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Finite Elastic Strain of Cubic Crystals*

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Murnaghan's theory of finite strain is developed for a medium of cubic symmetry subjected to finite hydrostatic compression, plus an arbitrary homogeneous infinitesimal strain. The free energy is developed for cubic symmetry to include terms of the third order in the strain components. The effect of pressure upon the second-order elastic constants is found and compared with experiment, with particular reference to the compressibility; the pressure-volume relation in several approximations is compared with the measurements to 100,000 kg/cm^2. The simplest approximation is shown to give a satisfactory account of most of the experimental data. The results are also compared with some of the calculations based on Born's lattice theory.

1. INTRODUCTION

MURNAGHAN[1] has published an exact treatment of finite deformation of elastic solids, with application to several questions involving isotropic media. The theory is not restricted to the case of isotropy, and it will be developed below for the case of cubic symmetry.

Finite *elastic* strain is in practice limited to finite hydrostatic strain plus superimposed infinitesimal strain of an arbitrary type. Excluding such special materials as rubber, non-hydrostatic strains large enough to require treatment as "finite" are generally beyond the elastic limit. On the other hand, hydrostatic strain of whatever magnitude is "elastic" and may be accompanied by elastic infinitesimal strain of any kind. The hydrostatic strain affects the response of the medium to the infinitesimal additional strain, giving rise to an effect of pressure upon the elastic constants. Such a strain is of fundamental interest in many problems concerning the interior of the earth, to a few of which the theory has been applied.[2] A large body of experimental data, almost entirely the work of Bridgman, may be used to find the change of compressibility with pressure; there are also a few determinations of the effect of pressure upon the rigidity of quasi-isotropic materials.

Born[3] has treated this kind of deformation from the point of view of lattice theory, and has carried out with several collaborators detailed computations for various monatomic cubic lattices. The results are of great interest, showing plausible pressure and temperature coefficients for the elastic constants. Born appears to have accepted as general the theorem of the classical theory of elasticity, which holds that the stress components are the partial derivatives of the free energy density with respect to the corresponding strain components. Murnaghan has shown that this is valid only for infinitesimal strain, and in consequence, some of the calculations according to Born's method are subject to a correction which increases with the amount of compression.

Another paper on this general topic has been published by Fürth,[4] who combines certain results of Born and Misra[5] concerning the third-order terms of the elastic potential with an incorrect application of Murnaghan's stress-strain relation. Except in the special case of hydrostatic pressure, Fürth's calculations are consequently wrong, and with the same exception, they deal with unrealizable examples of finite elastic strain.

In the following sections, the theory is developed for a medium of cubic symmetry subjected to a strain consisting of (1) a hydrostatic compression of any amount, plus (2) a homogeneous infinitesimal strain of general type. The exact stress-strain relations for this case are found and

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[1] F. D. Murnaghan, Am. J. Math. **49**, 235 (1937).

[2] F. Birch, Bull. Seis. Soc. Am. **29**, 463 (1939); K. E. Bullen, *ibid.* **30**, 235 (1940).

[3] Max Born, J. Chem. Phys. **7**, 591 (1939); also a series of papers in Proc. Camb. Phil. Soc.

[4] R. Fürth, Proc. Roy. Soc. **A180**, 285 (1942).

[5] Max Born and R. D. Misra, Proc. Camb. Phil. Soc. **36**, 466 (1940).

decomposed into a hydrostatic pressure plus a general stress related to the infinitesimal strain. A general form for the free energy is given, to the third order in the strain components, and used to find the variation of the elastic constants with pressure. Particular attention is given to the effect of pressure on compressibility and on volume, and to the relevant experimental data. Since there apparently exists some misunderstanding concerning the application of Murnaghan's theory, most of the developments are carried along according to both of the alternative methods which Murnaghan has formulated; this naturally lengthens the treatment, but it is perhaps worth while to show clearly that no ambiguity arises. The particular case of hydrostatic pressure could have been dealt with more directly, and indeed, since cubic crystals are isotropic with respect to such a stress, this case has already been covered in the studies of isotropic media.[1, 6] The general theory is given for the sake of comparison with Born's lattice theory, and with experimental data which should be obtainable.

2. THE STRAIN

Throughout the following, rectangular Cartesian coordinates are employed, the axes taken to coincide with the axes of fourfold symmetry; the same coordinate system is used for the description of the initial and final configurations. The usual notation of Cartesian tensors is used, repetition of an index signifying summation over the values 1, 2, 3 for this index. The coordinates of a point before strain are denoted by (a_1, a_2, a_3), after strain by (x_1, x_2, x_3). These points determine a displacement vector with components (x_1-a_1), (x_2-a_2), (x_3-a_3).

We now consider a special strain composed of two parts: (1) a hydrostatic compression by which every line in the crystal is shortened by the factor $(1-\alpha)$, where α, intrinsically positive, may have any value from 0 to 1; (2) a subsequent homogeneous strain expressed in terms of six coefficients β_{rs}, which will be treated as infinitesimals, whereas all powers of α are retained. By the hydrostatic strain, a point initially at (a_1, a_2, a_3) is brought to the point (x_1^0, x_2^0, x_3^0), given by $x_p^0=(1-\alpha)a_p$, with $p=1, 2, 3$. The additional displacements resulting from the strain β_{rs} will be

$$\begin{aligned} u_1' &= \beta_{11}x_1^0+\beta_{12}x_2^0+\beta_{13}x_3^0, \\ u_2' &= \beta_{21}x_1^0+\beta_{22}x_2^0+\beta_{23}x_3^0, \\ u_3' &= \beta_{31}x_1^0+\beta_{32}x_2^0+\beta_{33}x_3^0, \end{aligned} \qquad (1)$$

with $\beta_{rs}=\beta_{sr}$. The final coordinates are $x_r=x_r^0+u_r'$, or

$$\begin{aligned} x_1 &= (1-\alpha)[(1+\beta_{11})a_1+\beta_{12}a_2+\beta_{13}a_3], \\ x_2 &= (1-\alpha)[\beta_{21}a_1+(1+\beta_{22})a_2+\beta_{23}a_3], \\ x_3 &= (1-\alpha)[\beta_{31}a_1+\beta_{32}a_2+(1+\beta_{33})a_3]. \end{aligned} \qquad (2)$$

From these we find the partial derivatives:

$$\begin{aligned} \partial x_r/\partial a_s &= (1-\alpha)(\delta_{rs}+\beta_{rs}); \\ \partial a_r/\partial x_s &= (\delta_{rs}-\beta_{rs})/(1-\alpha); \\ r, s &= 1, 2, 3. \end{aligned} \qquad (3)$$

Here δ_{rs} is equal to 1 for $r=s$, to 0 for $r\neq s$; squares of β_{rs} have been neglected.

Putting ρ_0 for the initial unstrained density, ρ for the density in the strained state, with V_0 and V for the corresponding specific volumes, we have the mathematical identities,

$$\rho/\rho_0 = V_0/V = \begin{vmatrix} \dfrac{\partial a_1}{\partial x_1} & \dfrac{\partial a_1}{\partial x_2} & \dfrac{\partial a_1}{\partial x_3} \\ \dfrac{\partial a_2}{\partial x_1} & \dfrac{\partial a_2}{\partial x_2} & \dfrac{\partial a_2}{\partial x_3} \\ \dfrac{\partial a_3}{\partial x_1} & \dfrac{\partial a_3}{\partial x_2} & \dfrac{\partial a_3}{\partial x_3} \end{vmatrix}$$

$$= 1 \div \begin{vmatrix} \dfrac{\partial x_1}{\partial a_1} & \dfrac{\partial x_1}{\partial a_2} & \dfrac{\partial x_1}{\partial a_3} \\ \dfrac{\partial x_2}{\partial a_1} & \dfrac{\partial x_2}{\partial a_2} & \dfrac{\partial x_2}{\partial a_3} \\ \dfrac{\partial x_3}{\partial a_1} & \dfrac{\partial x_3}{\partial a_2} & \dfrac{\partial x_3}{\partial a_3} \end{vmatrix}. \qquad (4)$$

Using the relations (3) and neglecting squares and higher powers of the β_{rs}, we obtain

$$V_0/V=(1-\beta_{11}-\beta_{22}-\beta_{33})/(1-\alpha)^3. \qquad (5)$$

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[6] F. Birch, J. App. Phys. 9, 279 (1938).

For all β's equal to zero, we have the exact formula, $V=V_0(1-\alpha)^3$.

Murnaghan has shown how finite strain may be treated rigorously from either of two viewpoints; by analogy with the similar situation in hydrodynamics these are termed the "Lagrangian" and the "Eulerian." In the "Lagrangian" scheme, the strain is described with the initial or unstrained coordinates (a_p) as the independent variables; in the "Eulerian" scheme, the coordinates (x_p) of the strained state are taken as independent. The two alternative sets of strain components are then, using Murnaghan's notation,

the Lagrangian strain components,

$$\eta_{rs}=\tfrac{1}{2}\left(\frac{\partial x_p}{\partial a_r}\frac{\partial x_p}{\partial a_s}-\delta_{rs}\right), \qquad (6)$$

or the Eulerian strain components,

$$\epsilon_{rs}=\tfrac{1}{2}\left(\delta_{rs}-\frac{\partial a_p}{\partial x_r}\frac{\partial a_p}{\partial x_s}\right). \qquad (7)$$

Except for a factor of $\frac{1}{2}$ for $r\neq s$, the η_{rs} are identical with the strain components given by Love for finite strain. They are also equal to $\frac{1}{2}\xi_{rs}$, where ξ_{rs} are the strain components used by Born and Misra and by Fürth. For infinitesimal strains, the η_{rs} and ϵ_{rs} become identical and (except for the factor $\frac{1}{2}$ for $r\neq s$) equal to the strain components of the classical theory.

For the particular strain defined by (2), these become

$$\eta_{rs}=\delta_{rs}\eta+\beta_{rs}(1+2\eta),$$

and

$$\epsilon_{rs}=\delta_{rs}\epsilon+\beta_{rs}(1-2\epsilon), \qquad (8)$$

where η and ϵ are defined by

$$(1-\alpha)^3=(1+2\eta)^{\frac{3}{2}}=(1-2\epsilon)^{-\frac{3}{2}}. \qquad (9)$$

The relations between the quantities α, η and ϵ and the density for hydrostatic compression, are tabulated for convenience in Table 1.

TABLE I. Comparative values of ϵ, α, and η for hydrostatic compression.

ρ/ρ_0	V/V_0	$-\epsilon$	α	$-\eta$
1.0	1.0	0	0	0
1.1	.909	0.0328	0.0313	0.0308
1.2	.833	.0646	.0590	.0572
1.3	.769	.0955	.0837	.0802
1.4	.714	.1257	.1061	.1005
1.5	.667	.1551	.1264	.1185
2.0	.500	.2937	.2063	.1850
3.0	.333	.5400	.3067	.2596
4.0	.250	.7599	.3700	.3016
5.0	.200	.9620	.4152	.3290
∞	0	∞	1.0000	.5000

3. STRESS-STRAIN RELATIONS

Murnaghan's fundamental contribution is the discovery that for finite, elastic, isothermal strain, the exact relation between the stress components T_{rs} and the strain is of the form

$$T_{rs}=\rho\frac{\partial\phi}{\partial\eta_{pq}}\frac{\partial x_r}{\partial a_p}\frac{\partial x_s}{\partial a_q}\equiv-2\rho\frac{\partial\phi}{\partial j_{pq}}\frac{\partial a_p}{\partial x_r}\frac{\partial a_q}{\partial x_s}; \qquad (10)$$

$$r,\ s,\ p,\ q=1,\ 2,\ 3.$$

Here $j_{rs}=(\partial a_r/\partial x_p)(\partial a_s/\partial x_p)$, and tension is taken positive. In developing these expressions, all nine partial derivatives are to be formed; in this procedure we ignore the symmetry relations, $\eta_{pq}=\eta_{qp}$. Furthermore, it is supposed that the rotation has been removed from the strain, so that the matrix $\partial(x)/\partial(a)$ is symmetric.

The function ϕ is the Helmholtz free energy $(=E-TS)$ per unit mass; for a given material, it is assumed to depend only on the strain components η_{rs} and the temperature. The second equality in (10) is the Eulerian form of the first; the two are identically equal. ϕ is equivalent to the function A of Born, who, while using finite strain components equivalent to η_{rs}, has used the "infinitesimal" form of (10) for finding the stress.

In an isotropic medium, ϕ depends upon the strain components by way of the strain invariants (for arbitrary rotation of coordinate axes) of the first, second and third orders and their various products. In this simplest case, the Eulerian form becomes

$$T_{rs}=\rho\left(\frac{\partial\phi}{\partial\epsilon_{rs}}-2\epsilon_{rp}\frac{\partial\phi}{\partial\epsilon_{ps}}\right). \qquad (11)$$

Even in this case the stress matrix does not in general possess the same principal axes as the strain matrix η_{rs}, whereas the principal axes of the matrices T_{rs} and ϵ_{rs} coincide. Fürth's procedure amounts to taking the expression (11) for the isotropic medium, substituting η_{rs} for ϵ_{rs}, and finally applying this result, incorrect even for the isotropic case, to the problem of cubic symmetry. Only for the degenerate case of hydrostatic compression does this give a correct result.

4. THE FREE ENERGY FOR CUBIC SYMMETRY

In a crystalline medium, the form of the free energy ϕ must conform with the symmetry of the crystal; in other words, ϕ must be invariant for rotations of the coordinate axes corresponding to the covering operations. The forms of ϕ appropriate for the various classes of crystals have been developed for terms of the second order in the strain components, and constitute the basis of the classical theory of crystal elasticity. For the present work, it is desirable to extend the development to include terms of the third order in the strain components. The details of this process are given in the Appendix, where it is found that the third-order terms involve 6 new elastic constants for the most symmetrical classes of cubic crystals, 8 for the cubic classes of lower symmetry, and 56 for triclinic symmetry. Most actual cubic crystals belong to the class of highest symmetry and the further developments pertain to this case; the required modification for the other case is slight and easily made.

The free energy, including third-order terms but omitting terms independent of strain, is thus:

$$\begin{aligned}\rho_0\phi = {} & (c_{11}/2)(\eta_{11}^2+\eta_{22}^2+\eta_{33}^2)+c_{12}(\eta_{11}\eta_{22}+\eta_{22}\eta_{33}+\eta_{33}\eta_{11})+c_{44}(\eta_{12}^2+\eta_{21}^2+\eta_{23}^2+\eta_{32}^2+\eta_{13}^2+\eta_{31}^2)\\ & +C_{111}(\eta_{11}^3+\eta_{22}^3+\eta_{33}^3)+C_{112}\{\eta_{11}^2(\eta_{22}+\eta_{33})+\eta_{22}^2(\eta_{11}+\eta_{33})+\eta_{33}^2(\eta_{11}+\eta_{22})\}\\ & +C_{123}\eta_{11}\eta_{22}\eta_{33}+C_{456}(\eta_{12}\eta_{23}\eta_{31}+\eta_{21}\eta_{13}\eta_{32})+(C_{144}/2)\{\eta_{11}(\eta_{23}^2+\eta_{32}^2)+\eta_{22}(\eta_{13}^2+\eta_{31}^2)\\ & +\eta_{33}(\eta_{12}^2+\eta_{21}^2)\}+(C_{166}/2)\{(\eta_{11}+\eta_{22})(\eta_{12}^2+\eta_{21}^2)+(\eta_{22}+\eta_{33})(\eta_{23}^2+\eta_{32}^2)\\ & +(\eta_{33}+\eta_{11})(\eta_{13}^2+\eta_{31}^2)\}. \qquad (12)\end{aligned}$$

For ease in forming the relations (11) the equalities $\eta_{rs}=\eta_{sr}$ have been ignored in (12). Rather than ϕ, the product $\rho_0\phi$ has been expanded so that the second-order coefficients will equal those of Voigt, which are derived from the energy per unit volume. The C's with triple indices are the new "third-order" coefficients. For a given material, the c's and C's are functions only of the temperature. This differs from Born's development of the free energy in which the c's are functions of both pressure and temperature.

This expansion is based on the assumption that there is always a state of zero strain under no external forces for any temperature at which the crystal can exist. Energy dependent upon the temperature alone may be included in an additive term which, being independent of the strain, plays no part in the following treatment of isothermal processes. Thermal expansion does not constitute a strain in the sense of the present theory, and no special significance is attached to absolute zero.

The third-order terms of the free energy have been given by Born and Misra[5] for a cubic Bravais lattice with central forces between particles at absolute zero. In this special case, Cauchy's relation holds: $c_{12}=c_{44}$, and by comparison with (12) the following relations among third-order coefficients are found:

$$C_{456}=8C_{123};\quad C_{144}=2C_{123};\quad C_{166}=4C_{112}. \qquad (13)$$

Cauchy's relation is rarely satisfied by real crystals, and it seems probable that the relations (13) are also rarely valid.

When, however, (13) is assumed to hold, the third-order coefficients may be expressed in terms of the 5 lattice sums computed by Born and Misra, as follows:

$$\begin{aligned}c_{11}&=8\mathfrak{C}(2), & C_{111}&=8\mathfrak{C}(3),\\ c_{12}&=8\mathfrak{C}(1,1), & C_{123}&=48\mathfrak{C}(1,1,1), \qquad (14)\\ & & C_{112}&=24\mathfrak{C}(2,1).\end{aligned}$$

The expansion of ϕ in terms of the matrix j_{rs} might prove awkward in the general case, but for the particular strain (2) it is possible to express the j_{rs} in terms of the Eulerian strains,

ϵ_{rs}. Since

$$j_{pq}=\frac{\partial a_p}{\partial x_r}\frac{\partial a_q}{\partial x_r}, \quad \text{and} \quad \frac{\partial a_p}{\partial x_r}=(1-\alpha)^{-1}(\delta_{pr}-\beta_{pr}),$$

we find

$$j_{pq}=(1-\alpha)^{-2}(\delta_{pq}-2\beta_{pq})=\delta_{pq}-2\epsilon_{pq}. \tag{15}$$

Assuming that in this case, ϕ is expressible in terms of ϵ_{pq}, we may replace $\partial\phi/\partial j_{pq}$ by $-\frac{1}{2}(\partial\phi/\partial\epsilon_{pq})$. Also ϕ must have the same symmetry in terms of the ϵ_{rs} as in terms of the η_{rs}, and the second-order coefficients must be the same, since the expressions must coincide for infinitesimal strain, where ϵ_{rs} and η_{rs} become indistinguishable. Thus we obtain an expansion for $\rho_0\phi$ in terms for ϵ_{rs} exactly like (12), except that we write ϵ_{rs} instead of η_{rs}, and introduce new third-order coefficients, D_{111} and so on in place of the corresponding C's.

These expressions for ϕ must be identical, and hence there must be relations between the C's and the D's. One such relation is readily found by considering a hydrostatic strain, letting $\beta_{rs}=0$, and putting both expressions in terms of α. We have first, in terms of η,

$$\rho_0\phi=\tfrac{3}{2}\eta^2C_2+\eta^3C_3+\eta^4C_4+\cdots;$$

in terms of ϵ, (16)

$$\rho_0\phi=\tfrac{3}{2}\epsilon^2C_2+\epsilon^3D_3+\epsilon^4D_4+\cdots;$$

where

$$C_2=c_{11}+2c_{12};\quad C_3=3C_{111}+C_{123}+6C_{112};$$

$$D_3=3D_{111}+D_{123}+6D_{112};$$

and C_4, $D_4\cdots$ are possible coefficients of higher order terms. On substituting α for ϵ and η according to (9), and identifying the coefficients of like powers of α in the two expressions, we obtain:

$$D_3=C_3+6C_2;\quad D_4=C_4+6C_3+18C_2,\ \text{etc.} \tag{17}$$

Evidently the identity of the two formulations can be assured to any power of α by the addition of terms of higher order. Where C_3 has been calculated from lattice theory or otherwise, D_3 may be found by (17). Other relations may be found by taking other types of strain. Thus if we take $\beta_{12}\neq 0$, we find

$$D_{144}+2D_{166}=C_{144}+2C_{166}+16c_{44}+4c_{11}+8c_{12}. \tag{18}$$

In deriving this identity, care must be taken to include second-power terms of β_{12}; the approximations (8) should not be used.

These formulations of the free energy are not dependent upon the form of the potential between particles, except insofar as the numerical values of the coefficients, c's, C's, and D's, are concerned.

5. EFFECT OF PRESSURE ON ELASTIC CONSTANTS

The symmetry of a cubic crystal is preserved under hydrostatic compression, so that the relations between the additional stresses and the infinitesimal additional strains must have the same form as for a cubic crystal under infinitesimal strain at zero pressure, but the effective elastic "constants" will depend upon the pressure. These relations now follow; the algebra, which is tedious, is omitted. By substituting in (10) and noting that the density is given by (5) and (9), we find, for example,

$$T_{11}=(1+2\eta)^{-\frac{1}{2}}(1+\beta_{11}-\beta_{22}-\beta_{33})(\partial\phi/\partial\eta_{11}), \tag{19}$$

neglecting higher powers of the β's.

We now set $T_{11}=-P+T_{11}'$ and write T_{11}' in terms of the β's and a new set of elastic constants, c_{11}', c_{12}', and c_{44}', which depend upon P. Expanding (19) and identifying the coefficients, we find

$$T_{11}'=c_{11}'\beta_{11}+c_{12}'(\beta_{22}+\beta_{33}); \tag{20}$$

$$-P=\eta(1+2\eta)^{-\frac{1}{2}}(c_{11}+2c_{12}+\eta C_3+\cdots); \tag{21}$$

$$\left.\begin{aligned} c_{11}'&=(1+2\eta)^{-\frac{1}{2}}\{c_{11}+\eta(3c_{11}+2c_{12}+6C_{111}+4C_{112})+\eta^2(15C_{111}+C_{123}+14C_{112})+\cdots\};\\ c_{12}'&=(1+2\eta)^{-\frac{1}{2}}\{c_{12}+\eta(C_{123}+4C_{112}-c_{11})+\eta^2(C_{123}+2C_{112}-3C_{111})+\cdots\}.\end{aligned}\right. \tag{22}$$

Similarly, expanding $T_{12}=T_{12}'=2c_{44}'\beta_{12}$,

$$2c_{44}'=(1+2\eta)^{-\frac{1}{2}}\{2c_{44}+\eta(4c_{44}+2c_{11}+4c_{12}+C_{144}+2C_{166})$$
$$+\eta^2(6C_{111}+2C_{123}+12C_{112}+2C_{144}+4C_{166})+\cdots\}. \quad (23)$$

To the first power in η these become

$$c_{11}'=c_{11}+\eta(2c_{11}+2c_{12}+6C_{111}+4C_{112});$$
$$c_{12}'=c_{12}+\eta(C_{123}+4C_{112}-c_{11}-c_{12}); \quad (24)$$
$$c_{44}'=c_{44}+\eta(c_{44}+c_{11}+2c_{12}+C_{144}/2+C_{166});$$

also

$$c_{11}'+2c_{12}'=c_{11}+2c_{12}+2\eta C_3=C_2+2\eta C_3. \quad (25)$$

The three parameters c_{11}', c_{12}', and c_{44}' determine completely the response of the compressed crystal to the additional small strains. The constants for the bending, extension, or twisting of variously oriented bars or plates under pressure are found by substituting these parameters in Voigt's formulas in place of the c_{11}, c_{12}, and c_{44}. The equations of small motion in the compressed medium are found from T_{rs} in the usual way, the displacements being the u_p' defined in (1). For uniform pressure, the stress equations of equilibrium involve only the derivatives of T_{rs}'.

Parallel development in the Eulerian form leads to:

$$T_{11}=-P+T_{11}'=(1-2\epsilon)^{5/2}(1-3\beta_{11}-\beta_{22}-\beta_{33})(\partial\phi/\partial\epsilon_{11}); \quad (26)$$

$$-P=\epsilon(1-2\epsilon)^{5/2}[c_{11}+2c_{12}+\epsilon D_3+\cdots]; \quad (27)$$

$$c_{11}'=(1-2\epsilon)^{5/2}\{c_{11}-\epsilon(5c_{11}+6c_{12}-6D_{111}-4D_{112})-\epsilon^2(21D_{111}+3D_{123}+26D_{112})+\cdots\};$$
$$c_{12}'=(1-2\epsilon)^{5/2}\{c_{12}-\epsilon(c_{11}+4c_{12}-D_{123}-4D_{112})-\epsilon^2(3D_{111}+3D_{123}+14D_{112})+\cdots\};$$
$$2c_{44}=(1-2\epsilon)^{5/2}\{2c_{44}-\epsilon(4c_{44}+2c_{11}+4c_{12}-D_{144}-2D_{166})$$
$$-\epsilon^2(6D_{111}+2D_{123}+12D_{112}-2D_{144}-4D_{166})+\cdots\}. \quad (28)$$

To the first power in ϵ,

$$c_{11}'=c_{11}-\epsilon(10c_{11}+6c_{12}-6D_{111}-4D_{112}),$$
$$c_{12}'=c_{12}-\epsilon(c_{11}+9c_{12}-D_{123}-4D_{112}), \quad (29)$$
$$c_{44}'=c_{44}-\epsilon(7c_{44}+c_{11}+2c_{12}-D_{144}/2-D_{166});$$

also

$$c_{11}'+2c_{12}'=c_{11}+2c_{12}-\epsilon(12C_2-2D_3)=C_2-\epsilon(12C_2-2D_3). \quad (30)$$

In this form it is clear that the c''s will all increase with the pressure if the D's are sufficiently small.

Since for small compressions, α, η and ϵ are all equal to the first order, we obtain further identified among the C's and D's:

$$D_{123}+4D_{112}\equiv C_{123}+4C_{112}+8c_{12};$$
$$3D_{111}+2D_{112}\equiv 3C_{111}+2C_{112}+6c_{11}+4c_{12}; \quad (31)$$

as well as the relations (17) and (18) already given. Since it appears that the C's are usually negative, while the second-order coefficients must be positive, the D's will be numerically smaller than the C's.

The relations between pressure and volume, and between pressure and compressibility, are of special interest as they offer the possibility of rationalizing a large mass of experimental data. For hydrostatic strain, we may set all $\beta_{rs}=0$, or we may put $\beta=\beta_{11}=\beta_{22}=\beta_{33}$, with the other β's zero. The former method is more direct; the latter may serve as a check. With the β's all zero, we have from (21), with $V_0/V=(1+2\eta)^{-\frac{3}{2}}$,

$$P=\tfrac{1}{2}[(V/V_0)^{-\frac{1}{3}}-(V/V_0)^{\frac{1}{3}}][C_2-C_3/2+(C_3/2)(V/V_0)^{\frac{2}{3}}+\cdots]. \quad (32)$$

Denoting the ordinary compressibility, $-(1/V_0)(\partial V/\partial P)_T$ by χ_0 and its reciprocal, the "bulk modulus" or "incompressibility" by K_0, we find for the limiting case of zero pressure,

$$(\partial K_0/\partial P)_{P=0}=1-(2C_3/3C_2). \tag{33}$$

In terms of ϵ, with $V_0/V=(1-2\epsilon)^{\frac{3}{2}}$,

$$P=\tfrac{1}{2}[(V_0/V)^{7/3}-(V_0/V)^{5/3}][C_2+D_3/2-(D_3/2)(V_0/V)^{2/3}+\cdots]. \tag{34}$$

$$(\partial K_0/\partial P)_{P=0}=5-(2D_3/3C_2). \tag{35}$$

But since $D_3=C_3+6C_2$, (33) and (35) are identical.

The same result is of course obtained if we put $\beta_{rs}=\beta\delta_{rs}$, where β is a small constant. In this case, we have $-\Delta P=T_{11}'=\beta(c_{11}'+2c_{12}')$, and $\Delta V/V_0=3\beta(1-\alpha)^3=3\beta(1-2\epsilon)^{-\frac{3}{2}}$; $K_0=-(V_0\Delta P)/\Delta V$, so that $K_0=\frac{1}{3}[C_2-\epsilon(15C_2-2D_3)+\cdots]=C_2/3+P(5-2D_3/3C_2)+\cdots$. Thus in the limit, for $P=0$, we have again (35). The combination $3/(c_{11}'+2c_{12}')$, gives the "instantaneous" compressibility, that is, the compressibility referred to the volume at the pressure P, rather than to the volume at zero pressure.

We may remark that all of these expressions become identical with those of the isotropic medium[6] on setting $c_{11}=\lambda+2\mu$, $c_{12}=\lambda$, and $c_{44}=\mu$.

It is also noteworthy that (33) and (35) are unchanged by the introduction of higher order terms in the free energy; terms contributed by powers of the strain higher than the third, disappear in passing to the limit of zero pressure. Equation (33) has also been found by Fürth.[4]

6. RELATIONSHIP TO OTHER THEORIES

Since ϕ is the Helmholtz free energy, it must satisfy the thermodynamic relation, $-P=(\partial\phi/\partial V)_T=-\rho^2(\partial\phi/\partial\rho)_T$, when the stress system degenerates to a hydrostatic pressure P. In this case, the stress-strain equations (10) take the form

$$-P=T_{11}=\rho\frac{\partial\phi}{\partial\eta_{11}}(1+2\eta_{11})=\rho\frac{\partial\phi}{\partial\epsilon_{11}}(1-2\epsilon_{11}). \tag{36}$$

But

$$\rho/\rho_0=[(1+2\eta_{11})(1+2\eta_{22})(1+2\eta_{33})]^{-\frac{1}{2}}$$
$$=[(1-2\epsilon_{11})(1-2\epsilon_{22})(1-2\epsilon_{33})]^{\frac{1}{2}}.$$

Hence

$$\partial\rho/\partial\eta_{11}=-\rho(1+2\eta_{11})^{-1},$$

and

$$\partial\rho/\partial\epsilon_{11}=-\rho(1-2\epsilon_{11})^{-1}.$$

Since for this case,

$$\partial\phi/\partial\eta_{11}=(\partial\phi/\partial\rho)(\partial\rho/\partial\eta)_{11}$$

and

$$\partial\phi/\partial\epsilon_{11}=(\partial\phi/\partial\rho)(\partial\rho/\partial\epsilon_{11}),$$

we verify at once that $-P=-\rho^2(\partial\phi/\partial\rho)_T$.

We might also have proceeded to find the compressibility and its change with pressure by successive differentiation of this general equation. Thus we have

$$K_0=-V_0(\partial P/\partial V)_T=V_0(\partial^2\phi/\partial V^2),$$

and

$$(\partial K_0/\partial P)_{P=0}=-V_0(\partial^3\phi/\partial V^3)_0/(\partial^2\phi/\partial V^2)_0;$$

or if we take a linear dimension such that $V=r^3$, we find

$$(\partial K_0/\partial P)_0=2-r_0(\partial^3\phi/\partial r^3)_0/3(\partial^2\phi/\partial r^2)_0. \tag{37}$$

The partial derivatives with respect to the volume may be obtained from (12) or its equivalent in terms of ϵ or η by using (5) and (9); we return to the relations already found.

If, however, the form of ϕ is known or assumed in terms of the interparticle distances and force constants, additional relations may be derived. With the power-law favored by Born, where the potential between two isolated particles is of the form $-ar^{-m}+br^{-n}$, (37) leads at once to the well-known expression $(\partial K_0/\partial P)_0=(9+m+n)/3$; this is strictly valid only for $T=0$. Thus we find that $D_3/C_2=3-(m+n)/2$ and $C_3/C_2=-3-(m+n)/2$. Conversely, if $(\partial K_0/\partial P)_0$ is known, the sum $(m+n)$ is determined. This method has been applied by Fürth[7]

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[7] R. Fürth, Proc. Roy. Soc. **A183**, 87 (1944–45).

TABLE II. Relative values of third-order coefficients for power-law potential.

$(m+n)$	C_3/C_2	D_3/C_2	$(\partial K_0/\partial P)_0$
3	−4.5	+1.5	4.0
4	−5.0	+1.0	4.33
5	−5.5	+0.5	4.67
6	−6.0	0	5.00
7	−6.5	−0.5	5.33
8	−7.0	−1.0	5.67
9	−7.5	−1.5	6.00
10	−8.0	−2.0	6.33
11	−8.5	−2.5	6.67
12	−9.0	−3.0	7.00
14	−10.0	−4.0	7.67
16	−11.0	−5.0	8.33
18	−12.0	−6.0	9.00

in an effort to show that consistent values of m and n can be found from several independent experimental quantities.

As m and n are intrinsically positive, D_3 will always be smaller than C_3; values of the ratios of these coefficients to C_2 for various values of $(m+n)$ are shown in Table II. Since, as it will appear later, the most common experimental values for $(\partial K_0/\partial P)_0$ are in the neighborhood of 5, it may be justifiable for many purposes to neglect D_3/C_2 where the neglect of C_3/C_2 would introduce serious error. It is thus advantageous to treat most of the questions involving large compressions in terms of the Eulerian strain; the same results may be obtained with the Lagrangian form, but at the price of retaining terms of higher order.

Pressure-volume relations are furnished by Born and co-workers for a number of special cases, but the results are given in numerical form and comparison is not immediate, except for zero temperature. At $T=0$, however, it is readily found that the power-law potential leads to the general form,

$$P=\text{constant}\times\left[(V_0/V)^{(3+m)/3}-(V_0/V)^{(3+n)/3}\right]. \quad (38)$$

This equals (34) for $m=2$, $n=4$, in which case $D_3=0$. For other values of m and n, these expressions will be equal only with the inclusion of higher order terms in (34).

The higher order coefficients may be found for the special case of hydrostatic pressure by developing the power-law potential in terms of ϵ and of η. Putting $V_0/V=(r_0/r)^3$, we have $(r_0/r)=(1-2\epsilon)^{\frac{1}{2}}=(1+2\eta)^{-\frac{1}{2}}$. Then if

$$\rho_0\phi=A\left[\frac{1}{m}\left(\frac{r_0}{r}\right)^m-\frac{1}{n}\left(\frac{r_0}{r}\right)^n\right],$$

it follows that

$$\begin{aligned}\rho_0\phi=\text{constant}+A\{&(n-m)\epsilon^2/2!\\&-[(n-2)(n-4)-(m-2)(m-4)]\epsilon^3/3!\\&+[(n-2)(n-4)(n-6)\\&-(m-2)(m-4)(m-6)]\epsilon^4/4!-\cdots\};\end{aligned} \quad (39)$$

and also that, alternatively,

$$\begin{aligned}\rho_0\phi=\text{constant}+A\{&(n-m)\eta^2/2!\\&-[(n+2)(n+4)-(m+2)(m+4)]\eta^3/3!\\&+[(n+2)(n+4)(n+6)\\&-(m+2)(m+4)(m+6)]\eta^4/4!-\cdots\}.\end{aligned} \quad (39a)$$

Whenever m and n are both even integers, the development in ϵ becomes simply a polynomial; if either m or n is odd, (39) gives an infinite series which ultimately diverges for very high compressions (see Table I). It is hardly to be expected that the assumed power-law potential remains valid for such compressions, regardless of its suitability for small volume changes. The expression in η is always convergent, since $|\eta|$ never exceeds $\frac{1}{2}$, for compression; but also it is never a polynomial. The terminating property of (39) possibly accounts in part for its usefulness in dealing with reasonably large compressions. Except for ionic crystals, good approximations to the potential can probably always be obtained with even values of m and n (within the scope of usefulness of the power-law form of potential) and it seems unlikely that the larger of these

TABLE III. c_{44}'/c_{44} as function of volume.

ξ	-2ϵ	V_0/V	c_{44}'/c_{44} (Birch)	(Gow)
				$m=6$, $n=12$
0	0	1.000	1.000	1.000
0.05	0.0164	1.0247	1.125	1.193
.10	.0323	1.0488	1.247	1.405
.15	.0477	1.0724	1.363	1.635
				$m=4$, $n=8$
0.05	0.0247	1.0375	1.189	1.207
.10	.0495	1.075	1.378	1.436
.15	.0818	1.125	1.625	1.711

need ever exceed 12. For $n=12$, the expansion terminates with the sixth power of ϵ. Smaller values seem more suitable for most of the metals. The expansion in ϵ is given below for several pairs of values of m and n.

For $m=2$, $n=4$; $\rho_0\phi=\text{constant}+A\epsilon^2$.
For $m=2$, $n=6$; $\rho_0\phi=\text{constant}+A'\epsilon^2(1-\frac{2}{3}\epsilon)$.
For $m=4$, $n=8$; $\rho_0\phi=\text{constant}+A''\epsilon^2(1-2\epsilon+\epsilon^2)$.
For $m=1$, $n=8$; a good approximation for most of the alkali halides,[8] $\rho_0\phi=\text{constant}+A'''\epsilon^2 \times(1-\epsilon+\frac{3}{4}\epsilon^2+\frac{1}{4}\epsilon^3+\cdots)$.

These expressions are found from the power-law potential and hence possess the same restriction to zero temperature, but it appears probable that the differential effect of temperature upon the coefficients of the various powers of ϵ will not be great, at least for moderate temperatures, and hence that the values for such ratios as D_3/C_2, D_4/C_2 and so on, which are immediately obtainable from the above expansions for zero, will be approximately valid at higher temperatures. We notice that for $m=2$, $n=4$, we have D_3 and all higher order D's equal to zero, and the pressure is given by the relatively simple expression, $P=\text{constant}\times[(V_0/V)^{7/3}-(V_0/V)^{5/3}]$. D_3 depends only upon $(n+m)$ but the other terms depend upon the individual values of n and m. Thus for $m=2$, $n=6$, D_4 and higher coefficients are zero, while for $m=1$, $n=7$, $D_4/C_2=9/8$, $D_5/C_2=3/8$, and so on.

In treatments which deal only with the case of hydrostatic pressure, development of the potential in terms of strain components is of course unnecessary; any function of the volume may serve, subject to certain restrictions. Thus Slater expands the free energy in terms of $(1-r/r_0)$. This is equal to $1-(1+2\eta)^{\frac{1}{2}}$ which becomes approximately $-\eta$ for small compressions. If, however, the individual elastic constants are of interest and not merely the compression and its various derivatives, it is necessary to expand the free energy in terms of the strain components, as has been done by Born and his associates, using the equivalent of η_{rs}. It is possible that in the general case, as well as in the special case of hydrostatic compression, the use of the ϵ_{rs} instead of the η_{rs} might lead to more rapidly convergent results.

TABLE IV. Calculated effect of pressure on c_{44}' for several substances.

Substance	$7+(c_{11}+2c_{12})/c_{44}$	$\frac{1}{c_{44}}\frac{\partial c_{44}'}{\partial P}$ (P in bars)
Na	9.85	70.2×10^{-6}
Cu	12.60	2.97
Ag	13.86	4.63
Au	20.2	3.83
Al	15.28	6.59
W	13.02	1.41
Fe	11.46	2.22
MgO	10.0	2.15
NaCl	12.74	17.2
KBr	14.22	31.8
CaF_2	14.52	5.7

A paper by Miss Gow[9] gives the variation with pressure (and temperature) of all of the elastic constants for face-centered monatomic cubic lattices, using a potential of the form just considered; the lowest values of m and n for which calculations are presented are $m=4$, $n=8$. The results are given in numerical tables, in terms of a parameter ξ related to the volume by $(1+\xi)=(V_0/V)^{(n-m)/3}$. Comparison with the results of this paper can be carried out by computing the changes of the corresponding elastic constants for the same changes of volume. This has been done for c_{44} in Table III, where we have taken the approximate form of (29), neglecting the third-order coefficients D_{144} and D_{166}:

$$c_{44}'/c_{44}=1-\epsilon[7+(c_{11}+2c_{12})/c_{44}]. \tag{40}$$

As shown in Table IV, the coefficient of ϵ in (40) varies between 10 and 20 for various materials, most of the values falling near 14. In Table III, the figure 15.28, the value for aluminum, has been used.

Miss Gow gives

$$c_{44}/P_0=(V_0/V)[A_3/u+B_4T/\theta],$$

where A_3/u and B_4 are tabulated as functions of ξ; P_0, θ are constants, T the absolute temperature. This c_{44} is equivalent to our c_{44}'. For comparison with (29), we form the ratio for $T=0$, $c_{44}'(\xi)/c_{44}(0)=(V_0/V)[A_3(\xi)/A_3(0)]$; this ratio is not greatly affected by including the

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[8] J. C. Slater, *Introduction to Chemical Physics* (McGraw-Hill Book Company, Inc., New York, 1939), p. 393.

[9] Margaret M. Gow, Proc. Camb. Phil. Soc. **40**, 151 (1944).

TABLE V. Experimental values of change of compressibility with pressure: elements (pressure in bars).*

Element	t°C	10^6a	$10^{12}b$	$2b/a^2=(\partial K_0/\partial P)_0$
W	30	0.32	0.1	2
	75	.32	.2	4
Pt	30	.363	.3	5
Rh	30	.364	1.5	23
Cr	30	.525	.9	7
Ni	30	.535	.9	6
	75	.541	.8	5
Pd	30	.534	.9	6
Co	30	.546	.8	5
B	30	.558	.8	5
Au	30	.584	2.0	12
	75	.577	.8	5
Cb	30	.577	.9	5
Fe	24	.5941	.83	4.7 (to 30,000)
(Ebert)**	20	.603	1.37	7.5 (to 5,000)
V	30	.617	1.35	7.1
Cu	30	.729	1.6	6.0
		.7182	.9	4 (to 30,000)
(Ebert)**	20	.731	2.6	9.7 (to 5,000)
Mn	30	.803	4.2	13
Ag	30	1.002	3.7	7.4
(Ebert)**	20	1.025	1.9	3.6 (to 5,000)
Al	30	1.365	4.9	5.3
		1.328	3.7	4.2 (to 30,000)
(Ebert)**	20	1.370	3.1	3.3 (to 5,000)
(Birch)	23	1.378	7.2	7.6 (to 10,000)
Ge	30	1.435	4.8	4.6
Th	30	1.850	12	7
Pb	30	2.415	19.6	6.8
		2.340	10.2	3.7 (to 30,000)
(Birch)	20	2.354	14.3	5.1 (to 10,000)
(Ebert)**	20	2.448	14.5	4.9 (to 5,000)
Pr	30	3.451	12.2	2.0
La	30	3.578	13.9	2.2
Ca	30	5.805	65	3.9 see Table VIII
Sr	30	8.278	103	3.0
Ba	30	10.39	133	2.5

* Unless otherwise noted, the measurements are by P. W. Bridgman, and the range is 12,000 kg/cm². Several corrections have been applied to the values published in the original papers and in *The Physics of High Pressure* (Bell and Sons, London, England, 1931), notably for the new value of b for iron given in Proc. Am. Acad. Arts Sci. **74**, 11–20 (1940). See also Proc. Am. Acad. Arts Sci. **70**, 285–317 (1935), and Rev. Mod. Phys. **18**, 1 (1946). Corrected values, expressed as above in bars rather than in the original kg/cm², are tabulated in *Handbook of Physical Constants*, Special Paper No. 36, published by the Geological Society of America, Section 4. Values of a and b for the new measurements on Cu, Pb and Al, still unpublished, were computed by Birch. Entries marked "Ebert" are from H. Ebert, Physik. Zeits. **36**, 388 (1935). Those marked "Birch" are from F. Birch and R. R. Law, Bull. Geol. Soc. Am. **46**, 1219 (1935).

** Single crystal.

temperature terms. Values of the ratio, as a function of volume, are given in Table III, for $m=6$, $n=12$, and for $m=4$, $n=8$. Again it is clear that better agreement would exist for smaller values of m and n.

The magnitude of the neglected terms in (29), $(D_{144}+2D_{166})/2$, relative to the quantity retained, $(7c_{44}+c_{11}+2c_{12})$, may be estimated by using Fürth's evaluation[4] of the third-order coefficients, and the identity (18). The C's and the c's are given in terms of the quantity $\mathfrak{S}(2)$ for certain combinations of m and n. In this way, it may be estimated that for the face-centered cubic lattice, with $m=4$, $n=8$, the neglected terms would increase the pressure coefficient by about 14 percent; for $m=4$, $n=6$, the neglected terms would reduce the coefficient by about 4 percent. The few experimental determinations[10] of the effect of pressure on rigidity support the calculated values of Table IV: the measured values of the relative change of rigidity with pressure are $2.7\cdot 10^{-6}$ for copper, $7.6\cdot 10^{-6}$ for aluminum, and $2.36\cdot 10^{-6}$ for steel (P in bars). However, these are for polycrystalline materials, and are not strictly comparable with the calculated values for a particular direction in the crystal, although it seems probable that the effect will not differ greatly for different orientations.

The correction to Born's theory arising from the stress-strain relation (10) for finite strain will apply only to the expressions for the elastic constants; the pressure-volume relation escapes this correction, since it is based on the exact thermodynamic relation for the pressure as volume derivative of the free energy. The relation (10) should be regarded as the exact extension of this thermodynamic relation to the general finite strain.

7. COMPARISON WITH MEASUREMENTS OF COMPRESSION

The compression of a large number of materials crystallizing in the cubic system has been measured over pressure ranges sufficiently great to establish a definite departure from linearity. Most of the measurements have been made by Bridgman, who has extended the working range from about 12,000 kg/cm² in his early work to 100,000 kg/cm² in recent publications. The results for the lower ranges are usually given in the form, $-\Delta V/V_0=aP-bP^2$, where ΔV is the change of volume from the initial volume V_0 at zero pressure, to the pressure P; a and b depend upon the temperature. Thus, at constant temperature, $(\partial K_0/\partial P)_0=2b/a^2$. Table V includes the measurements for all of the elements of cubic symmetry except for those of high compressibility (Table VII and VIII), and several (Mo, Ta, Ce) which show anomalous

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[10] P. W. Bridgman, Proc. Am. Acad. **63**, 401 (1929); F. Birch, J. App. Phys. **8**, 129 (1937).

negative values of b. Table VI includes measurements for a number of cubic compounds. Measurements made before 1940 have been corrected to the new value determined for iron at that time; this correction amounts to a reduction of the former values for b by about $1.5 \cdot 10^{-12}$ and is thus of importance for the materials of low compressibility.

Most of the values of $2b/a^2$ in both Table V and Table VI lie between 4 and 7; if the distribution is considered to represent a normal probability curve, the most probable value for the elements is about 4.5 with a half-width of about 0.5, an amount not inconsistent with the experimental uncertainty when reasonable allowance is made for such defects of material as initial strains and porosity. Occasional deviations seem to be of this character, as for gold, where an erratic value occurs for 30°C, a normal one for 75°C. The values for rhodium and for manganese are almost certainly erratic. The most probable value for the compounds is between 5 and 6. The only significant deviation is for the sulfides and perhaps certain fluorides, where $2b/a^2$ is about 12. It is noteworthy that the latest and most precise measurements, to 30,000 kg/cm², show even lower values for $2b/a^2$ than the earlier ones for such relatively reliable materials as Al, Pb, and Cu. Figures lower than 5 mean positive values of D_3, and correspond to very small exponents in the power-law potential (Table II). Low values occur both at the beginning and end of Table V, which is arranged in the order of increasing compressibility. Not too much weight should be attached to the low value for tungsten, where the experimental error must be relatively large; but the same reasoning would suggest that the values for Ca and Sr should be very reliable. Other data for Ca in Table VIII demonstrate a more "normal" variation.

Slater[11] has concluded that 5 is probably the best general value of $2b/a^2$ for the metals; this leads to a figure of 1.833 for Gruneisen's constant, as compared with about 2.4 preferred by Fürth. An outstanding feature of Tables V and VI is the evidence that $(\partial K_0/\partial P)_0$ has approximately the same value for such diverse materials as metals and various types of ionic compounds. This is understandable if the ratio $(-D_3/C_2)$, which is the part of $(\partial K_0/\partial P)_0$ which depends upon the individual peculiarities of the interparticle forces, is generally no greater than unity, or in other terms, $(m+n)$ no greater than 8 or 9.

TABLE VI. Experimental values of change of compressibility with pressure: compounds. Measurements at 30°C (P in bars).*

Compound	10^6a	$10^{12}b$	$2b/a^2$	
TiN	0.334	0.87	16	
TiC	.477	.8	7	
Pyrope (garnet)	.545	.9	6	
Fe_3O_4	.547	.82	5.5	
MgO	.598	1.0	5.5	
Andradite (garnet)	.673	.86	3.8	
Fe_2S	.68	.87	3.8	
CoAsS	.767	1.88	6.4	
CdF_2	1.120	7.5	12	
ZnS	1.303	1.28	1.5	
	1.258	5.4	6.8	(to 50,000)
CaF_2	1.226	6.49	8.7	
LiF (S)	1.53	7.6	6.5	
	1.52	5.5	4.8	
SrF_2	1.607	9.4	7.3	
PbS	1.869	7.43	4.3	
Cu_2O	1.943	19.3	10.1	
BaF_2	1.964	14	7.3	
NaF	2.11	17	7.7	
CaS	2.321	39	14.5	
SrS	2.426	38.8	13.2	
CuCl	2.508	13.3	4.2	
CuI	2.802	24.8	6.3	
BaS	2.946	52.8	12.1	
Ag_2S	3.265	49.5	9.4	
KF (S)	3.30	32	5.9	
LiCl (S)	3.40	32.3	5.6	
NaCl	4.260	51	5.6	see Table IX
LiBr (S)	4.30	51	5.6	
$NaBrO_3$	4.401	76	7.8	
$NaClO_3$	5.033	95	7.5	
NaBr (S)	5.07	63	4.9	see Table IX
KCl (S)	5.62	75	4.8	
CsCl	5.94	99.5	5.7	see Table IX
LiI	6.00	110	6.1	
KBr (S)	6.70	105	4.7	
CsBr	7.05	149	6.0	see Table IX
RbBr (S)	7.93	137	4.4	
KI (S)	8.53	155	4.3	
CsI	8.565	209	5.7	see Table IX
RbI (S)	9.56	204	4.5	

* All measurements by P. W. Bridgman (see references for Table V) except those marked "S," which are by J. C. Slater, Phys. Rev. **23**, 488 (1924).

The same conclusion may be reached by examining the striking body of data for compressions up to 100,000 kg/cm² given in two papers by Bridgman, as well as some earlier results to 45,000. The data are given as $-\Delta V/V_0$ for various pressures. In a number of instances the density was more than doubled, and in many cases, raised by 25 percent or more. Taking the pressure-volume relation in the form (34), we

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[11] J. C. Slater, Phys. Rev. **57**, 744 (1940).

TABLE VII. Compression of the alkali metals to 45,000 kg/cm², and values of F/P.*

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	641	0.929	113	0.884	210	0.826	374	0.818	401
10	.926	599	.883	107	.817	202	.767	301	.729	397
15	.899	584	.852	98	.770	196	.721	280	.674	387
20	.875	581	.818	100	.732	194	.684	271	.628	395
25	.855	573	.791	100	.699	196	.655	264	.586	417
30	.835	577	.767	100	.671	197	.629	261	.568	392
35	.816	581	.746	100	.647	199	.607	259	.542	400
40	.798	591	.727	101	.627	199	.587	259	.519	409
45	.782	597	.710	101	.604	206	.569	260	.499	417

* P. W. Bridgman, Phys. Rev. **57**, 237 (1940); Proc. Am. Acad. Arts Sci. **72**, 207 (1938).

TABLE VIII. Compressions to 100,000 kg/cm² and values of F/P.*

P in 10^3 kg/cm²	Li		Na		K		Rb		Ca	
	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
10	0.926	598	0.883	106	0.817	202	0.767	301	0.942	449
20	.875	581	.818	100	.732	194	.684	271	.897	451
30	.835	575	.767	100	.671	197	.629	261	.861	449
40	.798	591	.727	101	.627	199	.587	259	.832	443
50	.763	621	.690	104	.581	216	.538	288	.805	447
60	.728	668	.657	108	.543	232	.499	313	.780	454
70	.695	720	.628	112	.508	252	.461	351	(Transition)	
80	.664	776	.603	116	.478	272	.425	401		
90	.634	842	.581	120	.451	293	.392	459		
100	.606	913	.560	124	.427	316	.362	527		

* P. W. Bridgman, Proc. Am. Acad. Arts Sci. **74**, 425 (1942); or Phys. Rev. **60**, 351 (1941).

see that if it is permissible to neglect D_3/C_2, we obtain the simpler form,

$$P=FC_2/2,$$

with

$$F=[(V_0/V)^{7/3}-(V_0/V)^{5/3}]. \tag{41}$$

The ratio F/P is in this case a constant, $2/C_2=2\chi_0/3$. The following test has been applied to the measurements of Tables VII, VIII, and IX: F has been formed from the measured values of V_0/V and divided by the corresponding measured pressures. The test is extremely sensitive since F varies rapidly with V_0/V. All, or nearly all, of the measurements of inorganic cubic materials have been included except those which show polymorphic changes in the pressure range, a fairly large fraction of the whole.

Let us first examine the alkali metals in the 45,000 kg/cm² range, shown in Table VII. F/P is constant within the precision of the measurements for all of these metals except Rb, where there is an abnormally high initial compressibility; the first value for Li also deviates widely. For the others, the initial compressibility can be obtained with an error of less than about 10 percent from any single volume determination. There is no particular trend which would suggest that improved agreement would result from the next approximation, with a non-zero D_3.

The measurements on the alkali metals to 100,000 kg/cm² (Table VIII), do show a definite trend, with F/P increasing beyond 50,000, by roughly 50 percent for Li and K, nearly 100 percent for Rb, and about 20 percent for Na. The values above 50,000 can be fitted by including a term in D_3, as in (34), but D_3 turns out to be large and positive and far beyond any value compatible with the measurements below 50,000. It seems fairly clear that the determinations for these two ranges are not mutually consistent. Bridgman has discussed the possible sources of fairly large errors in the higher range. In view of later determinations to 100,000, we may conclude that the abnormal behavior of the alkali metals above 50,000 is somehow connected with the method of correcting the data, which was improved in the later work. For example, as shown in Table IX, if the data for indium (a tetragonal crystal) given in the two papers (1942 and 1945) are reduced in the same way, we find that F/P increases in the former, though much less than for the alkali metals, whereas it decreases in the latter.

A decrease or approximate constancy of F/P is characteristic of the 1945 determinations, shown in Table IX. The decrease is readily accounted for by restoring D_3, which may be evaluated by plotting P/F *versus* $(V_0/V)^{\frac{2}{3}}$; according to (34) this should be a straight line. In a fairly typical case, we find $D_3/C_2=-0.8$ for CsI. This corresponds to a value of 5.53 for $2b/a^2$, whereas from Table VI, we find 5.7; and from Table II, $(m+n)$ between 7 and 8.

With the retention of the constant D_3, the measurements of Table IX can all be reproduced with an error not exceeding about 3 percent on the pressure. This is probably less than the experimental error of pressure determination for this range, and there is some indication from the data that the experimental pressures may be perhaps 10 percent lower than supposed. We reach this conclusion by observing that the ratio $(F/P)_{10,000}$ to $(F/P)_{100,000}$ is close to 1.1 for 9 of the 14 materials of Table IX; it is nearly constant for AgCl and CsBr and equal to about 1.2 for CsCl and $TlNO_3$. There appears to be no correlation with the amount of compression.

The approximate form (41) thus gives the pressure corresponding to the extreme compression in terms of the measured compression at 10,000 with an error not exceeding 20 percent, and generally less than 10 percent for the entries of Table IX. This is probably not far from the limits of experimental precision for this range of pressure.

Bardeen[12] has calculated the zero-point energy as function of density for Li and Na by approximate quantum-mechanical methods, obtaining the energy in the form, $\phi = Ay^3 + By^2 - Cy$, with $y = (V_0/V)^{\frac{1}{3}}$. A, B, and C are constants which he calculates and compares with the experimental values. This leads to a formula for the pressure which is approximately,

$$P = \text{constant}[(V_0/V)^{5/3} - (V_0/V)^{4/3}], \quad (42)$$

equivalent to the form for a power-law potential with $m=1$, $n=2$. Comparison with experiment requires a somewhat uncertain reduction to absolute zero, and the numerical agreement for the constants is not very close. If, however, the constant of (42) is determined from the measured initial compressibility, the agreement with the measured compression of the alkali metals to 45,000 is very nearly as close as for (41). Fürth[7] has applied the power-law potential to some of the measurements to 100,000, with values of m and n larger than are implied by (41); the agreement with the experimental values is less good. It appears that larger values of the exponents in the force law are required to satisfy the experimental determinations of temperature effects than to fit the measurements of pressure effects. It may be questioned whether this is mainly the consequence of an inadequacy of this form of potential, of some approximation in Born's treatment of the entropy of the lattice, or of more fundamental causes, as suggested by Bridgman in a discussion of the implications of Schottky's theorem.[13]

8. CONCLUSION

Besides the application of the theory of finite strain to find the effect of pressure upon the elasticity of cubic crystals, we have attempted a clarification of certain questions regarding the

TABLE IX. Compressions of cubic compounds and values of F/P. Compression of indium.*

P in 10^3 kg/cm^2	V/V_0 NaCl	F/P	V/V_0 CsCl	F/P	V/V_0 TlCl	F/P	V/V_0 AgCl	F/P	V/V_0 NaBr	F/P	V/V_0 CsBr	F/P	V/V_0 NH_4Br	F/P
10	0.962	279	0.952	362	0.962	279	0.979	145	0.957	321	0.947	405	0.951	370
20	.932	270	.914	359	.929	285	.960	149	.922	319	.905	406	.912	369
30	.907	264	.882	359	.901	285	.942	150	.893	315	.870	409	.880	367
40	.885	260	.856	353	.877	284	.926	149	.868	313	.840	411	.853	364
50	.865	258	.834	348	.856	282	.910	152	.847	309	.814	416	.830	361
60	.848	254	.816	338	.838	279	.896	152	.829	303	.792	413	.811	354
70	.832	253	.801	329	.823	274	.883	153	.814	296	.773	411	.795	346
80	.817	253	.788	319	.809	270	.871	152	.801	288	.757	405	.781	338
90	.803	252	.777	309	.798	262	.860	151	.789	282	.742	402	.768	332
100	.790	252	.767	301	.787	258			.778	277	.728	400	.756	327
	$TlNO_3$		NaI		CsI		TlI		1940		Indium 1942		1945	
10	0.963	271	0.944	429	0.935	513	0.950	379	0.978	155	0.977	166	0.9760	170
20	.932	270	.902	424	.887	508	.910	379	.958	156	.955	168	.9558	164
30	.905	271	.868	417	.849	505	.877	378	.940	155	.936	167	.9381	162
40	.882	266	.840	411	.818	501	.848	381	.925	152	.919	167	.9219	159
50	.863	264	.816	406	.792	496	.823	384	.913	146	.903	166	.9068	157
60	.848	255	.795	404	.770	490	.802	382			.888	167	.8928	157
70	.835	246	.777	398	.751	484	.784	378			.874	168	.8798	158
80	.824	238	.761	393	.734	479	.768	373			.860	170	.8676	156
90	.815	228	.747	388	.719	473	.755	366			.847	172	.8561	158
100	.806	222	.734	383	.706	467	.744	356			.835	173	.8451	157

* P. W. Bridgman, Proc. Am. Acad. Arts Sci. **76**, 1 (1945), (Halogen compounds and indium); **74**, 425 (1942), (Indium); **74**, 21 (1940), (Indium).

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[12] J. Bardeen, J. Chem. Phys. **6**, 372 (1938).

[13] P. W. Bridgman, Rev. Mod. Phys. **7**, 1 (1935).

scope of this theory. It is shown that there is no ambiguity: the alternative methods developed by Murnaghan lead to identical results for comparable approximations. The choice of method is a matter of convenience; for studies of large compressions, the Eulerian form furnishes simpler, more compact relations. Lattice theory does not conflict with this method; in cases where it can be sufficiently developed, it furnishes numerical values for the elastic constants in terms of atomic parameters, but many relations of a general nature are obtainable without a detailed specification of lattice structure and forces. The present method is valid for elastic strain at any constant temperature, and hence avoids the complexities which arise in lattice theory when temperatures other than zero are considered. It is shown that a relatively simple approximation accounts for practically all of the measurements at high pressure. The fact that this first approximation is also a good one, is shown to imply values for the exponents in a power-law form of potential considerably lower than have commonly been adopted.

9. ACKNOWLEDGMENTS

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APPENDIX

Derivation of Third-order Terms of the Free Energy for Cubic Crystals

The general methods of taking into account the symmetry of a crystal for various properties are described in Voigt,[14] Wooster[15] and other texts on crystal physics, and the application to the second-order elastic coefficients is given in considerable detail in Love.[16] The symmetry of all classes of cubic crystals is such as to reduce the 21 possible second-order coefficients to 3. There are 56 possible distinct third-order coefficients, and this is the actual number for a triclinic crystal. Using the customary short notation, where we write 1 for the pair of indices 11, 2 for 22, 3 for 33, 4 for 23 and 32, 5 for 31 and 13, and 6 for 12 and 21, the 56 third-order terms are as follows where evidently $C_{pqr}=C_{prq}=C_{qpr}$ and so on:

$$\begin{array}{llllll}
C_{111}\eta_1^3 & +C_{112}\eta_1^2\eta_2 & +C_{113}\eta_1^2\eta_3 & +C_{114}\eta_1^2\eta_4 & +C_{115}\eta_1^2\eta_5 & +C_{116}\eta_1^2\eta_6 \\
 & +C_{122}\eta_1\eta_2^2 & +C_{123}\eta_1\eta_2\eta_3 & +C_{124}\eta_1\eta_2\eta_4 & +C_{125}\eta_1\eta_2\eta_5 & +C_{126}\eta_1\eta_2\eta_6 \\
 & & +C_{133}\eta_1\eta_3^2 & +C_{134}\eta_1\eta_3\eta_4 & +C_{135}\eta_1\eta_3\eta_5 & +C_{136}\eta_1\eta_3\eta_6 \\
 & & & +C_{144}\eta_1\eta_4^2 & +C_{145}\eta_1\eta_4\eta_5 & +C_{146}\eta_1\eta_4\eta_6 \\
 & & & & +C_{155}\eta_1\eta_5^2 & +C_{156}\eta_1\eta_5\eta_6 \\
 & & & & & +C_{166}\eta_1\eta_6^2 \\
 & +C_{222}\eta_2^3 & +C_{223}\eta_2^2\eta_3 & +C_{224}\eta_2^2\eta_4 & +C_{225}\eta_2^2\eta_5 & +C_{226}\eta_2^2\eta_6 \\
 & & +C_{233}\eta_2\eta_3^2 & +C_{234}\eta_2\eta_3\eta_4 & +C_{235}\eta_2\eta_3\eta_5 & +C_{236}\eta_2\eta_3\eta_6 \\
 & & & +C_{244}\eta_2\eta_4^2 & +C_{245}\eta_2\eta_4\eta_5 & +C_{246}\eta_2\eta_4\eta_6 \\
 & & & & +C_{255}\eta_2\eta_5^2 & +C_{256}\eta_2\eta_5\eta_6 \\
 & & & & & +C_{266}\eta_2\eta_6^2 \\
 & & +C_{333}\eta_3^3 & +C_{334}\eta_3^2\eta_4 & +C_{335}\eta_3^2\eta_5 & +C_{336}\eta_3^2\eta_6 \\
 & & & +C_{344}\eta_3\eta_4^2 & +C_{345}\eta_3\eta_4\eta_5 & +C_{346}\eta_3\eta_4\eta_6 \\
 & & & & +C_{355}\eta_3\eta_5^2 & +C_{356}\eta_3\eta_5\eta_6 \\
 & & & & & +C_{366}\eta_3\eta_6^2 \\
 & & & +C_{444}\eta_4^3 & +C_{445}\eta_4^2\eta_5 & +C_{446}\eta_4^2\eta_6 \\
 & & & & +C_{455}\eta_4\eta_5^2 & +C_{456}\eta_4\eta_5\eta_6 \\
 & & & & & +C_{466}\eta_4\eta_6^2 \\
 & & & & +C_{555}\eta_5^3 & +C_{556}\eta_5^2\eta_6 \\
 & & & & & +C_{666}\eta_6^3.
\end{array}$$

The crystallographers have amused themselves by inventing a variety of ways of designating the 32 crystal classes and of describing the elements of symmetry. Table X shows in parallel form a few of the proposals with regard to the 5 classes of cubic or isometric symmetry. Only two of these classes are characterized by the tetragonal symmetry about the three cubic axes which one might expect to be a common property; the other three classes possess digonal symmetry

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[14] W. Voigt, *Lehrbuch der Kristallphysik* (B. G. Teubner, Leipzig, Germany, 1928).

[15] W. A. Wooster, *A Textbook on Crystal Physics* (The Cambridge University Press, New York, New York, 1938).

[16] A. E. H. Love, *A Treatise on the Mathematical Theory of Elasticity* (The Cambridge University Press, New York, New York, 1937).

TABLE X. Designations and elements of symmetry of the isometric classes.

Name or symbol of class Dana (Groth-Rogers)	Miers	Lewis	Hermann-Mauguin	Schoenflies	Elements of symmetry
Hexoctahedral (galena)	Ditesseral central	Cubic II	$\frac{4}{m}\ \bar{3}\ \frac{2}{m}$	$O^{(h)}$	C, $3A_4$, $4A_3$, $6A_2$
Gyroidal (cuprite)	Tesseral holoaxial	Cubic I	$4\ 3\ 2$	O	$3A_4$, $4A_3$, $6A_2$
Hextetrahedral	Ditesseral polar	Cubic V	$\bar{4}\ 3\ m$	$T^{(d)}$	$4A_3$, $3A_2$
Diploidal (pyrite)	Tesseral central	Cubic IV	$\frac{2}{m}\ \bar{3}$	$T^{(h)}$	C, $4A_3$, $3A_2$
Tetartoidal	Tesseral polar	Cubic III	$2\ 3$	T	$4A_3$, $3A_2$

Note: In the last column, C denotes a center of symmetry, A_4 an axis of fourfold symmetry, A_3 an axis of threefold symmetry, A_2 an axis of twofold symmetry. The numbers before the A's denote the number of such axes. This notation is used in Dana and Hurlbut's *Manual of Mineralogy* (John Wiley and Sons, Inc., New York, 1941) and is by far the most intelligible and useful to the reader unversed in crystallography. The Hermann-Mauguin symbols are to be found in the first volume of *International Tables for the Determination of Crystal Structures* (Borntraeger, Berlin, Germany, 1935). The other notation has been extracted from Love.

about these axes. All classes possess trigonal symmetry with respect to the 4 cube diagonals. This is expressed analytically as an invariance of properties under cyclic permutation of indices. Thus if the three original axes of coordinates are $X_1\,X_2\,X_3$, coinciding with a set of cubic axes, then rotation of 120° about a trigonal axis defines a new set of axes, $X_1'\,X_2'\,X_3'$, say, such that X_2' coincides with X_1, X_3' with X_2 and X_1' with X_3, for example. This corresponds to the scheme:

$$\begin{array}{c|ccc} & X_1' & X_2' & X_3' \\ \hline X_1 & 0 & 1 & 0 \\ X_2 & 0 & 0 & 1 \\ X_3 & 1 & 0 & 0. \end{array}$$

The strain components referred to the new axes, η_{rs}', will be related to the strain components referred to the original axes by the general transformation equation for second-order tensors, $\eta_{rs}'=\alpha_{pr}\alpha_{qs}\eta_{pq}$, p, q, r, $s=1, 2, 3$, where α_{11} is the cosine of the angle between X_1 and X_1', and so on. For this transformation, this becomes simply

$$\begin{array}{ll} \eta_1'=\eta_3 & \eta_4'=\eta_6 \\ \eta_2'=\eta_1 & \eta_5'=\eta_4 \\ \eta_3'=\eta_2 & \eta_6'=\eta_5. \end{array}$$

TABLE XI. Effect of the elements of symmetry upon the third-order elastic constants.

Trigonal symmetry 4 axes	Diagonal symmetry 3 axes	Tetragonal symmetry 3 axes
$C_{111}=C_{222}=C_{333}$	C_{111}	C_{111}
$C_{112}=C_{133}=C_{223}$	C_{112}	C_{112}
$C_{113}=C_{332}=C_{122}$	C_{113}	$=C_{112}$
$C_{114}=C_{225}=C_{336}$	$=0$	
$C_{115}=C_{226}=C_{334}$	$=0$	
$C_{116}=C_{224}=C_{335}$	$=0$	
$C_{444}=C_{555}=C_{666}$	$=0$	
$C_{445}=C_{664}=C_{556}$	$=0$	
$C_{446}=C_{665}=C_{554}$	$=0$	
$C_{124}=C_{136}=C_{235}$	$=0$	
$C_{125}=C_{134}=C_{236}$	$=0$	
$C_{126}=C_{135}=C_{234}$	$=0$	
$C_{144}=C_{366}=C_{255}$	C_{144}	C_{144}
$C_{244}=C_{166}=C_{355}$	C_{166}	C_{166}
$C_{344}=C_{266}=C_{155}$	C_{155}	$=C_{166}$
$C_{145}=C_{364}=C_{256}$	$=0$	
$C_{146}=C_{356}=C_{245}$	$=0$	
$C_{156}=C_{345}=C_{246}$	$=0$	
C_{123}	C_{123}	C_{123}
C_{456}	C_{456}	C_{456}
Non-zero distinct constants 20	8	6

Now the free energy must possess the same form with respect to the new axes as to the old; thus we must have

$$C_{111}\eta_1^3+C_{112}\eta_1^2\eta_2+\cdots=C_{111}\eta_1'^3+C_{112}\eta_1'^2\eta_2'+\cdots,$$

the C's being necessarily the same on both sides. Substitution for the η_{rs}' of their values in terms of η_{rs}, as given above, leads to equalities among the C's. By this process, the 56 constants are reduced to 20, as shown in Table XI.

In addition to the trigonal symmetry, all 5 isometric classes possess digonal symmetry about the 3 cubic axes. The corresponding transformation scheme for rotation of 180° about the X_3 axis is:

$$\begin{array}{c|ccc} & X_1' & X_2' & X_3' \\ \hline X_1 & -1 & 0 & 0 \\ X_1 & 0 & -1 & 0 \\ X_3 & 0 & 0 & 1\ , \end{array}$$

so that

$$\begin{array}{ll} \eta_1'=\eta_1 & \eta_4'=-\eta_4 \\ \eta_2'=\eta_2 & \eta_5'=-\eta_5 \\ \eta_3'=\eta_3 & \eta_6'=\ \ \eta_6. \end{array}$$

Application of this transformation, taking into account the equalities already found, gives, for example, $C_{114}\eta_1^2\eta_4=-C_{114}\eta_1^2\eta_4$, and hence $C_{114}=0$. By this process, the 20 constants are reduced to a maximum of 8.

Finally, for two of the classes, the cubic axes are axes of tetragonal symmetry. For a rotation of 90°, we have the typical scheme

$$\begin{array}{c|ccc} & X_1' & X_2' & X_3' \\ \hline X_1 & 0 & -1 & 0 \\ X_2 & 1 & 0 & 0 \\ X_3 & 0 & 0 & 1 \end{array},$$

leading to

$$\begin{aligned} \eta_1' &= \eta_2 & \qquad \eta_4' &= -\eta_5 \\ \eta_2' &= \eta_1 & \eta_5' &= \eta_4 \\ \eta_3' &= \eta_3 & \eta_6' &= -\eta_6. \end{aligned}$$

We find two additional equalities, $C_{112}=C_{113}$, and $C_{155}=C_{166}$; the number of constants is thus reduced to 6. This is the minimum obtainable from considerations of symmetry alone, although further reduction may result from special assumptions about lattice structure and forces, as Born and Misra have shown.