AN EQUATION OF STATE FOR THE CORE OF THE EARTH

by

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Summary

Recent shock wave measurements upon the compressibility of iron and eight other metals, at pressures up to five megabars, permit an investigation of the equation of state of the Earth's core. The density of iron at $T = 0$ at 1·4 megabars (core–mantle boundary pressure) is 11·8. The density at the core boundary is estimated to be between 9·1 and 10·1, depending upon the particular Earth model. The temperature correction is small. The discrepancy can only be resolved by stating that the core is not pure iron, but rather that it contains significant amounts of alloying elements of lower atomic number than iron. The seismic velocity in pure iron at core pressures is also significantly different from the velocity in the core and also indicates the existence of lighter components within the core. A material of mean atomic number 23 in the core is consistent with the shock wave velocity and density measurements and with seismic observations.

1. Introduction

The discovery of the core of the Earth by Oldham in 1906 has since provoked much speculation as to the physical and chemical properties of the core. The difficulty of determining, with any degree of definiteness, the physical and chemical nature of the Earth's core is connected with the difficulty of compressing surface materials to the pressures of the Earth's core. The pressures and densities in the Earth's core are reasonably well known (Bullen 1953). Bullard (1957) investigated permissible density distributions within the Earth and concluded that the assigned density of the core at the core–mantle boundary (9·7 g/cm³) should not be in error by more than 0·5 g/cm³. If ordinary materials, taken from the surface of the Earth, could be compressed to core pressures and elevated to core temperatures, then the densities could be compared and a selection made from among the likely candidates for the composition of the core. Until recently, the highest pressures obtained in the laboratory for jacketed specimens have been approximately 100000 atmospheres (Bridgman 1946); these pressures correspond to a depth of only 250 km in the Earth.

It was suggested by Jensen (1938) that the Thomas–Fermi model for the degenerate state of atoms at extremely high pressures might provide an indication as to the state to which ordinary Earth materials would be compressed at these extreme pressures. Jensen suggested the possibility that laboratory compressibilities of Earth materials could be extended to the Thomas–Fermi equations of state as

asymptotes. At that time, little high pressure data on compressibility of Earth materials was available. Elsasser (1951) took much of the data of Bridgman and extrapolated it to the Thomas–Fermi model and was able to assign an atomic number for the core of the Earth; the atomic number he obtained was 29. This number should be compared with 26 for iron and 28 for nickel. Ever since a suggestion by Wiechert, it has been more or less accepted that the Earth's core is principally iron–nickel.

Bullen (1952) criticized Elsasser's extrapolation of the high pressure results to low pressures and showed that an Earth model based on Elsasser's calculations becomes internally inconsistent. Bullen concluded that the atomic number to be associated with the material of the outer portion of the Earth's core should be of the order of about 23, a figure somewhat less than the atomic number for iron.

The extreme gap in pressure between the laboratory data of Bridgman and the region of validity of the high pressure equation of state of the Thomas–Fermi model makes the interpolation between these two regions extremely uncertain. Knopoff & Uffen (1954) suggested that the interpolation can be substantially improved by extending the high pressure data by the use of the Birch–Murnaghan semi-empirical theory of finite strain. This procedure gave an improved interpolation between the experimental data and the high pressure theoretical models. The results obtained showed again that the atomic number associated with the core was less than that of iron, and in substantial agreement with the value of 23 obtained by Bullen.

MacDonald & Knopoff (1958) compared the abundances of the elements in the solar system, meteorites and solar spectra. They showed that a significant amount of silicon could not be accounted for on the assumption of the preservation of the iron plus magnesium to silicon ratio within the solar system. If this excess silicon is assumed to be present in the core of the Earth, then again the atomic number of such an iron–silicon mixture in the core will be of the order of 23, a number in substantial agreement with the previous estimates.

Other models have been suggested for the composition of the core. The most notable of these include the model of Ramsey (1948, 1949, 1950) who suggested that the seismic discontinuity at the core represents a phase transition from a solid phase of olivine to a metallic liquid phase of the same material. A second and alternate hypothesis which challenges the assumption of an iron core was presented by Kuhn & Rittman (1941) who proposed a core made up of undifferentiated solar matter rich in hydrogen. However, it was shown by Wigner & Huntington (1935) and Kronig, de Boer & Korringa (1946) that significant amounts of hydrogen at the core pressures would yield a material whose density was not sufficiently great compared with that obtained in the core of the Earth. Birch (1952) reviewed the latter two hypotheses and concluded that the core is indeed mainly iron–nickel, although he noted that the density of the core is perhaps 10 to 20 per cent less than that of iron or iron–nickel at core conditions.

2. High pressure experiments

All speculations as to the composition of the core must inevitably be compared with high pressure experiments. The results of compressibility measurements will ultimately determine which of the available constituent materials for the Earth's core can be compressed to the density appropriate to the core.

Recently, measurements have been made of the compressibility of iron and several other metals to pressures of the order of 4 million atmospheres (Altshuler & others, 1958a,b). These measurements of compressibility, to pressures of an order of magnitude higher than any hitherto reported, provide the comparison sought for. The measurements have been made using the technique of shock waves obtained from the detonation of high explosives in the vicinity of a sample. A summary of the development of the method, the methods of interpretation of the data, and results of measurements to pressures of the order of 400 kb* is given by Rice, McQueen & Walsh (1958).

In order properly to interpret the data, the equation of state as determined from the shock wave data must be reduced to a reference temperature. The temperatures in the shock front are not generally known and some auxiliary measurements must be made. The equation of state in the shock front is the Hugoniot, a condition which interrelates the conservation of momentum and energy in the shock front; this is neither an adiabatic nor an isothermal condition. The pressure–density data obtained in the shock wave experiments can be reduced to those at absolute zero if Grüneisen's ratio γ is known. Grüneisen's ratio is

$$\gamma = \frac{\alpha}{c_v \beta \rho} \tag{1}$$

where c_v is the specific heat at constant volume, ρ is the density, α is the coefficient of thermal expansion and β is the compressibility. If $P_h(\rho/\rho_0)$ is the Hugoniot pressure at density ρ, then the pressure at absolute zero P_c can be written as

$$P_c = -\tfrac{1}{2}\gamma^2(\rho/\rho_0)^{\gamma+1} \int_1^{\rho/\rho_0} P_h(x)(x-h)x^{-\gamma-2}dx - \tfrac{1}{2}\gamma\left(\frac{\rho}{\rho_0} - h\right)P_h(\rho/\rho_0) \tag{2}$$

where $h = (2/\gamma) + 1$ and Grüneisen's ratio is taken to be constant over the pressure range of interest (Altshuler & others). ρ_0 is the density at zero pressure. The reduction of the data therefore depends upon a measurement of Grüneisen's ratio. Altshuler & others, by a rather ingenious experiment, have directly measured Grüneisen's ratio at approximately 1 million atmospheres. Grüneisen's ratio for iron at this pressure is about 1·6. The measurement, involving the compressibility of metallic iron in a dense state and metallic iron in a "porous" state, has not been carried out for the other materials subjected to the high shock experiments. Therefore, for the materials, copper, zinc, silver, cadmium, tin, gold, lead and bismuth, also compressed by shock waves in the Hugoniot pressure range of 400 kb to 4 Mb an estimate of Grüneisen's ratio has to be made.

The equation of state for iron reduced to absolute zero (Figure 1) shows that the experimental data yield a density somewhat in excess of the density of the core at the core–mantle boundary pressure. Corrections have to be made to the experimental data to account for (1) the thermal expansion of iron to the temperatures of the core, and (2) the volume change upon melting. It will be shown that these two corrections are insufficient to account for the discrepancy between the experimental determination of the density of iron at the core pressure and the density of the Earth at this same pressure.
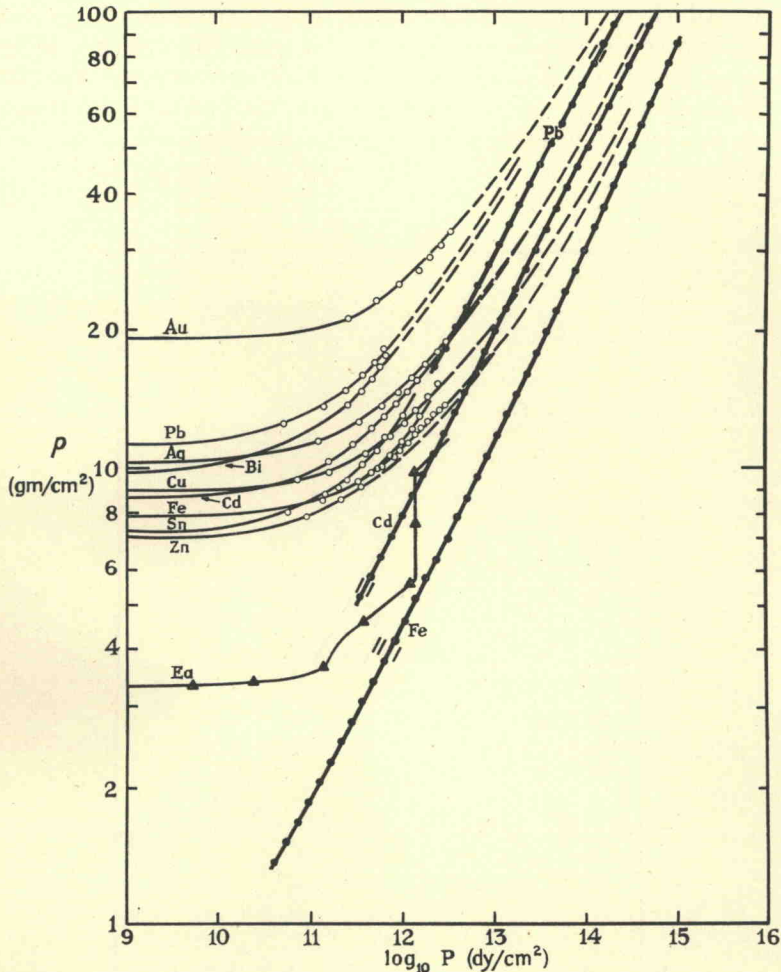
* 1 b (bar) = 10^6 dyn/cm^2.

FIG. 1.—Experimentally determined equation of state of nine elements (open circles) reduced to absolute zero, compared with the Thomas–Fermi equation of state at absolute zero (closed circles) and the equation of state for the Earth on Bullen's model (triangles). Extrapolation of the experimental data (dashes) is obtained by integration of the velocity equation of state.

3. Grüneisen's ratio at high pressure

The reduction of the Hugoniot equation of state to an equation of state at absolute zero depends very critically upon the value of the Grüneisen ratio γ. The Grüneisen ratio must be evaluated in the pressure range of interest, and therefore may have little relationship to its value at low pressures. The correction to the experimental data is given in Equation 2. The derivation of Equation 2 is made under the assumption that γ is a constant over the pressure range of interest. Unfortunately, γ is not a constant over the entire pressure range, but is itself a function of the state of the material (Rice, McQueen & Walsh 1957).

Grüneisen's ratio at pressures of the order of megabars has been measured experimentally by Altshuler & others. No evaluation of this parameter has been made for the other eight materials. In order to determine the value of γ for the

materials for which no experimental measurements exist, we use the technique already used in preceding studies of equations of state. We calculate the value of this parameter for extremely high pressures by determining its value from the Thomas–Fermi equation of state. We then attempt to correct these values in the intermediate pressure range using some experimental data; in this case the experimental determination of γ for iron is used to correct the value of γ for the remaining materials.
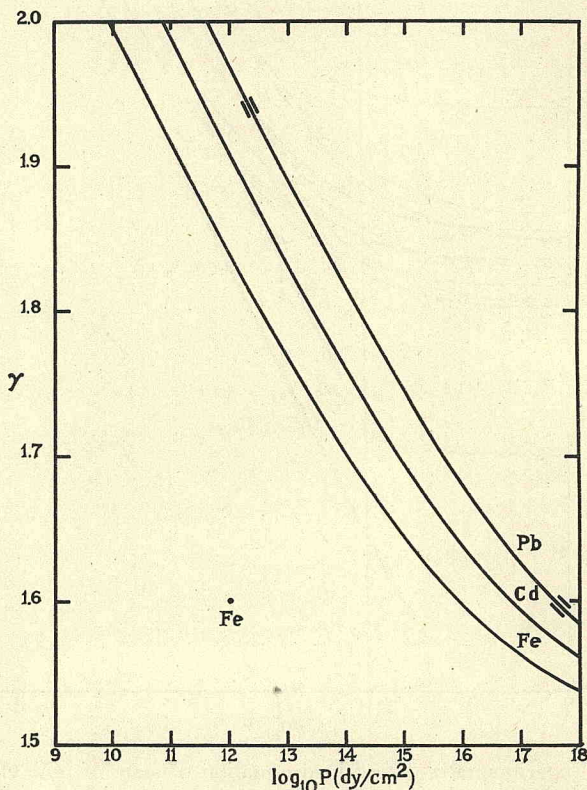

FIG. 2.—The variation of Grüneisen's ratio as a function of pressure for the Thomas–Fermi model of lead, cadmium, and iron. The experimental determination by Altshuler & others is shown as a point.

Although Equation 2 was derived under the assumption that γ is a constant, the corrections to the data at low pressures, pressures of the order of 400 kb or less, are not significant and it will suffice to determine a single value for Grüneisen's ratio in the pressure range of the order of 2 or 3 Mb. This should be accurate enough to cover the entire range of the experimental data of Altshuler & others, taken over the pressure range from zero to 4 Mb.

In order to determine the quantum-mechanical values of γ, we need not only the pressure–density equation of state at absolute zero, but also the way in which the state functions vary with temperature. This is necessary in order to be able to evaluate c_v and α. Expansions of the state functions, valid for low temperatures, have been given by Gilvarry (1954).

The quantum-mechanical calculation for γ yields numbers, in the pressure range where the quantum-mechanical model becomes significant, of the order of the values of γ determined experimentally at low pressures (Figure 2).

It is now not a difficult matter to construct the correction to the quantum-mechanical values for γ as a function of pressure, as in Figure 2. From these values we can now select values of γ appropriate to the pressure range of the order of megabars and apply the corrections to the Hugoniot equations of state by the method of Equation 2.

The experimental data of Altshuler & others, have been taken for nine materials ranging in atomic number from that of iron (26) to bismuth (83). The metals experimentally measured fall into three groups of atomic numbers: iron (26), copper (29), zinc (30); silver (47), cadmium (48), tin (50); gold (79), lead (82), bismuth (83). The Thomas–Fermi data on all the figures have been plotted only for representative members of each of the three groups; the curves for the remaining elements are sufficiently close to those for which the appropriate curves have been drawn.

4. The velocity equation of state

The experimental data of the Hugoniot equation of state for the nine materials have been corrected using Equation 2 and a value of γ as determined in the preceding section. The values of γ used all fall in the range 1·3 to 1·6. The experimental equations of state at absolute zero have been drawn as the lines with open circles in Figure 1, along with their quantum-mechanical counterparts, valid at extremely high pressures.

It is now possible to interpolate between the experimental data for the nine materials and their quantum-mechanical asymptotes. In order to do this, we construct a velocity equation of state relating velocity in the fluid state of the metal to the pressure. For pressures less than 2 or 3 Mb numerical differentiation has been applied to the corrected experimental data. At extremely high pressures numerical differentiation has been applied to the Thomas–Fermi equation of state. These curves have been drawn in Figure 3. It is now seen that the velocity equation of state determined from the experimental data approaches the quantum-mechanical velocity equations of state at pressures much lower than those at which the corresponding density equations of state approach their quantum-mechanical asymptotes. It would appear that the experimental velocity equation of state approaches the quantum-mechanical equation of state at pressures less than 1 Mb. Thus the quantum-mechanical velocity equation of state can be used at pressures in excess of about 1 Mb. Using the experimentally determined density equation of state, numerical integration can now take place using the quantum-mechanical velocities at the appropriate pressures and the extension of the experimental curves can be made. This has also been done in Figure 1; the dashed curves represent the numerical integration of the experimentally determined density equations of state for the nine materials where the numerical integration has taken place using the quantum-mechanical values of the velocities for each of these materials.

The velocity distribution in the Earth can also be compared with the experimental determinations of the velocities in the nine metals since the pressure range is similar. In Figure 3, the velocity in the Earth has been compared with the velocities at absolute zero for the nine metals. An expansion of the region of interest, pertinent to the core of the Earth, has been made in Figure 4. The velocity distribution in the core of the Earth seems to be in excess of the experimental values of the velocity in iron at absolute zero and is roughly identical to the Thomas–Fermi
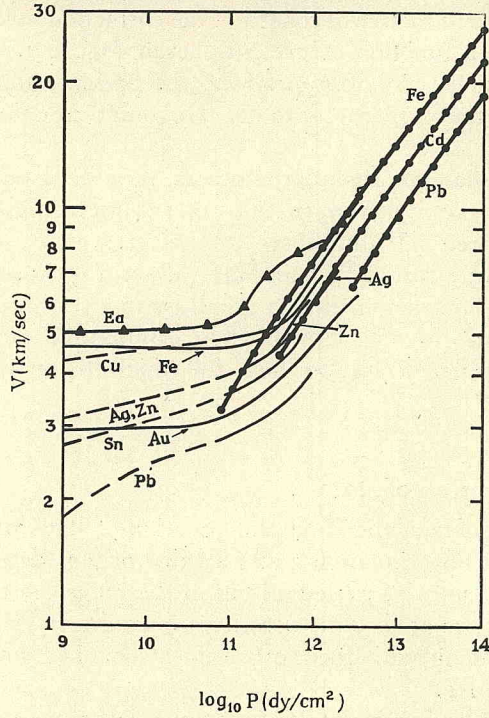
FIG. 3.—The variation with pressure of the velocity of sound in the fluid state. Velocities derived from the Thomas–Fermi model (closed circles) are compared with those obtained from the reduced data of shock wave measurements (solid curves). The seismic velocity distribution given by Bullen (triangles) is also shown for comparison. The dotted curves represent the extrapolation to the zero pressure value of $V = (\alpha^2 - \frac{4}{3}\beta^2)^{\frac{1}{2}}$.
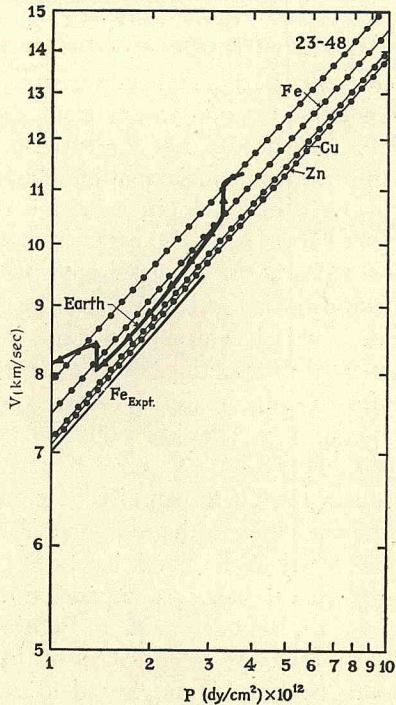

FIG. 4.—Velocity of sound in the fluid state at core pressures.

values of the velocity in iron. The velocity of seismic waves in the core of the Earth is about 0·4 km/s higher than the experimental values for metallic iron. Quantum-mechanical velocity equations of state have also been drawn for materials of atomic number 23 and for copper and zinc. The difference in velocity between a material of atomic number 23 and iron, and in turn between iron and copper, is again about 0·4 km/s. If there are no corrections for temperature, it is highly likely that the velocity in the core of the Earth is more appropriate to the material having atomic number 23 than to iron.

5. Density equation of state of the core of the earth

From the experimental velocity data it seems highly likely that the Earth's core has a density less than that of iron. A similar conclusion can be drawn from
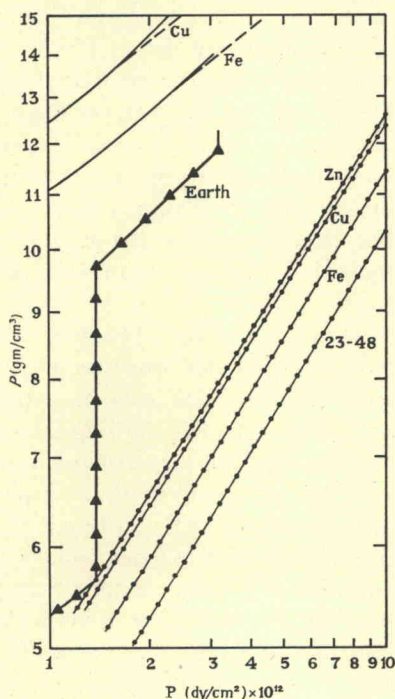

FIG. 5.—Equation of state for iron, copper, zinc and a hypothetical material of atomic number 23, atomic weight 48 in the core pressure range. The values derived from shock wave measurements (solid) are compared with those obtained from the Thomas–Fermi theory (closed circles). Bullen's density distribution is shown for comparison (triangles).

the density equation of state. The absolute zero experimental equations of state of the nine metals and the quantum-mechanical equations of state can be compared with the density equation of state for the Earth. This has been done in Figure 1. The portions of the curves in the pressure range appropriate to the core of the Earth have been extracted and the data replotted in Figure 5. The experimental data for iron and copper at the top of the graph show densities somewhat in excess of those for the Earth. If no corrections were applied, the density of iron would be of the order of about 1·8 g/cm³ larger than that for the Earth's core. The quantum-mechanical equations of state for zinc, copper, iron and a material of atomic number 23 (atomic weight 48) have been plotted and are found in the lower portion of

Figure 5. If no corrections were to be applied, again it would seem highly likely that the core of the Earth has an atomic number less than that of iron.

Strong (1959) has measured the change in the melting point of iron to a pressure of 96 000 atmospheres. Extrapolating his data and using Simon's equation, he obtains a minimum core temperature of 2340 °C. The derived value of Grüneisen's ratio is 0·4, in disagreement with the experimental result of Altshuler & others for core pressures. Strong's data are not inconsistent with a value of $\gamma = 1·6$, if Simon's equation for the melting curve is used. An extrapolation of Strong's melting point curve using $\gamma = 1·6$ leads to a melting point of iron at 1·4 Mb of 4 000 °C. If the core were pure iron, the temperature of the core would be in excess of 4 000 °C. The presence of alloying elements tends to reduce the melting point.

The density of solid iron at 0 °K derived from shock wave data must be corrected for thermal expansion and the volume change on melting before a meaningful comparison can be made with geophysical data. The thermal expansion of iron over the temperature range 20°–900 °C is $1·5 \times 10^{-5}$/deg C. Birch (1952) estimates, on the basis of the classical theory of specific heat, the change in thermal expansion with compression. Applying his results to the thermal expansion of iron, we expect a reduction of about one half in the zero pressure value of α for an increase in pressure of a megabar. Adopting an average value of 1×10^{-5}/deg C for the thermal expansion of iron, we see that a temperature on the order of a few thousand degrees Celsius would result in a decrease in the room temperature density of iron of only a few per cent.

The change of volume on melting of iron at a pressure of one bar is $3 \pm 0·5$ per cent (Gilvarry 1957) though the quoted uncertainty may be much too small. The volume change at core conditions also may be estimated from the Simon equation provided some assumption is made regarding the entropy of fusion. Since the latter quantity is most uncertain, it appears that the best guess is that a change in volume on melting of iron of 2 to 3 per cent might be expected at core conditions.

The combined effects of thermal expansion and melting on the volume of iron are such as to reduce the density by about 5 to 6 per cent. The discrepancy between solid iron at 0 °K and the density of the core is about 20 per cent. Though the corrections for thermal expansion and melting may be in error by a factor of two, it appears unlikely that these corrections are large enough to reduce the apparent discrepancy in the densities of the core and of pure iron. Furthermore, any nickel alloyed with iron would increase the discrepancy since the density of pure nickel is 8·6 g/cm³ at room conditions, and the density of nickel is greater than that of iron at extremely high pressures.

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