus we have independent support for the interpretation of the high value of $1 - g^{-1}\, d\phi/dr$ of layer C as indicating the introduction of new phases.

Table 15 also shows that admixture of heavy metals, such as iron, with silicates or oxides will generally reduce the resultant (K_T/ρ); if free iron exists in layer D, then an even higher value than 60 (km/sec)^2 is required for the other components. Even when combined as silicate, iron has the effect of reducing (K_T/ρ), by comparison with magnesium (for example, forsterite *versus* fayalite, after Adams, 1931).

TABLE 16—*Estimates of parameters of layer D at various depths*

Parameter (and unit)	Depth in kilometers		
	0	800	2,800
ϕ, (km/sec)^2	51	71	115
ρ, (gm/cm^3), after Bullen	4	4.5	5.6
P, (megabars), after Bullen	0	0.3	1.3
K_S, (megabars)	2.0	3.2	6.4
f, (dimensionless)	0	0.04	0.13
$\alpha/\gamma = C_P/\phi$, (10^{-6}/deg)	24	17	10
γ, estimated, (dimensionless)	1.5	1.2	0.8
α, (10^{-6}/deg), from C_P/ϕ	36	20	8
from $\alpha_0\beta/\beta_0$	36	23	11
$\alpha\phi$, (10^7 cm^2.sec^{-2}.deg^{-1})	1.8	1.4	0.9
γ/ϕ, (10^{-12} sec^2.cm^{-2})	3.0	1.7	0.7
$\tau\alpha\phi/g$, for $\tau = 1°$/km, (dimensionless)	0.18	0.14	0.09
For $T = 10^3\, q$ degrees:			
$-(dT/dr)_S = Tg\gamma/\phi$, (deg/km)	$0.30q$	$0.17q$	$0.07q$
$T\alpha\gamma$, (dimensionless)	$0.054q$	$0.025q$	$0.008q$

On the supposition that layer D is homogeneous, Table 16 gives estimates of various parameters according to the considerations of the preceding section. The uncertainty arising from the estimate of γ may be tentatively set at ±30 per cent; this affects α and quantities proportional to α directly, but $T\alpha\gamma$ is proportional to γ^2. With the aid of Bullen's densities, we find an initial compressibility of about 5×10^{-13} cm^2/dyne, somewhat less than that of iron, with an initial density of about 4, at the temperature of the layer.

The variation of ϕ in layer D is consistent with uniformity and adiabaticity, the necessary conditions for the application of the Adams-Williamson method. This interpretation has the advantage of simplicity, and there is no evidence that it is wrong. It is difficult, however, to give precise answers to such questions as the following: Just how great an excess of gradient above the adiabatic is permissible? What are the permissible limits on the mean temperature? How much departure from uniformity can be reconciled with the data? Such questions involve a number of considerations: (1) The meaning of the scatter of the "observed" $\Delta\phi/\Delta r$; (2) the possibility of compensation of non-adiabatic gradients by non-uniform composition; (3) the possibility of a rate of change of incompressibility with pressure somewhat different from the value adopted as most probable. Most of these points must be left for future discussion, preferably with the aid of different kinds of information.

As an example, however, of the degree of discrimination which these methods possess, let us consider whether a temperature of 10,000° at the core boundary is acceptable. We then estimate $T\alpha\gamma$ at this level as 0.08, $5T\alpha\gamma = 0.4$; the excess gradient would be roughly 2 to 3°/km, and the correction, $2\tau\alpha\phi/g$ about 0.4. Thus, we would expect $1 - g^{-1}\Delta\phi/\Delta r$ to be about 0.8 less than $(\partial K_T/\partial P)_T$, rather than about 0.1 to 0.2 less. So large a difference at such high compression seems improbable in the light of the experimental data. A temperature of 5,000° produces no serious discrepancy. The present treatment can hardly justify a more precise statement about temperature. We notice that a supra-adiabatic gradient of 3°/km would require a reduction of the order of 30 to 60 per cent in the rate of increase of density given by the Adams-Williamson equation, even for a homogeneous layer.

Figure 6 shows also the variation of Poisson's ratio σ with depth, as found from Jeffreys' velocities (see Table 12). Though we know little about the variation to be expected for this quantity, the reversal of trend which takes place in the neighborhood of 500 km is striking, and we may say at least that this is not the kind of variation which we would expect to find as the result of compression of a uniform layer. Below 900 km, however, there is a regular rise with depth which seems consistent with uniformity. The total change is small, only about 10 per cent of σ over the whole range, in which the compressibility changes by a factor of ~ 2. Expressed differently, the rigidity does not rise as rapidly as the incompressibility, though the maximum difference is just sufficient to raise σ from about 0.28 to 0.30 in layer D. The slight flattening of the velocity curves in the neighborhood of the core is such as to reduce σ slightly; that is, to increase the rigidity in proportion to the bulk modulus. The reality of this feature has been questioned above.

The Core: Layers E, F, and G

We approach the question of uniformity, as before, by forming the quantity $1 - g^{-1}\Delta\phi/\Delta r$. Several new complications now arise. First, we have only a single velocity, V_P; this fact, combined with the low effective rigidity of the core required by the variation of latitude, leads to the conclusion that layer E, at least, is liquid. The thermodynamics of a homogeneous layer developed above is valid for liquids as well as solids, but we know very much less about the behavior of liquids at high compressions. In the second place, the acceleration g now begins to decrease as the radius decreases, vanishing at the center; but Bullen's 1942 values, used in these estimates, are probably not subject to a greater uncertainty than the differences of ϕ or V_P^2.

For velocities, we take the values of Jeffreys (1939c) at intervals of 347.3 km (one-tenth of the radius of the core), as well as the recent values of Gutenberg (1951), published only as a curve. The calculations are summarized in Table 17 and plotted in Figure 7. The principal difference between these two sets of data comes toward the base of layer E, where the absolute velocities differ by as much as 3 per cent.

Jeffreys' velocities yield a mean value for $1 - g^{-1}\Delta\phi/\Delta r$ in layer E of about 3.6, to be compared with 3.0 from Gutenberg's 1951 velocities. This means that a

TABLE 17—*Variation of ϕ in layer E*

Radius	ϕ	$-\Delta\phi/\Delta r$	g	$1 - g^{-1}\Delta\phi/\Delta r$
km	$(km/sec)^2$	cm/sec^2	cm/sec^2	
		(*1*) *Jeffreys, 1939c*		
3473	65.6			
		2070	1000	3.1
3126	72.8			
		2500	930	3.7
2778	81.5			
		2200	850	3.6
2431	89.1			
		1900	780	3.4
2084	95.7			
		1800	700	3.6
1737	102.0			
		2000	640	4.1
1389	109.0			
Mean	. . . .			3.6
		(*2*) *Gutenberg, 1951*		
3400	65.6			
		2100	980	3.1
3000	74.0			
		2120	880	3.4
2500	84.6			
		1900	770	3.5
2000	94.1			
		1180	680	2.3
1500	100.0			
		800	620	2.3
1250	102.0			
Mean	. . . .			3.0

curve satisfying the equation of state (14) can be fitted to Gutenberg's curve with good precision, while Jeffreys' velocities show a more rapid increase with depth. It is evidently difficult to obtain high precision in the core, and we can conclude only that the rate of change of velocity is about what we expect for a homogeneous and nearly isothermal layer at the corresponding pressures, on the assumption that under these conditions there is little difference in the change of compressibility of liquid and solid. The small change of $1 - g^{-1}\Delta\phi/\Delta r$ across the core boundary is indeed the principal basis of Bullen's "pressure-compressibility" theory (Bullen, 1949).

Layer *E* has already been treated as homogeneous and adiabatic by Bullen, in calculating the change of density by the Williamson-Adams method. Estimates of the adiabatic gradient, the thermal expansion, and the quantity $T\alpha\gamma$ are hazarded in Table 18. Grüneisen's ratio γ is taken as unity, a value probably not in error by

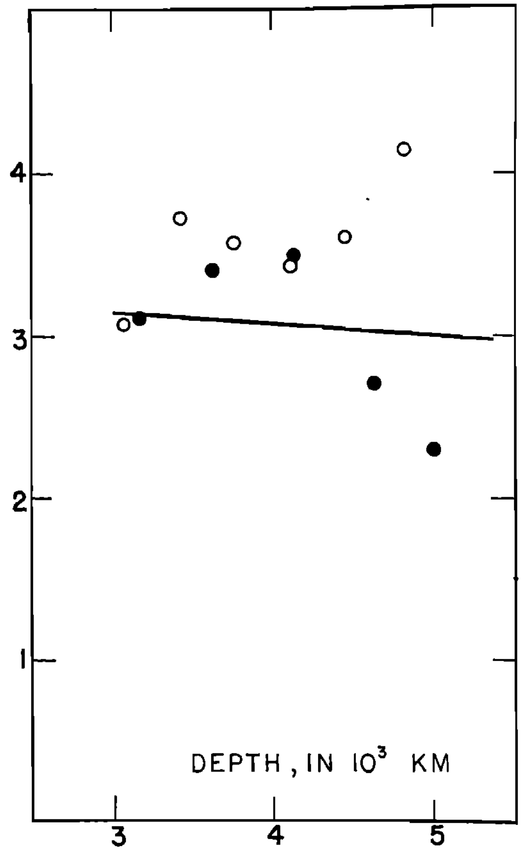

FIG. 7—THE FUNCTION, $1-g^{-1}\Delta\phi/\Delta r$, FOR LAYER E

Table 18—*Estimates of certain parameters in layer E*

Depth	ϕ	g	α	$T\alpha\gamma$	$Tg\gamma/\phi = -(\partial T/\partial r)_S$
km	*(km/sec)²*	*cm/sec²*	*per degree*		*°/km*
2900	66	1000	9×10^{-6}	$0.009q$	$0.15q$
4600	100	700	6×10^{-6}	$0.006q$	$0.08q$

Assumptions: $T = q \times 10^3$ degrees; $\gamma = 1$; $C_P = 6 \times 10^6$ erg/gm.deg.

more than 50 per cent. We notice (1) that the difference between the adiabatic and isothermal compressibilities is only a few per cent; (2) that if the rate of change of temperature is approximately adiabatic, and the temperature of the order of several thousand degrees, the rise of temperature in layer *E* is probably less than 1,000°; (3) a rise of temperature of 1,000° will affect the density by less than one per cent. Thus the Williamson-Adams method is likely to give the change of density in this region with good precision unless, improbably, the temperature deviates widely from the adiabatic.

The variation of the velocity in layers F and G is even less well determined than in layer E. The most recent paper (Gutenberg, 1951) shows a sharp change of slope of velocity *versus* radius, at about 1,250 km radius; thereafter, for smaller radii, it shows a rapid rise toward a limiting value of about 11.15 km/sec, which is reached at a radius of more than 1,000 km; the velocity remains constant below this point. Now we may expect the velocity to have a zero slope at $r = 0$, but it is unlikely to show no change throughout the whole inner core. Jeffreys' 1939 solution shows an increase of velocity with depth in the inner core, but has the disturbing feature of a decrease of velocity by about 0.8 km/sec between $r = 1{,}390$ and $r = 1{,}250$ (layer F), followed by a sudden jump from about 9.6 km/sec to 11.1 km/sec at the boundary of layer G, $r = 1{,}250$ km. Jeffreys believes that a decrease of velocity with depth is required by the travel times, but remarks of this particular solution: "Presumably there are an infinity of others, but there is no apparent way of deciding which is the right one, and the first question to decide was whether the times could be fitted at all." Gutenberg, on the other hand, concludes that there is no "decrease of velocity nor a strictly vertical segment" (p. 389, 1951).

The point is not without interest, as far-reaching conclusions have been built up on this somewhat arbitrary feature of Jeffreys' solution. Ramsey has argued that this decrease of velocity is evidence of a phase change of "olivine" in spite of its dissimilarity to the minor and possibly illusory change of slope of the velocity just outside layer E, which is also cited as "positive proof" of the transition of olivine to a metallic phase. Bullen believes that the reduction of velocity must indicate a comparable rise of density, since he has already adopted the "pressure-compressibility" hypothesis, according to which all materials have the same compressibility at pressures above perhaps 0.4 megabar. Still another explanation must then be found for the rise of velocity at the boundary of layer G. Aside from the questionable premises in both instances, the seismological evidence seems hardly adequate as yet to support these deductions.

Gutenberg's latest solution bears a resemblance to the variation of velocity found in the neighborhood of the melting point, in the few cases where such measurements have been made (Birch and Bancroft, 1940; Siegel and Cummerow, 1940; Hunter and Siegel, 1942) and perhaps the simplest interpretation of the inner core is that it represents a crystalline phase, mainly iron (Birch, 1940). The change of temperature throughout the core being slight, the melting point may be approached as the pressure diminishes, and reached at the radius of 1,250 km; in ordinary experience, the melting point is usually approached by a rise of temperature at constant pressure, but the phenomena which take place near the melting curve should be exhibited in either case. The available data, even for pure iron at one atmosphere, are unsatisfactory, but with improvement of data and perhaps of theory, it may become possible to obtain an estimate of the temperature of the core with the aid of this hypothesis.

Another straw of evidence may be brought to its support. If the inner core is crystalline, then the observed velocity is given by $V_P^2 = (K/\rho)(3 - 3\sigma)/(1 + \sigma)$; on the other hand, we can calculate K/ρ for iron at the pressures of the inner core

(Table 22), and by combining the observed V_P and the calculated K/ρ, we obtain a value for Poisson's ratio. A negative value, or one greater than 0.5, would indicate incompatibility of these data; in fact, this method gives $\sigma = 0.37 - 0.38$ at $r = 0$, a reasonable figure. In making this calculation, we have ignored the effects of temperature, of phase changes, and of alloying elements on the compressibility of iron, and the satisfactory result may well be fortuitous.

In this connection, there is a minor correction to be made to Elsasser's (1950*a*) calculation of Poisson's ratio for the inner core, on the assumption that density and compressibility have the same values as just outside, in layer *E*. With $V_P = 10.44$ km/sec $= (K/\rho)^{1/2}$ outside, and $V_P = 11.16$ km/sec $= [(K/\rho)(3 - 3\sigma)/(1 + \sigma)]^{1/2}$ inside, it follows that $\sigma = 0.45$, instead of 0.37. This is a possible but high value for a solid, and would lead to a velocity of shear waves V_P of about 3.4 km/sec, instead of about 5.2 km/sec for $\sigma = 0.36$. The value of σ for a liquid is 0.50, instead of 0, as given by Elsasser.

Ramsey and Bullen have also concluded that the inner core is probably crystalline and Bullen (1950*b*) has computed tables for the travel times of phases which traverse the inner core as shear waves. If any of these can be reliably identified, the theory of the inner core will be placed on a firmer basis.

Another possibility, pointed out by Elsasser and Isenberg (1949) is that the inner core represents a new phase of iron, corresponding to rearrangement of electronic orbits of the kind postulated by Sternheimer (1949) to account for the transition found by Bridgman in cesium at 45,000 bars; in this case, the inner core also might be liquid. In cesium, the density change accompanying this transition is about 11 per cent of the density of the low-pressure phase, at the transition point, where the density is about twice the value at zero pressure. It is not unreasonable to suppose that a similar effect may take place in iron at roughly twice its initial density; but a comparable compression does not induce the transition in potassium or rubidium.

CHEMICAL COMPOSITION

Modern discussions of the internal composition of the Earth are usually based on the assumption that the relative abundances of the chemical elements in the Earth may be found by suitable weighting of the analyses of meteorites. Many writers have discussed the characteristics of meteoritic material which suggest its origin in masses of planetary dimensions. Except for the lightest elements, there is fair agreement between the meteoritic and solar abundances (Brown, 1949; Elsasser, 1950*a*). Although Kuhn and Rittmann have proposed an Earth consisting largely of hydrogen, the orthodox view is that the principal constituents are the four elements oxygen, silicon, magnesium, and iron, which predominate in the meteorites.

The most striking characteristic of meteorites is that they display two sharply differentiated "phases"—the silicates, mainly olivines and pyroxenes, and free metal, approximately 90 per cent metallic iron. These phases occur intermingled in nearly every proportion, from stones with no free metal, to irons with no silicates. Such facts long ago led to the hypothesis that the Earth might possess an iron core surrounded by a silicate mantle, an idea developed by Wiechert to explain the high mean density and central condensation. Qualitatively, this concept is highly satisfactory, and its age should not be regarded as a sufficient reason for easy rejection.

On advancing beyond this broad generalization, however, we encounter the practically indeterminate problem of giving weights to the several hundred analyses of meteorites of all types. Aside from the dubious value of many of these analyses, the major difficulty is to find the correct ratio between silicates and iron. The range of estimates of the ratio of masses of stony to iron meteorites is illustrated in Table 19 (see also Watson, 1941, p. 177; Rankama and Sahama, 1950, p. 30) which includes the resulting proportions for the major elements.

TABLE 19—*Weighted composition of meteorites (per cent by weight)*

		Washington	*Watson*	*Goldschmidt*	*Brown*
Ratio of masses, silicate/iron =		35/1	9/1	5/1	1·5/1
Resulting proportions for major elements	O	32	33	32	25
	Fe + Ni	26	34	30	49
	Mg	17	13	12	10
	Si	18	16	16	12
	Rest	7	4	10	4

Ramsey (1949, p. 424), adopting Washington's estimates, has argued that an iron core would lead to a proportion of iron "larger than the average content of meteorites," and "much larger than would be expected if the earth originated from solar matter." At the other extreme, Brown has used the hypothesis of an iron core to find the correct ratio for the meteorites, which turns out to be about 1.5/1 (silicate/iron), with an assumed 10 per cent of free iron in the mantle. It seems evident that no serious quantitative argument either for or against an iron core can be drawn from such data. The "cosmic" or solar ratio of iron to silicon must be uncertain by a factor of 10 or more (see Brown, 1949, Fig. 2; Urey, 1951*a*; Table 1).

There is much less uncertainty about the composition of the "average stony meteorite," particularly if we consider only the silicate phase. This is expressed in

TABLE 20—*Composition of the average stony meteorite*

Element (1)	Per cent by weight (2)	Oxides (3)	Molecular ratio SiO_2 = 100 (4)	Normative minerals (5)	Per cent by weight (6)
O	41.02				
Mg	15.82	MgO	93	Olivine	47.34
Si	20.57	SiO_2	100	Pyroxene	32.40
Fe, Ni, etc.	16.53	FeO	32.4	Anorthite	3.73
Al	1.74	Al_2O_3	4.5	Albite	8.20
Ca	1.97	CaO	6.7	Orthoclase	1.24
S	1.79	(FeS)	7.6	Troilite	5.58
Na	0.78	Na_2O	2.3	Chromite	0.78
K	0.20	K_2O	0.4	Apatite	0.73
P	0.16	P_2O_5	0.3		

References: Columns 1 and 2, after Brown, 1949, p. 626; columns 5 and 6, metal-free chondrites, after Daly, 1943, p. 411.

various ways in Table 20, where the abundances of the elements are taken from Brown (1949, p. 626) and the calculation as normative minerals is from Daly (1943, p. 411). All elements are retained which are more abundant than 0.1 per cent by weight; this just excludes Cl, with 0.09 per cent. Mn, Ti, Cr have been grouped with Fe, and account for 0.75 per cent.

Brown gives relative abundances for all the elements, and it is worth noticing that beyond the iron group (transition metals), no element is as much as one-thousandth as abundant as iron. Even with a very generous allowance for error in these estimates, we must reject Bullen's suggestion that the density in the inner core (*G*) may be "too high to be compatible with the presence of much iron," and that there may be "an accumulation of denser materials." The mass of the inner core is roughly one-tenth of the mass of the core, or one-thirtieth of the mass of the Earth. No element denser than iron occurs in one-hundredth of the required proportion (see also Elsasser, 1950*a*, pp. 11, 15).

Inspection of Table 20 suggests another general comment. The proportions of metal oxides to silica do not correspond to the proportions in an orthosilicate; this is not surprising, as the silicates of the average stony meteorite are fairly evenly divided between olivines and pyroxenes. Washington, for example (in Gutenberg, Editor, 1939, p. 113) says of the average stony meteorite: "In terms of minerals, this corresponds to olivine, 35 (per cent); pyroxene, 42; anorthosite, 4; troilite, 5; nickel–iron, 13. The silicate portion is principally an olivine–pyroxene mixture, i.e., essentially a peridotite." The notion that the mantle consists exclusively of olivine, or dunite, finds no support in the chemistry or mineralogy of the meteorites.

We have seen that new phases are required to account for the high elasticity of layer *D* and, in part, of layer *C*. If these phases are stable only at pressures corresponding to depths of several hundreds of kilometers or more in the Earth, their absence in meteorites is automatically accounted for; whether the high-pressure phases ever existed in the meteorites depends upon the size of the parent body. They would not exist in the Moon, nor, probably, in Mercury; they might comprise a minor fraction in a body as large as Mars. For present purposes, it is sufficient to suggest that the absence of such phases from meteorites is not an argument against their existence in the Earth, even if we adopt the plausible view that the meteorites provide a rough sample of the Earth's chemical composition.

Somewhat different problems arise when we attempt to reconcile the data with respect to the shallow region between the base of the crust and a depth of several hundred kilometers with the meteoritic mineralogy. Here we have ϕ_0 between 34 (km/sec)^2 (Jeffreys, 1939*a*) and 37 (km/sec)^2 (Gutenberg, 1948). Either value probably excludes peridotite, or the average stony meteorite, even without allowance for the effect of temperature; forsterite barely meets the requirement. Even a small allowance for temperature or for iron content gives a value for olivine below the latest seismic values, though it is difficult to be sure that the difference is significant, all errors considered. As Table 15 shows, thanks to the measurements of Adams and Gibson and of Bridgman, there are a number of possibilities which do not so greatly strain the data. In particular, the garnets and the pyroxene minerals, jadeite and spodumene, show higher values of ϕ than do the olivines, and there seems to be reason to consider a form of the "eclogite" hypothesis (see Bowen, 1928, pp. 305, 318). Yoder (1950) has recently reviewed the problem of the origin of jadeite, and Yoder and Weir (1951) have found that jadeite is slightly more stable than its chemical equivalent, albite + nepheline, at ordinary conditions, and increasingly more stable as the depth increases. (A related question is the range of existence of feldspars, as the pressure increases. It seems unlikely that such relatively "loose" structures would either form or persist at high pressures.) We need not suppose that the composition of layer *B* is identical with that of any particular eclogite, and indeed this term appears to designate a variable group of rocks (Eskola, 1921), but an assemblage of olivines, pyroxenes, such as jadeite and its potassium equivalent, and garnets can evidently have the required ϕ, and this will be termed "eclogite" for present purposes.

A property of the eclogite hypothesis is that it accommodates the appreciable "sialic" fraction of the stony meteorite, that is, the alumina, lime, and alkalis. As is easily seen from Table 20, a mass of the average chondrite equal to the mass of the Earth's mantle would contain enough lime, alumina, soda, and potash to form a layer of "sial" several hundred kilometers deep, containing about 10 per cent of the mass of the mantle, and some ten times the mass of the crust; this supposes the separation of all the feldspars of Table 20 toward the surface. On the other hand, if differentiation in this sense proceeded only to the point of forming the actual crust, the remainder would have nearly its original average composition, namely, that of a peridotite with roughly one-half olivine. But the seismic evidence is unmistakable that no appreciable proportion of the minerals, quartz, orthoclase, or albite can be present below the crust. These considerations have seemed an objection to acceptance of the meteoritic composition as the prototype for the Earth's mantle. If, however, most of the alumina, alkalis, and lime, though segregated toward the surface, exist in such forms as jadeites and garnets, this particular difficulty disappears. As layers *B* and *C* comprise roughly 40 per cent of the mass of the mantle, we are at liberty to suppose that all of the alumina, lime, and alkalis have been concentrated in these layers and the crust, with a remainder of silicates of magnesium and iron.

Another attractive feature of the eclogite hypothesis is that the chemical composition of eclogite may be fairly close to that of basalt. The provision of a copious supply of basaltic magma is a fundamental requirement for petrogenesis and has proved a difficult one to reconcile with the seismic and laboratory evidence against a "basaltic substratum" (Birch and Bancroft, 1942; Daly, 1946). With a layer several hundred kilometers thick of "eclogite," in which the temperature may reach several thousand degrees, a satisfactory account of the origin of basaltic magma does not seem impossible.

The density of eclogite might well exceed the figure of 3.32 adopted by Bullen for the top of layer *B*, with highly magnesian olivine in mind. We have already seen that the Adams-Williamson equation is probably not applicable in layer *B*, either because of heterogeneity or because of the high gradient of temperature, and that the density may be nearly uniform between the base of the crust and the somewhat indefinite lower limit of layer *B*.

The variation of properties through the transitional layer *C* may depend upon two effects not easily disentangled. First, there may be a change of gross composition; for example, the proportion of the alumina-bearing phases may gradually diminish as the depth increases, with an increase of the ferro-magnesian portion. Second, the olivines and pyroxenes, which are the stable phases at low pressure, may gradually give way to increasing proportions of high-pressure phases as the depth increases. It has already been proposed that orthorhombic olivine may, at high pressures, transform to a cubic olivine having a spinel structure (Bernal, 1936; Jeffreys, 1937*c*); it is still unknown, however, whether such a modification would show the necessary increase of ϕ, as compared with the ordinary olivine structure. Furthermore, the transitional layer is some 500 kilometers deep. Instead of attributing this spread to "impurities" (Jeffreys, 1937*b*, p. 38; 1937*e*, p. 250), we may perhaps more reasonably imagine a system of several major components, for example, MgO–FeO–SiO_2. The gradual change may then be interpreted as a shift with pressure in the relative proportions of high-pressure and low-pressure phases.

On this hypothesis, the transformation to high-pressure phases is complete at about 900 km. This depth coincides approximately with the "Repetti discontinuity," from which reflected waves have been identified by a number of seismologists (Macelwane, Chapter 10, in Gutenberg, Editor, 1939 or 1951; Caloi and Peronaci, 1951). The seismic nature of this discontinuity remains uncertain; not even a discontinuity of velocity-gradient appears in Jeffreys' 1939 solution. It is clear, however, that a large change of velocity-gradient takes place between depths of about 800 and 1,000 km.

A few specific proposals may be offered concerning possible high-pressure phases, but, needless to say, they require analysis by the methods of chemical physics. It is necessary to investigate the stability, density, and compressibility, a task not yet accomplished for any of the high-pressure phases so far suggested. We have already noticed (Table 15) that several oxides, such as corundum and rutile, have values of ϕ_0 of about the right order. It is conceivable that pyroxene, for example, enstatite, $MgSiO_3$, might adopt a structure of the corundum (Al_2O_3) type; or SiO_2 might exist at high pressure in the rutile (TiO_2) structure. The orthosilicates such as Mg_2SiO_4 might transform to the spinel structure, or break down to high-pressure phases having the compositions MgO and $MgSiO_3$, and so on. These are questions for further study. The principal points are that high-pressure phases are required, and that oxide structures are known which have the required elastic ratios.

The classical view that the Earth's core is chemically similar to the iron meteorites has been challenged by Kuhn and Rittmann (1941), who propose an interior of "solar material," largely hydrogen, and by Ramsey (1948, 1949, 1950*a*), who regards the core as a metallic phase of olivine. These writers agree only on the rejection of iron; on this point, Ramsey accepts the principal argument of Kuhn and Rittmann, namely, that separation of iron from a silicate melt would be prevented by viscosity, and adds several new ones. In view of the geochemical importance of this question, these arguments will be considered in some detail.

The most damaging evidence against a high hydrogen content is the work of Kronig, de Boer, and Korringa (1946), who start out to show, in support of Kuhn and Rittmann, that the mantle-core discontinuity may be identified with the molecular hydrogen-metallic hydrogen transition suggested by Wigner and Huntington (1935). The calculations lead to a density for metallic hydrogen of about one at the pressure of the core, and it is clear that the hydrogen content must be limited to a small fraction, probably even less than the 10 per cent by mass proposed by Kronig, de Boer, and Korringa (see also Ramsey, 1949; Elsasser, 1950*a*). It is evidently more reasonable to reserve hydrogen for the giant planets, which have mean densities in the neighborhood of one, than to attempt the construction of small planets having mean densities between 4 and 5.5 of so light a component.

While the theory of Kuhn and Rittmann has been much discussed and rather generally rejected, Ramsey's ingenious theory has not yet received wide attention (see, however, Elsasser, 1950*a*, 1950*b*, 1951; Bullen, 1949; Jeffreys, in Gutenberg, Editor, 1951). The inner planets are regarded by Ramsey as consisting exclusively of "olivine," the different layers (excluding the Earth's crust), resulting from phase changes alone. In order to maintain this view, he is forced to modify Bullen's densities by an arbitrary increase of density with depth, attributed to a concentration of heavy elements, particularly of iron orthosilicate, towards the center. The inconsistency of such a concentration with his acceptance of the thesis of Kuhn and Rittmann, that segregation of metallic iron is impossible, does not seem to be remarked.

Let us first consider the objection to the possibility of separation of an iron core. The processes of condensation of the Earth envisioned by Jeffreys (1929, pp. 29–31), Eucken (1944), Edgeworth (1949), and others provide for the separation of iron before the consolidation of the mantle as a viscous liquid. It is clear, furthermore, that if for good reasons we decide that the core *is* iron, this conclusion will condition our theories of origin. Suppose, however, that the iron was originally distributed uniformly. A dry melt having the composition of the "average stony meteorite" would have a viscosity, not far above its melting range and at one atmosphere, of the order of 10 to 100 poise. An estimate has to be made of the effects of pressure, an unknown temperature, and unknown amounts of dissolved water, and other "volatiles," all highly uncertain, but offering little support for the figure adopted by Kuhn and Rittmann, 10^{20} poise, which appears to depend upon estimates of the present "viscosity" of the Earth as a whole. Whether or not free iron is capable of sinking through the mantle at the present time, as suggested by Urey (1951*b*), it is sufficient for the hypothesis of the iron core that the possibility of separation existed at some earlier epoch.

But there is another aspect to this problem. If the iron were uniformly distributed, the central pressure would be lower, the average pressure on the iron would be lower, and the iron would occupy a larger fraction of the volume than does the present core, roughly one-quarter instead of about one-sixth of the whole volume. Rather than the separation of small volumes of iron from a much greater volume of "silicate," we should perhaps consider the separation of silicate or oxide crystals from liquid iron. So far as we can judge from experience with mercury, the viscosity of liquid metals is little affected by pressure; estimates of the present viscosity of the core based on the damping of compressional waves give about 10^9 poise as an upper limit (Jeffreys, 1929, p. 266); a theoretical estimate for molten iron in the core is 10^{-2} poise (Bullard, 1948, p. 256). In either case, we have to do with a relatively fluid component. In the present state of ignorance regarding the processes of origin, the thesis of the impossibility of segregation of iron may be regarded as wholly unproved.

Another objection raised by Ramsey, not only against an iron core but against a core chemically distinct from the mantle, is based on his discussion of the mean densities of the inner planets. Some recent values for these densities are collected in Table 21; Ramsey adopts the values of Russell, Dugan, and Stewart. This argument is vitiated by the recent determinations of the mass of Mercury by Clemence (1949) and Rabe (1950), leading to values about 25 per cent higher than the old ones. Even the density of Venus shows an appreciable fluctuation. It seems advisable to limit arguments based on the densities of other planets to qualitative generalizations.

Table 21—*Mean densities of the inner planets*

Authority	Venus	Mars	Mercury
Russell, Dugan, and Stewart, 1945	4.9	3.85	4.1
Jeffreys, 1937	5.04 ± 0.12	3.958 ± 0.031	4.30 ± 0.95
Wildt, 1942	4.86	3.84	2.86
Whipple, 1941	4.86	3.96	3.8
Urey, 1950		4.16	
Rabe, 1950*	4.99 ± 0.15	3.93 ± 0.04	5.3 ± 0.5
Smart, 1951	5.21	3.94	3.73
Ramsey, 1948†, theoretical			3.7

*These are calculated with masses according to Rabe, and diameters according to Jeffreys (1937).
†After adjustment of densities to give a density of 3.93 for Mars.

In the earlier discussion of the inner planets by Jeffreys (1937*d*), the desired mean densities were obtained by adjustment of the cores, treated as chemically distinct; this procedure, which still seems most reasonable, gave as the ratios of core mass to total mass for Mars, 0.16, and for Venus, 0.22; the value for the Earth is 0.32. No core was required for Mercury when the density was taken as about 4, but the new value of 5.3 demands a core ratio of about 0.5 (or an equivalent amount of distributed heavy material). It is not clear why there need be a greater degree of chemical similarity than is indicated by these figures.

Ramsey gives a surprising argument against the possibility of a sharp boundary between a silicate mantle and an iron core. Remarking that at 10,000°, a rough estimate of the temperature at this depth, the energy kT is equivalent to the energy required to lift an iron atom a distance of 300 km in the Earth's gravitational field, Ramsey concludes that "if gravity were the controlling factor, then the jump in density would not be sharp, as indicated by seismology, but would be spread over at least 300 km." This implies that a blast furnace must be at least 60 km high. Gravity is not the factor which controls the distribution of atoms between these phases; it merely controls the relative positions of the phases, while the distribution of the elements depends upon chemical potentials. A sharp interface is not incompatible with diffusion in both directions, and the peculiarity of the velocity variation just outside the core, if real, might perhaps be accounted for by such a process.

Ramsey also postulates an increasing concentration of iron silicate, relative to magnesian silicate, toward the base of the mantle, and, indeed, toward the center of the Earth. Instead of a gravitative concentration of iron silicate, it is more probable that iron would be concentrated in last-forming crystals in layers B and C, the corresponding magnesian silicates or oxides having not only higher velocities but also higher crystallizing temperatures. Part of the abnormal rise of velocity in layer C might be attributed to a shift toward *lower* proportions of iron as the depth increases.

A final argument concerns the density of the core. The point of departure is generally one of Bullen's density-pressure relations, and the usual procedure, aptly characterized by Jeffreys as "rather risky," is to extrapolate to zero pressure. The data refer to pressures between 1.3 and 3 megabars, and are subject to the effects of all of the special assumptions necessary for the construction of the density curves. With the evolution of the seismic velocities and of their interpretation in terms of "discontinuities," widely ranging zero-pressure densities have been published. These values are usually compared with the density of iron under ordinary conditions or of liquid iron near the melting point.

Extrapolation to zero pressure may be carried out graphically (Bullen, 1937) or with the aid of various formulas for the relation of density or compressibility to pressure. For example, Ramsey has relied on the assumption, very nearly correct for a limited pressure range, that $\partial K/\partial P$ is a constant; on applying this to his "corrected" density distribution, he finds a density of 4.8 for $P = 0$, but this low value is a result of his "condensation of heavier elements" toward the center. Without this condensation, he obtains 6.4, which is considered to be too high by as much as 0.5 because of the method of extrapolation. This value is interpreted as excluding the possibility that the core is iron.

Inspection of the seismological values of K/ρ shows that they also are closely linear with pressure in layer E. Integrating $K/\rho = a + bP = dP/d\rho$, and determining a and b by means of Jeffreys' velocities and Bullen's pressures, we find $\rho - \rho_0 = (1/b) \log (1 + bP/a)$, with $\rho_0 = 6.5$ and $K_0 = 2.08$ megabars. We may also apply the equation of state (14) to determine ρ_0 and K_0. It is possible to obtain a good approximation to Bullen's (1942) curve for any value of ρ_0 between 6 and 7; the best fit is for $\rho_0 = 6.4$, $K_0 = 1.63$ megabars, for which the standard deviation of a single point of calculated density is 0.014, for eight calculated points. This includes the effect of initially high compressibility. The densities used for all these calculations are subject to revisions which may easily amount to several tenths of a unit.

Having found an initial density, however, we still have the problem of its significance. The extrapolation gives at best the density at zero pressure, but at some unknown temperature, possibly not greatly different from the temperature of the core. The density of pure liquid iron near the melting point is variously given as between 6.9 and 7.2, and its thermal expansion as between 100×10^{-6}/deg. and 400×10^{-6}/deg. A density of 6.4 might thus be expected at no more than 1000° above the melting point, even for "pure iron."

Another approach to this problem is by calculation of the expected density for iron with the aid of (14) and the known compressibility at ordinary temperature.

TABLE 22—*Estimated density, pressure, and incompressibility of iron*

f	ρ	P	K	K/ρ
		megabars	*megabars*	$(km/sec)^2$
0	7.87	0	1.68_4	21.4
0.02	8.35	0.111	2.12	25.5
0.04	8.83	0.245	2.61	29.7
0.06	9.32	0.402	3.17	34.2
0.08	9.83	0.586	3.81	38.9
0.10	10.35	0.798	4.52	43.8
0.12	10.87	1.039	5.31	49.0
0.14	11.39	1.312	6.18	54.4
0.16	11.93	1.617	7.14	60.0
0.18	12.48	1.962	8.21	65.9
0.20	13.03	2.342	9.37	72.1
0.22	13.61	2.765	10.64	78.5
0.24	14.18	3.232	12.03	85.1
0.26	14.78	3.742	13.53	92.0
0.28	15.34	4.298	15.16	98.8
0.30	15.93	4.916	16.91	106.1

The results are tabulated in Table 22 and plotted in Figure 8; it has been assumed that $\xi = 0$, in agreement with the latest measurements on iron to 30,000 kg/cm^2 (Bridgman, 1940, 1949; see also Table 4 above) and with the large compressions of the alkali metals. The densities obtained in this way are about 20 per cent higher than Bullen's 1942 values for layer *E*. The allowance to be made for the temperature of the core is uncertain, but might be set roughly at no more than 10 per cent. Phase changes may increase the density; for example, we know that body-centered (alpha) iron transforms to the denser, face-centered (gamma) structure at a relatively shallow depth (Birch, 1940); the change of density accompanying this transformation is, however, only $\sim$1 per cent. The only other type of transformation likely to occur would be a cesium-like transition, which has been suggested to account for the inner core. It seems possible that the density of layer *E* is perhaps 10 to 20 per cent lower than the density of iron or nickel-iron under the same conditions.

Jensen's curve of density *versus* pressure (Fig. 8) has been much quoted in this connection, but Jensen assigns an uncertainty of about 10 per cent to the interpolated portion, which depends, furthermore, upon the use of the seismic velocity in the core (Jensen, 1938, p. 377).

In view of all the uncertainties of these comparisons, either by extrapolation from high pressures to low, or from low to high, a discrepancy of 10 to 20 per cent can hardly be said to condemn the hypothesis of the iron core, especially when the density appears to be slightly smaller than we expect for iron. While it is difficult to find enough heavy elements in the cosmic chemistry to account for a density substantially greater than that of iron, any of the most abundant elements will reduce the density of iron. The effects of carbon and silicon are perhaps the most familiar, a reduction of density by 10 per cent requiring only small percentages of these elements. A more important discrepancy, so far as "pure iron" is concerned, is that the calculated values of K/ρ are somewhat too low for layer *E*. Thus we require an alloying element which will not only reduce the density slightly but raise the ratio K/ρ. The suggestion of Kronig, de Boer, and Korringa that the core might contain a small proportion of metallic hydrogen is worth consideration, as the ratio K/ρ, which can be formed from the pressure-density table calculated by Ramsey (1950*b*) as $\Delta P/\Delta\rho$, is extraordinarily high, of the order of 700 (km/sec)^2. The properties of alloys are often unpredictable, but it seems likely that a small amount of this component would alter the properties of iron in the right direction.

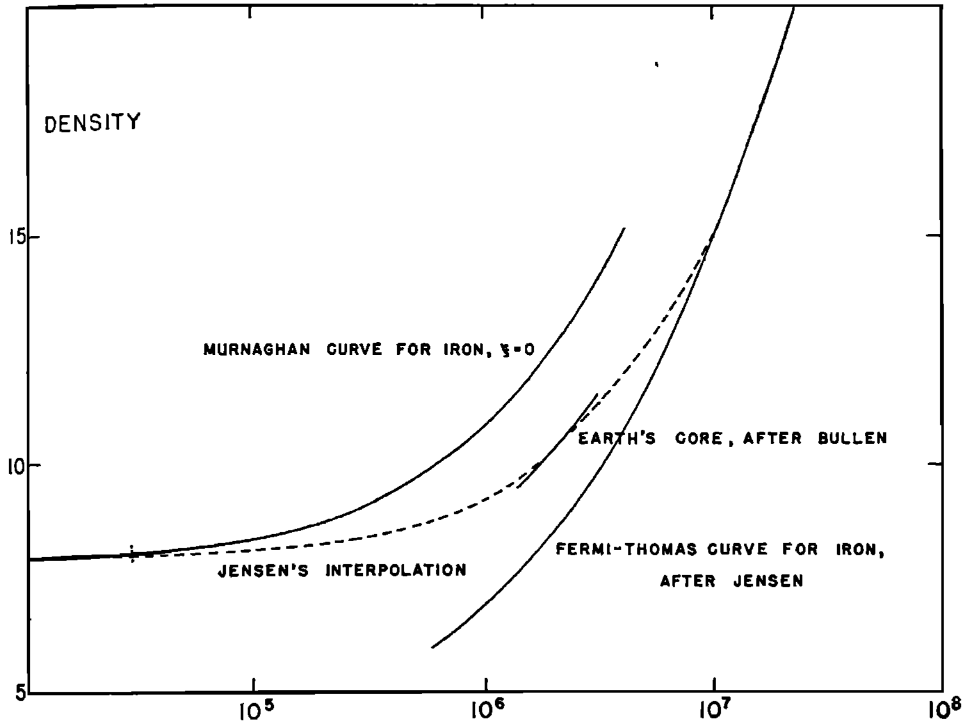

FIG. 8—ESTIMATED DENSITY OF IRON AS FUNCTION OF PRESSURE

Although the geophysical arguments against a predominantly iron core are unconvincing, and the astronomical argument has been invalidated by the new studies of Mercury, Ramsey's proposal of a phase change, rather than a chemical change, at the core boundary deserves consideration on its own merits. The prediction of phase changes, even of more familiar kinds, is notoriously hazardous, and to demand a calculation of the pressure and change of density to be expected for the transition from an ionic compound to a metallic form is perhaps unreasonable. Calculations have been presented only for the transition of hydrogen from the molecular to the metallic form, and as the predicted pressure is beyond the range of experiment, the accuracy of these calculations remains unknown, though the plausibility of the process has been increased by Ramsey's studies (1950*b*) of the giant planets and white dwarfs. With respect to the proposed transition of olivine in the Earth, Ramsey shows only that the work done by the pressure for the change of specific volume on crossing the core boundary, on the supposition that this corresponds to a phase change, is roughly equivalent to the excitation energy of the first conduction band of quartz. But the same amount of work could be associated with a smaller change of volume at a higher pressure.

There are reasons for believing that the density of a material made up chiefly of light elements must be lower than that of the core at the corresponding pressures, regardless of the degree of ionization. The Thomas-Fermi method gives densities for completely ionized elements and, in this sense, gives maximum values of the density obtainable by pressure ionization. Curves for a number of elements have been published (Feynman, Metropolis, and Teller, 1949; Elsasser, 1951), and it is noteworthy that the density of the core is approached, even at pressures of the order of 10 megabars, only by elements of atomic number of nearly 30. We know that this theory fails at low pressures, where the density depends upon atomic and lattice structures; for example, Jensen's curve for iron ($Z = 26$) gives a Thomas-Fermi density at one megabar slightly below the real density of iron at one atmosphere. It is difficult to estimate exactly where these curves begin to attain a reasonable precision, but it seems highly unlikely that a compound of magnesium ($Z = 12$), silicon ($Z = 14$), and oxygen ($Z = 8$) will reach a density of 10 at a pressure of several megabars. The density of silicon alone, the heaviest of these elements, can hardly exceed 6. These calculations suggest that a compound such as Mg_2SiO_4, of mean atomic number equal to 10, would reach a density of 10 only at a pressure ten times as great as the pressure at the core boundary, even if in the fully ionized condition.

The inner core is considered by Ramsey to represent still another modification of olivine. Bullen prefers the hypothesis of a chemically distinct inner core, nickel-iron or denser material. We have seen above that the predicted properties of crystalline iron, calculated on the assumption that iron follows the same law of compression as the alkali metals, are consistent with the velocities in the inner core. On this hypothesis, the central density would be about 14.8, and the density near the boundary would be about 14.3. There is no necessity for the rapid rise of density near the center proposed by Bullen, and the change of density from layer *E* to layer *G* would be merely the difference of 10 to 20 per cent, which has already been discussed. This leaves the peculiarity of Jeffreys' velocity distribution (layer *F*) unaccounted for, on the ground that it is not necessarily real. If there were no change of Poisson's ratio in layer *G*, the total rise of V_P in this layer would be about 0.3 km/sec. The rise shown by Jeffreys' curve is about 0.16 km/sec, and corresponds to an increase of σ from about 0.35 at the edge to 0.37 at the center. Gutenberg's curve shows no change in velocity, and this corresponds to a rise of σ from 0.35 at the edge to 0.38 at the center. In view of the behavior of σ in layer *D*, approximate constancy in layer *G* seems most likely, the change of pressure in this region amounting only to about 10 per cent. It is evident that improving the velocity distribution in this small central region will be a matter of great difficulty.

CONCLUSION

In the foregoing analysis, we have attempted to answer certain questions about the Earth's interior by direct comparison of a quantity obtained from the seismic velocities with the theoretical value of this quantity for a homogeneous layer. This theoretical value was found in its general form by purely thermodynamical reasoning, but for the numerical evaluation of the various parameters, it was necessary to review the theoretical and experimental work bearing on the equation of state of solids. The numbers adopted for the parameters may be considered as normal or typical, in the sense that they are representative of the experimental values for a wide variety of materials and conditions; the measurements on highly compressed materials and at temperatures above the Debye temperatures are of the greatest value. The parameters of importance for this purpose show relatively little dependence upon pressure, upon temperature (at high temperatures), or upon the chemical composition or type of chemical bond. Nevertheless, it is impossible to be sure in advance that any particular material will conform to these typical specifications, and a reasonable margin of uncertainty must be accepted. When the comparison of observed and expected quantities is carried out, however, the result is a striking agreement throughout most of the interior of the Earth with the expectation for uniform layers at relatively low and uniform temperatures; a strong presumption of uniformity is established for each of the layers D, E, and G. In layer C, and possibly part of layer B, the observed rate of change of ϕ is so great that no plausible adjustment of parameters can bring it into agreement with the rate expected for a uniform layer. The extreme "abnormality" of layer C, and the remarkable "normality" of the other layers, are exhibited in Figures 5 and 7; this contrast is second in importance only to the striking change of properties at the boundary of the core.

Further examination of layer D leads to the conclusion that it consists of high-pressure phases, possibly close-packed oxides of magnesium, silicon, and iron, similar in structure to corundum, or rutile, or spinel; further study by the methods of chemical physics is required. Layer C, in which the abnormal rise of velocity occurs, is thus interpreted as a layer of transition, from familiar silicate minerals in layer B to the high-pressure phases of layer D. The great depth of this transitional layer is thought to indicate a shift of equilibrium, induced principally by increase of pressure, in a multicomponent system. It is also suggested that there may be important changes of chemical composition within this layer, alumina-rich "eclogitic" minerals such as garnet and jadeite in layer B giving way gradually to magnesium-rich high-pressure forms as the depth increases. The variation of velocity in layer B still seems to be uncertain, but the recent results of Gutenberg may be accounted for in terms of the effect of temperature, a gradient of about 6°/km probably sufficing to produce a shadow zone at a depth of 80 to 100 km.

The transitional layer C, between about 300 and 900 km, is possibly the key to a number of geophysical problems. The deepest earthquakes originate at about 700 km below the surface. Cooling by conduction from the surface cannot have penetrated below about 1,000 km, and is now a maximum at about 500 km. It is natural to look for an association of deep-focus shocks with the phase changes of layer C, and to expect that the amount of contraction, as calculated by Darwin and Jeffreys, may be considerably increased if it results to an appreciable degree from change of phase rather than simple thermal contraction. The source of lavas may have to be sought in this deep but evidently active region. The nature of layer *C* has also an important bearing on the question of convection within the mantle (Birch, 1951*b*). Changes of composition or even of phase alone, in layer *C*, necessarily affect the possibility of through-going currents involving the whole mantle. These questions must be left for future discussion.

If, as this analysis suggests, layer *D* is homogeneous, how could it have reached such a condition? There seem to be at least two possibilities. The whole mantle was originally homogeneous, and layer *D* has remained unchanged, differentiation having affected only the layers above and including layer *C*; or differentiation has affected the whole mantle, with settling out of a uniform aggregate of the highest-melting components as high-pressure phases and rejection of lower-melting components toward the surface. For reasons discussed elsewhere (Urry, 1949; Birch, 1951*a*), a stage of general fusion in the early history of the Earth seems likely even on the hypothesis of a relatively cold origin, and the second alternative is preferred.

Consideration of the deviations of Figure 5 leads to a rough estimate of the internal temperature, but the margin of uncertainty is large. The data are easily consistent with temperatures of the order of several thousand degrees in layer *D*; a temperature of 10^4 degrees at the base of the mantle seems improbably high.

Some of the recent proposals concerning the core have been considered. Ramsey's theory of a metallic phase of a magnesian silicate is rejected, as is Bullen's suggestion of an appreciable concentration of heavy elements in the inner core. New support has been found for the classical idea of a predominantly iron core, although alloying with lighter elements, conceivably including metallic hydrogen, may be required for layer *E*. The properties of the inner core are consistent with the predicted properties of crystalline iron, and there seems to be no reason to imagine a central density greater than about 15. A system composed of a crystalline iron core, surrounded by a layer of liquid iron, and then by the mantle, would constitute a virtual thermostat, the addition or loss of heat serving only to displace the solid-liquid interface, whose temperature would be controlled by the melting curve. This possibility has implications for the "hydromagnetic" theories of the Earth's magnetism.

Attention has been directed to several regions for which improvement of the seismic velocities is required for further progress; these are layer *B*, and especially the transition zone from *B* to *C*, and the transition zone from layer *E* to the inner core. It is essential that the best seismological solutions be sought without reference to their physical significance; at the same time, each solution has its own meaning, in terms of materials and temperatures, and conceivably non-seismological arguments may be needed to discriminate where seismology reaches an impasse. It seems premature to revise Bullen's density distributions before clarification of the seismic uncertainties.

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