Approximate Compressibility of Elements and Compounds*

L. Knopoff
Department of Physics and Institute of Geophysics, University of California, Los Angeles, California

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The zero-pressure incompressibilities and volumes per atom for metals and solid nonmetals are found to fit the relation

$$(K_0Z^{-10/3})(Zv_0)^{7/3}=(\pi^{10/3}6^{2/3}/15)a_0{}^3e^2$$

to good accuracy. The relation is derived by an empirical attempt to interpolate between the finite-strain equation of state and the Thomas-Fermi equation of state. The strain energy is quadratic in the finite strain for the heavier alkali metals but higher order terms are important for the silicates, at least to twofold compression.

The finite-strain function ϵ is defined[1] in terms of the density ρ as

$$\epsilon=\tfrac{1}{2}\{(\rho/\rho_0)^{2/3}-1\}. \tag{1}$$

If $\rho/\rho_0=1+\delta$, then in the limit as ρ approaches the zero-pressure density ρ_0, the function ϵ approaches $\delta/3$, the linear elastic strain. It has been shown[2] that the Bardeen[3] isothermal equation of state can be written as a power series in ϵ:

$$\begin{aligned}P&=3K_0[(\rho/\rho_0)^{5/3}-(\rho/\rho_0)^{4/3}]\\&=3K_0(\rho/\rho_0)^{5/3}\sum_{n=1}^{\infty}(-1)^{n+1}\\&\qquad\times(1\times3\times5\cdots(2n-1)/n!)\epsilon^n.\end{aligned} \tag{2}$$

The leading item of the series expansion is the Birch[4] isothermal equation of state

$$P=\tfrac{3}{2}K_0[(\rho/\rho_0)^{7/3}-(\rho/\rho_0)^{5/3}]. \tag{3}$$

The proof of (2) comes by deriving the pressure from a strain-energy function

$$E=a[\epsilon-(1+2\epsilon)^{1/2}], \tag{4}$$

where a is a constant proportional to the zero-pressure incompressibility K_0 and

$$K=\rho(\partial P/\partial\rho)|_T. \tag{5}$$

In a generalization, it can be shown that isothermal equations of state of the form $P=f(\rho/\rho_0)$ can be written as a power series in ϵ with (3) as the leading term, by substituting for ρ/ρ_0 from (1).

In the earth $\epsilon<0.3$, and at the upper value of ϵ, the pressure computed by (3) is 43% greater than that computed by (2). At the bottom of the mantle $\epsilon\sim0.13$; the pressure from (3) is about 19% greater than that from (2). More pertinent is the value of dK/dP. From (2)

$$\frac{dK}{dP}=\frac{25(1+2\epsilon)^{1/2}-16}{15(1+2\epsilon)^{1/2}-12}, \tag{6}$$

while from (3)

$$\frac{dK}{dP}=\frac{1}{3}\times\frac{12+49\epsilon}{1+7\epsilon}. \tag{7}$$

At zero pressure, these quantities are 3 and 4, respectively. At the maximum pressure in the mantle, these two values are 2.50 and 3.21, respectively; at the center of the earth, they are 2.24 and 2.88. Recent evidence[5] shows that the value of dK/dP differs somewhat from that derived from the Bullen[4] model of density. Thus the higher order terms in an expansion of the energy in a power series may be important for the determination of the state and constitution of the mantle and core. Birch has shown that these terms are vanishingly small for the alkali metals for ϵ up to 0.3 and has made the assumption that this holds for the silicates for ϵ up to 0.13.

In this paper, an independent determination of the isothermal pressure-density equation of state is sought in which an interpolation is made between low-pressure finite-strain theory, as described by (3) as a leading term, and the Thomas-Fermi model as a high-pressure limit. This procedure was suggested by Elsasser[6] although he suggested that experimental data rather than (3) be used as starting values for the interpolation.

If the strain-energy function E is constrained to be a quadratic function of the finite strain, then the interpolation can proceed by a generalization of the definition of the finite strain.[2] Since the finite-strain function (1) is defined in terms of a series of geometrical operations, the generalization can be used to parametrize the system as long as the generalization is reducible to (1) in the small-finite-strain limit. An alternative approach is to retain (1) as the definition of finite strain and to allow the strain-energy function to be appropriately chosen so that the interpolation can take place and so that it is

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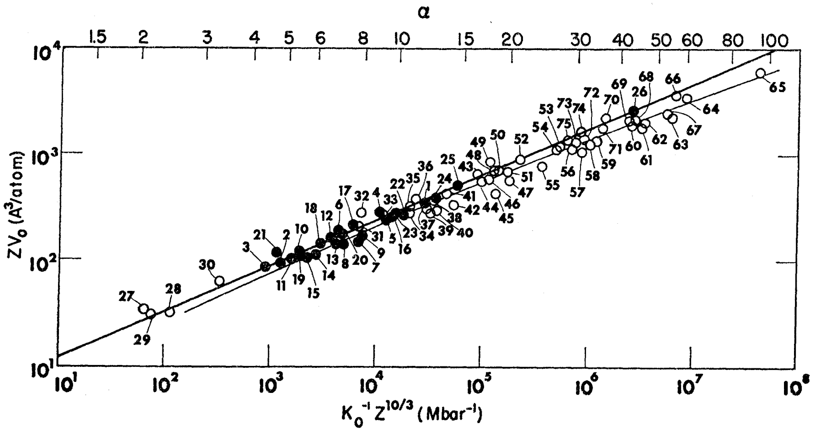

FIG. 1. Graphs of relations (14) (upper curve) and (15) (lower curve). Also shown are the tabulated values of scaled bulk modulus and density at zero pressure for metallic elements (open circles) and ionic compounds (closed circles). The identification numbers are listed in Table I.

quadratic for small ϵ. The latter procedure is simpler and is adopted here. Both procedures are equivalent.

Let the strain-energy function be

$$E=g(\epsilon). \tag{8}$$

Then the pressure-density equation of state at constant temperature

$$P=-(\partial E/\partial v)|_T$$

becomes

$$P=3K_0(g'(\epsilon)/g''(0))(\rho/\rho_0)^{5/3};\quad g'(0)=0, \tag{9}$$

after an application of (5) to determine K_0. Since $g''(0)\neq 0$ and $g'(0)=0$, then $g(\epsilon)$ is quadratic for small ϵ.

The asymptotic solution to the Thomas-Fermi (TF) equation is[7]

$$PZ^{-10/3}=\frac{(3\pi^2)^{2/3}}{5}a_0e^2(Zv)^{-5/3}\left\{1-\frac{(4Zv)^{1/3}}{2\pi a_0}+\cdots\right\}, \tag{10}$$

where v is the volume per atom and a_0 and e are the usual Bohr radius and electronic charge. Z is the atomic number; for compounds Z is computed in this limit by the expression[8]

$$Z^{2/3}=\sum n_iZ_i^{5/3}/\sum n_iZ_i, \tag{11}$$

where n_i is the number of times the element with atomic number Z_i appears in the chemical formula.

Comparing (9) and (10), we see that

$$g'(\infty)=\alpha,$$

where α is a constant determined by the parameters above. This condition, plus $g'(0)=0$ are the only conditions upon $g'(\epsilon)$. Clearly a unique choice of $g'(\epsilon)$ is impossible. If we require that $g'(\epsilon)$ be governed by the first two terms of (10), then one function that can be selected is

$$\begin{aligned} g'(\epsilon)&=\alpha\{1-(1+2\epsilon/\alpha)^{-1/2}\},\\ P&=3K_0\alpha\{1-(1+2\epsilon/\alpha)^{-1/2}\}(\rho/\rho_0)^{5/3}. \end{aligned} \tag{12}$$

The term-by-term comparison of (10) and (12), to two orders at high pressures, gives

$$P=\frac{(3\pi^2)^{2/3}a_0e^2Z^{5/3}}{5v_0^{5/3}}(\rho/\rho_0)^{5/3}\times\left[1-\left(1+\frac{30\epsilon K_0v_0^{5/3}}{(3\pi^2)^{2/3}a_0e^2Z^{5/3}}\right)^{-1/2}\right] \tag{13}$$

with the auxiliary condition

$$\begin{aligned}(K_0Z^{-10/3})(Zv_0)^{7/3}&=(\pi^{10/3}6^{2/3}/15)a_0^3e^2\\ &=3.417\times10^{-43}\text{ cgs units}\\ &=34.17\text{ megabars Å}^7. \end{aligned} \tag{14}$$

If the interpolation formula (12) is accurate, then (14) is a universal relation between the zero-pressure compressibility and volume. McMillan[9] has pointed out that

$$-5(K_0Z^{-10/3})(Zv_0)^{-1}=\left.\frac{d(P_{\text{TF}}Z^{-10/3})}{d(Zv)}\right|_{v=v_0} \tag{15}$$

may also be a reasonable relation of this type. In Fig. 1 (Table I), formulas (14) and (15) are compared. The laboratory data for $K_0Z^{-10/3}$ for metals and compounds are also shown. Z for compounds is computed from (11). The relation (14) is considerably simpler to apply than (15) and fits the observations with comparable fidelity.

An interpolation formula of the type

$$g'(\epsilon)=b_1\{1-(1+(2N\epsilon/b_1)+\sum_{j=2}^{N}b_j\epsilon^j)^{-1/2N}\}$$

could also have been used. The parametrization would then allow the fit to the asymptotic TF formula (10) to be made to any degree of exactness desired; relation (14) could not then have been obtained. Thus (14)

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TABLE I. Identification of entries in Fig. 1.

Number	Name	Formula	Z	Number	Name	Formula	Z
1	Salt	$NaCl$	14.4	39	Cobalt	Co	27
2	Periclase	MgO	10.3	40	Manganese	Mn	25
3	Corundum	Al_2O_3	10.4	41	Sodium	Na	11
4	Magnetite	$FeOFe_2O_3$	20.1	42	Copper	Cu	29
5	Hematite	Fe_2O_3	19.6	43	Molybdenum	Mo	42
6	Rutile	TiO_2	15.5	44	Ruthenium	Ru	44
7	Quartz	SiO_2	10.7	45	Zinc	Zn	30
8	Albite	$Na_2OAl_2O_3 6(SiO_2)$	10.6	46	Rhodium	Rh	45
9	Orthoclase	$K_2OAl_2O_3 6(SiO_2)$	11.6	47	Gallium	Ga	31
10	Jadeite	$Na_2OAl_2O_3 4(SiO_2)$	10.5	48	Columbium	Cb	41
11	Spodumene	$Li_2OAl_2O_3 4(SiO_2)$	10.2	49	Calcium	Ca	20
12	Anorthite	$CaOAl_2O_3 2(SiO_2)$	11.7	50	Germanium	Ge	32
13	Diopside	$CaOMgO2(SiO_2)$	12.0	51	Palladium	Pd	46
14	Enstatite	$MgOSiO_2$	10.5	52	Zirconium	Zr	40
15	Forsterite	$2(MgO)SiO_2$	10.5	53	Tungsten	W	74
16	Fayalite	$2(FeO)SiO_2$	17.7	54	Iridium	Ir	77
17	Andradite	$3(CaO)Fe_2O_3 3(SiO_2)$	15.1	55	Silver	Ag	47
18	Grossularite	$3(CaO)Al_2O_3 3(SiO_2)$	12.6	56	Platinum	Pt	78
19	Pyrope	$3(MgO)Al_2O_3 3(SiO_2)$	11.7	57	Cadmium	Cd	48
20	Almandite	$3(FeO)Al_2O_3 3(SiO_2)$	14.8	58	Indium	In	49
21	Beryl	$3(BeO)Al_2O_3 6(SiO_2)$	10.0	59	Gold	Au	79
22	Marcasite	FeS_2	20.3	60	Praseodymium	Pr	59
23	Pyrite	FeS_2	20.3	61	Uranium	U	92
24	Oldhamite	CaS	18.2	62	Cerium	Ce	58
25	Sphalerite	ZnS	24.8	63	Thallium	Tl	81
26	Galena	PbS	69.0	64	Rubidium	Rb	37
27	Diamond	C	6	65	Cesium	Cs	55
28	Boron	B	5	66	Barium	Ba	56
29	Beryllium	Be	4	67	Lead	Pb	82
30	Lithium	Li	3	68	Neodymium	Nd	60
31	Aluminum	Al	13	69	Lanthanum	La	57
32	Silicon	Si	14	70	Strontium	Sr	38
33	Magnesium	Mg	12	71	Hafnium	Hf	72
34	Chromium	Cr	24	72	White Tin	Sn	50
35	Vanadium	V	23	73	Tantalum	Ta	73
36	Titanium	Ti	22	74	Gray Tin	Sn	50
37	Iron	Fe	26	75	Potassium	K	19
38	Nickel	Ni	28				

appears to be a reasonable interpolation using a small number of parameters.

It is now possible to determine the importance of higher order terms at low pressures. From (12)

$$P=3K_0(\rho/\rho_0)^{5/3}\epsilon[1-\tfrac{3}{2}(\epsilon/\alpha)+\cdots].$$

The quantity α is

$$\alpha^{7/2}=\frac{1}{15}\left(\frac{9}{32\pi^{11}}\right)^{1/3}\frac{e^2}{a_0{}^4K_0Z^{-10/3}}$$

$$=0.1932(K_0Z^{-10/3})^{-1}\text{ megabars}^{-1}\qquad(16)$$

if (14) holds exactly. From Fig. 1 it is seen that the silicates, the likely constituents of the earth's mantle, have values of α derived from (16) of the order of $5\frac{1}{2}$ while for the alkali metals, it is of the order of 27 for Na and 80 for Rb. Evidently the Birch equation (3) will hold for the elements with the greater scaled compressibility $(K_0Z^{-10/3})^{-1}$ but the higher order corrections become important for lower scaled compressibilities. To values of $\epsilon=0.13$, the error in neglecting terms of order higher than the first in (15) is negligible, even taking into account the lower value of ϵ for silicates.

As indicated above, dK/dP is a more crucial diagnostic term than the relation for pressure itself. Birch[4] inferred that, because (3) fitted the experimental data to $\epsilon=0.3$ for the alkali metals, (3) also was applicable to the silicates. But the success of the inference for the alkali metals depends crucially upon the data for Rb, K, and Cs and less so for Na. To 100 kbar, the data are not discriminatory for Li. However, dK/dP may be more intimately dependent upon this precise vanishing of higher order terms than is P itself. From (12) we obtain the formula

$$\frac{dK}{dP}=\frac{25R([1+2\epsilon/\alpha]^{1/2}-1)+12-3R^{-1}}{3+15R([1+2\epsilon/\alpha]^{1/2}-1)},\quad R=\frac{\alpha+2\epsilon}{1+2\epsilon}.$$

In the range of ϵ and α of interest, a useful approximation is

$$dK/dP=(dK/dP)_B-1/\alpha,$$

where $(dK/dP)_B$ is the value derived [Eq. (7)] by Birch. Thus, for the silicates, the corrections in the mantle are of the order of 0.2 while for the alkali metals, they are negligible. Thus the interpolation (12) tends very closely to the one-term equation (3) for pressure and is intermediate to Eqs. (6) and (7) for dK/dP.