

ever seen at any voltage. That breakdown within the electrode system actually occurred was evident in many cases by direct visual observation, although the precise location of a given discharge could seldom be determined.

From the data given herein it seems reasonable to conclude that the initiating mechanism of high-voltage electrical breakdown *in vacuo* is not a process whereby charged particles reproduce themselves by a series of secondary chain reactions involving electrons striking the anode, with an efficiency which depends continuously on voltage and which rises to unity at breakdown. Note that no direct statement can be made about chain reactions not involving electrons, as, for instance, a positive ion-negative ion reaction, for which in one case over-all efficiencies as high as one percent have been

observed.⁷ Aside from the latter type of reaction, the mechanisms left as possibilities appear to be those triggered by random events originating within or without the gap, such as electrostatically detached clumps,⁸ excitation from some external source, e.g., cosmic rays, or cumulative resistive heating at field-emitting points of high-current density.²

ACKNOWLEDGMENTS

The writer wishes to thank Dr. E. J. Sternglass, who suggested the possibility of using the method of this paper as a test for the photoelectric chain reaction efficiency, and Dr. R. L. Longini (both of these Laboratories) for discussions and criticism which made this work possible.

⁷ M. Inghram, University of Chicago (private communication).

Temperature-Dependent Equations of State of Solids

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(Received July 10, 1957)

An isothermal equation of state of a solid is considered, which contains as special cases the equations of Birch, Murnaghan, Bardeen, and others. The equation is generalized to arbitrary temperature by replacing two constants of the equation by temperature-dependent parameters, whose functional form is determined by considerations of thermodynamic consistency. The thermal properties of the solid implied by this equation of state are examined. It is shown that the generalized equation is consistent with the Mie-Grüneisen relation for the thermal pressure of the lattice, and that the corresponding Grüneisen parameter is only slightly dependent on temperature, in general. The form of the generalized equation of state at low temperature is exhibited as an explicit function of volume and temperature for a solid whose heat capacity obeys the Debye law. A comparison with pressure-volume data of Swenson for potassium at low temperatures shows excellent agreement of the generalized equation of state with experiment.

I. INTRODUCTION

SINCE the time of Murnaghan's successful application of the theory of finite strain to obtain equations of state for solids at high pressure,¹⁻³ considerable attention has been devoted to the general problem he initiated. Additional equations of state have been derived by later investigators from Murnaghan's formulation of the theory of finite strain.⁴⁻⁷ The salient example is perhaps the equation of Birch,⁵ which has been used very successfully to represent pressure-volume relations for solids, at large pressures⁸ and at

constant temperatures extending to low values.⁹ The relation has been used widely in geophysical applications, for extrapolation of compression data for elements and compounds beyond the experimental range, and in the inference of physical properties of the earth's interior.^{8,10,11} Murnaghan's equation has been applied in a discussion of the effect of shock waves on solids.¹²

A wider development has proceeded in the derivation of equations of state of solids from quantum mechanics and from lattice models. As an example among many in the former class, one can cite Bardeen's equation.¹³ In principle, the limitations on accuracy in the quantum-mechanical calculation of an equation of state are set only by mathematical complication in the solution of

¹ F. D. Murnaghan, *Am. J. Math.* 59, 235 (1937).

² F. D. Murnaghan, in *Applied Mechanics, Theodore von Kármán Anniversary Volume* (California Institute of Technology, Pasadena, 1941), p. 121.

³ F. D. Murnaghan, *Finite Deformation of an Elastic Solid* (John Wiley and Sons, Inc., New York, 1951), Chap. 4.

⁴ F. Birch, *J. Appl. Phys.* 9, 279 (1938).

⁵ F. Birch, *Phys. Rev.* 71, 809 (1947).

⁶ A. Keane, *Nature* 172, 117 (1953); *Australian J. Phys.* 7, 322 (1954).

⁷ Y. Shimazu, *J. Phys. Earth* 2, 55 (1954).

⁸ F. Birch, *J. Geophys. Research* 57, 227 (1952).

⁹ C. A. Swenson, *Phys. Rev.* 99, 423 (1955).

¹⁰ L. Knopoff and R. J. Uffen, *J. Geophys. Research* 59, 471 (1954).

¹¹ J. J. Gilvarry, *Nature* 178, 1249 (1956); *J. Atmospheric and Terrest. Phys.* 10, 84 (1957).

¹² G. E. Duvall and B. J. Zwolinski, *J. Acoust. Soc. Am.* 27, 1054 (1955).

¹³ J. Bardeen, *J. Chem. Phys.* 6, 372 (1938).

Schrödinger's equation for a many-body problem. In practice, the necessary approximations generally limit the validity of a result to a particular class of elements (the alkali metals in the case of Bardeen's equation). As a consequence, equations of state derived from the theory of finite strain generally have the advantage of applicability to a wider range of elements and compounds than is possible for those obtained from quantum mechanics (or from a lattice model). These statements do not apply, of course, to the range of extremely high pressure (greater than a limit in the order of megabars) where use can be made reliably of the methods of quantum-statistical mechanics,¹⁴ as represented by the statistical atom model of Thomas and Fermi.

In applications of Birch's equation and others of similar type, the restriction of validity to isothermal conditions is a serious shortcoming, since any temperature correction must be estimated separately. For this purpose, the Mie-Grüneisen equation of state for the thermal pressure of the lattice,¹⁵ or the specific form of this relation corresponding to the Debye model,¹⁶ has been used in a number of geophysical discussions.^{7,8,10,17} This method is the one used by Walsh and co-workers to determine the effect of temperature on Hugoniot curves obtained by measurements on shock waves in solids, and thus to obtain isothermal equations of state experimentally.^{18,19}

The purpose of this paper is to determine by a thermodynamic argument the modification produced by variable temperature in a general class of isothermal equations of state. Special cases include the equations of Birch and others. The explicitly temperature-dependent equation of state will be shown consistent with the Mie-Grüneisen relation for the thermal pressure of the lattice.

II. ISOTHERMAL EQUATIONS OF STATE

In another context, the author has given an isothermal equation of state for a solid, which can be expressed as

$$P = (n-m)^{-1}K_0[(V_0/V)^n - (V_0/V)^m], \quad (1)$$

where P is the pressure corresponding to the volume V , K_0 is the bulk modulus corresponding to the normal volume V_0 , and n and m are constants.²⁰ The corresponding value of the bulk modulus (incompressibility) K is

$$K = (n-m)^{-1}K_0[n(V_0/V)^n - m(V_0/V)^m], \quad (2)$$

¹⁴ J. J. Gilvarry, Phys. Rev. 96, 934, 944 (1954).

¹⁵ J. C. Slater, *Introduction to Chemical Physics* (McGraw-Hill Book Company, Inc., New York, 1939), pp. 201, 222, 238, 394, 451.

¹⁶ C. Kittel, *Introduction to Solid State Physics* (John Wiley and Sons, Inc., New York, 1953), first edition, p. 80.

¹⁷ P. E. Valle, Ann. geofis. (Rome), 5, 41 (1952); 8, 189 (1955).

¹⁸ Walsh, Rice, McQueen, and Yarger, Phys. Rev. 108, 196 (1957).

¹⁹ Rice, McQueen, and Walsh, in *Solid State Physics* (Academic Press, Inc., New York, to be published).

²⁰ J. J. Gilvarry, Phys. Rev. 102, 331 (1956).

which verifies the identification of K_0 . For the purposes of this paper, the usefulness of Eq. (1) lies in the fact that it can be considered the generic member of a wide class of equations of state for solids at constant temperature.

If one assumes that

$$n=7/3, \quad m=5/3, \quad (3)$$

one obtains the Birch equation of state,

$$P = (3/2)K_0[(V_0/V)^{7/3} - (V_0/V)^{5/3}], \quad (4)$$

from Eq. (1). This equation was derived by Birch from Murnaghan's theory of finite strain, by assuming merely that the strain energy of an elastic body is proportional in first order to the square of the strain. The form (4) presupposes that a multiplicative correction of the form

$$1 - \xi[(V_0/V)^{2/3} - 1] + \dots \quad (5)$$

be taken as unity, where ξ is a temperature-dependent parameter which is small in general. A slightly different choice of exponents in Eq. (1) yields Bardeen's equation

$$P = 3K_0[(V_0/V)^{5/3} - (V_0/V)^{4/3}], \quad (6)$$

where again a factor of the order of unity has been ignored.¹³ The original derivation of this equation from quantum mechanics applies specifically to the alkali metals, but considerations by Gombas suggest the possibility of a wider application in the case of metals.²¹

The choice $m=0$ yields the equation of state

$$P = n^{-1}K_0[(V_0/V)^n - 1] \quad (7)$$

obtained by Murnaghan³ from the "integrated linear theory of finite strain." Murnaghan introduced the constant n empirically into the theory, and chose its value in special cases by a fit to the experimental data. The author has shown that this quantity can be interpreted physically as

$$n = 2\gamma_{AV} + \frac{1}{3}, \quad (8)$$

where γ_{AV} is an average value of the Grüneisen parameter γ of the solid over the range of interest on its $P-V$ diagram.²² If the Grüneisen parameter shows only small variation over the range in question, which is true in general for a relatively incompressible solid, γ_{AV} in Eq. (8) can be replaced by the value γ corresponding to the initial volume.²³ The special case of Eq. (7) for a vanishing value of the Grüneisen constant is

$$P = 3K_0[(V_0/V)^{\frac{1}{3}} - 1], \quad (9)$$

which is the form derived by Murnaghan from the linear theory of finite strain.³

The general form (1) includes also the equations of

²¹ P. Gombas, *Die Statistische Theorie des Atoms und ihre Anwendungen* (Springer-Verlag, Vienna, 1949), pp. 299-337.

²² J. J. Gilvarry, Phys. Rev. 102, 325 (1956).

²³ J. J. Gilvarry, Phys. Rev. 104, 908 (1956).

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Grüneisen,²⁴ Born,²⁵ and Fürth²⁶ corresponding to the Mie form for the potential energy U of an atom in the interatomic force field, given by

$$U = -A/r^{3(m-1)} + B/r^{3(n-1)}, \quad (10)$$

where r is the interatomic distance, and A and B are either interaction constants or lattice sums. In this case, the constants n and m are chosen either from theoretical considerations (e.g., to correspond to a Lennard-Jones potential) or from the requirement of a fit to thermodynamic parameters (such as the lattice energy) of the solid at normal pressure. To a large extent, these equations of state from lattice models have been supplanted for applications at high pressure by the forms discussed previously.

Some discussion of the relative merits of these various special forms of Eq. (1) is in order. Because of the generality of the underlying assumptions, one might expect Birch's equation of state to have a wide range of applicability, and such appears to be the case. The equation in the form (4) seems to reproduce the majority of Bridgman's experimental data on the isothermal equations of state of inorganic solids, within about the experimental uncertainty⁸ (exclusive of the occurrence of polymorphic phase transitions). In the case of the highly compressible alkali metals, for example, this statement appears true for normal temperature up to the limit of Bridgman's pressure measurements (about 10^5 bars, where, in the case of potassium, the fractional compression is about $\frac{1}{2}$). The fact that it contains only one disposable parameter, and fits such a wide range of data, makes Eq. (4) extremely useful.

On the other hand, use of Birch's equation entails some minor drawbacks at the lower pressures. For sufficiently low pressure, the equation of state of any solid can be described by the Bridgman equation

$$-(V - V_0)/V_0 = aP - bP^2, \quad (11)$$

where $a(=K_0^{-1})$ and b are constants.¹⁶ By means of the Lorentz-Slater relation^{15,22}

$$\gamma = -\frac{1}{2}(\partial \ln K / \partial \ln V)_T - \frac{1}{6} \quad (12)$$

for the Grüneisen constant as evaluated from compressibility parameters at fixed temperature T , one can obtain this constant for the solid at zero pressure as

$$\gamma = b/a^2 - \frac{2}{3}, \quad (13)$$

from the Bridgman equation. However, the Lorentz-Slater relation yields

$$\gamma = \frac{1}{2}(n + m - \frac{1}{3}), \quad (14)$$

²⁴ E. Grüneisen in *Handbuch der Physik* (Verlag Julius Springer, Berlin, 1926), Vol. 10, pp. 1-59.

²⁵ M. Born, *J. Chem. Phys.* 7, 591 (1939). The equation of state contains a temperature-dependent term which can be omitted for purposes of the present discussion.

²⁶ R. Fürth, *Proc. Roy. Soc. (London)* A183, 87 (1944). The equation of state contains a temperature-dependent term which can be omitted for purposes of the present discussion.

from Eq. (1), which corresponds to $\gamma = 11/6$ for the Birch equation. Unless the Grüneisen constant of the solid in question has this particular value, which corresponds to $2b/a^2 = 5$ from²⁷ Eq. (13), the Birch equation fails to yield the correct curvature of the $P-V$ curve at zero pressure. For the alkali metals, specifically, the Birch values for the Grüneisen constant and the parameter $2b/a^2$ seem definitely high, and the constant values from Bardeen's equation of 4/3 and 4, respectively, are closer to corresponding averages over these metals obtained by means of Grüneisen's law.²⁸ On the other hand, it can be noted that the average value of the Grüneisen constant over most solids has closely the Birch value, since Slater²⁹ has estimated the average value of the ratio $2b/a^2$ over most materials as 5. Finally, one can observe that the modified Murnaghan equation, with n evaluated in terms of γ by Eq. (8), can be reduced exactly to the Bridgman equation by means of Eq. (13) when the pressure is small. Thus, the equation of Murnaghan as modified by the author is capable of yielding identically the correct curvature of the $P-V$ curve of a solid at zero pressure.

One sees that the equations of Birch, of Murnaghan, and of Bardeen are subsumed under the general equation of state represented by Eq. (1). Various equations (or special cases thereof) treated by Gombas fall into the general class of Eq. (1) also.²¹ The temperature dependence of all these special forms can be obtained by determining the proper temperature dependence of Eq. (1).

III. GENERAL TEMPERATURE-DEPENDENT EQUATION

The special forms of Eq. (1) which have been discussed yield reasonable approximations to the pressure at fixed temperature, when the constants K_0 and V_0 correspond to the temperature in question. For all these forms, it is consistent with experimental results to assume that the exponents n and m are constants, and that the entire volume dependence of the pressure is contained in the powers V^{-n} and V^{-m} appearing. The former assumption for the case of Murnaghan's equation will be examined in Sec. IV. To generalize Eq. (1) to arbitrary temperature, it will be postulated that the constants V_0 and K_0 are replaced by parameters \mathcal{V} and \mathcal{K} , respectively, which are functions only of temperature (aside from dependence on constants fixed by an initial state).⁸ The generalization of Eq. (1) becomes

$$P = (n-m)^{-1} \mathcal{K} [(\mathcal{V}/V)^n - (\mathcal{V}/V)^m], \quad (15)$$

and that of Eq. (2) is

$$K = (n-m)^{-1} \mathcal{K} [n(\mathcal{V}/V)^n - m(\mathcal{V}/V)^m]. \quad (16)$$

²⁷ Birch has shown (reference 4) that the value $2b/a^2 = 5$ follows directly from certain approximations in the theory of finite strain.

²⁸ J. J. Gilvarry, *J. Chem. Phys.* 23, 1925 (1955).

²⁹ J. C. Slater, *Phys. Rev.* 57, 744 (1940).

The temperature dependence of \mathcal{U} and \mathcal{K} will be determined by considerations of thermodynamic consistency; dependence solely on temperature will be verified *a posteriori*.

Any valid equation of state, applicable for variable absolute temperature T , must conform to the thermodynamic identity

$$(\partial P/\partial T)_V = K\alpha, \quad (17)$$

where $K = -V(\partial P/\partial V)_T$ is the isothermal bulk modulus, and $\alpha = V^{-1}(\partial V/\partial T)_P$ is the volumetric coefficient of thermal expansion. Also, the equation must obey the relation

$$(\partial K/\partial T)_V = K'\alpha + K^2(\partial\alpha/\partial P)_T, \quad (18)$$

obtained by differentiation of Eq. (17), where

$$K' = -V(\partial K/\partial V)_T. \quad (19)$$

It is convenient to define a dimensionless parameter η by

$$\eta = -K\alpha^{-1}(\partial\alpha/\partial P)_T, \quad (20)$$

which ranges, numerically, from about 2 to perhaps 12 for different solids.⁸ By virtue of the identity

$$K^{-1}(\partial K/\partial T)_P = K(\partial\alpha/\partial P)_T, \quad (21)$$

one can write Eq. (18) as

$$(\partial K/\partial T)_V = (K' - K\eta)\alpha. \quad (22)$$

The general forms (15) and (16) will be required to meet the conditions of the two identities (17) and (22). This procedure corresponds to requiring that

$$P = -(\partial F/\partial V)_T,$$

where F is the Helmholtz function, rather than

$$P = -dE/dV,$$

where E is the energy; note that $(\partial P/\partial T)_V$ in Eq. (17) equals $(\partial S/\partial V)_T$, where S is the entropy.

On the assumptions made, differentiation of Eqs. (15) and (16) with respect to temperature to obtain $(\partial P/\partial T)_V$ and $(\partial K/\partial T)_V$, respectively, and substitution of the results into Eqs. (17) and (22) yield two linear algebraic equations in $\partial \ln \mathcal{U}/\partial T$ and $\partial \ln \mathcal{K}/\partial T$, whose solutions are

$$\partial \ln \mathcal{U}/\partial T = \alpha[K^2 + P(K\eta - K')]/(K^2 - PK'), \quad (23a)$$

$$\partial \ln \mathcal{K}/\partial T = -\eta\alpha K^2/(K^2 - PK'). \quad (23b)$$

One notes that these equations imply that \mathcal{U} and \mathcal{K} cannot depend solely on the temperature, as presupposed by the derivation [in the first instance, in the volume differentiation to obtain K of Eq. (16)]. It will be shown that, actually, \mathcal{U} and \mathcal{K} are each a function only of temperature, to a certain approximation.

For most solids, P is considerably smaller than K up to relatively high pressures, although K and K' are comparable, in general. By means of the binomial

theorem, one can write Eq. (23a) to first order in the ratio P/K as

$$\partial \ln \mathcal{U}/\partial T = \alpha(1 + \eta P/K). \quad (24)$$

Now, Birch has shown that the pressure dependence of $\alpha(T)$ at fixed temperature T is given approximately by⁸

$$\alpha = \alpha_0(1 - \eta_0 P/K), \quad (25)$$

where $\alpha_0(T)$ is the value of α at zero pressure and at temperature T , and $\eta_0(T)$ is the corresponding value of η . This equation is simply an approximate integral of the differential relation (20), but it agrees fairly well with Bridgman's experimental results on the change of thermal expansion (over the range 0–95°C) of the alkali metals with pressure up to the limit of measurement⁸ (about 2×10^4 bars). Hence, to first order in the ratio P/K , Eq. (24) becomes

$$d \ln \mathcal{U}/dT = \alpha_0(T), \quad (26)$$

where the right-hand side is a function of the temperature alone. The integral of this relation is

$$\mathcal{U} = V_0 \exp \int_{T_0}^T \alpha_0 dT, \quad (27)$$

where V_0 is the initial volume corresponding to the temperature T_0 and zero pressure.

By a binomial expansion, Eq. (23b) can be expressed as

$$\partial \ln \mathcal{K}/\partial T = -\eta\alpha(1 + K'P/K^2) \quad (28)$$

to first order in P/K . The partial derivative of η with respect to pressure at constant temperature can be obtained as

$$\eta^{-1}(\partial\eta/\partial P)_T = (K\eta + K')/K^2 - (K/\eta\alpha)(\partial^2\alpha/\partial P^2)_T, \quad (29)$$

from the definition (20). In this equation, the second derivative appearing can be neglected consistently with the approximation (25) of Birch. In this case, use of Birch's result (25) and the analogous approximate integral of Eq. (29) yields

$$\partial \ln \mathcal{K}/\partial T = -\eta_0\alpha_0(1 + 2K'P/K^2), \quad (30)$$

from Eq. (28). One can reduce this relation approximately to

$$\partial \ln \mathcal{K}/\partial T = -\eta_0\alpha_0[1 + 2(n+m)P/K] \quad (31)$$

for P small, by replacing the ratio K'/K by its limiting value $n+m$ for normal volume, as obtained from Eq. (2). In contrast to the case with \mathcal{U} , it is seen that \mathcal{K} can be dependent solely on temperature and the assumptions thus self-consistent, only in the limit $P \ll K$. Presupposing this limit, one can restrict the right-hand side of Eq. (31) to its leading term, and one obtains

$$\mathcal{K} = K_0 \exp \left[- \int_{T_0}^T \eta_0\alpha_0 dT \right], \quad (32)$$

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where η_0 and α_0 correspond to temperature T and pressure zero, and K_0 is the bulk modulus at temperature T_0 and at zero pressure.

Accordingly, Eqs. (27) and (32) yield for Eq. (1) the generalization

$$P = \frac{K_0}{n-m} \exp\left[-\int_{T_0}^T \eta_0 \alpha_0 dT\right] \times \left[\left(\frac{V_0}{V} \exp \int_{T_0}^T \alpha_0 dT\right)^n - \left(\frac{V_0}{V} \exp \int_{T_0}^T \alpha_0 dT\right)^m\right], \quad (33)$$

which exhibits the temperature dependence explicitly and reduces to Eq. (1) when the exponentials appearing are set equal to unity. This equation yields

$$(\partial P / \partial T)_V = K \alpha_0 - P \eta_0 \alpha_0 = K \alpha(T) \quad (34)$$

directly, which shows that $\alpha_0(T)$ must be taken as strictly independent of pressure; the pressure dependence of the thermal expansion demanded by Eq. (25) is taken into account by the exponential in P which involves $\eta_0 \alpha_0$. One concludes from Eq. (26) that the generalization (33) yields correctly the temperature dependence of the pressure through terms of first order in P/K as a parameter of smallness, but, from Eq. (31), that the temperature dependence of the bulk modulus is given correctly only to zero order in this parameter. Note that the role of the exponential involving $\eta_0 \alpha_0$ in Eq. (33) is to ensure that Eq. (17) be fulfilled at nonvanishing pressure; if this exponential be set equal to unity while the exponential involving only α_0 be retained, Eq. (17) is met only to zero order in the parameter P/K . Finally, the physical interpretations of the parameters \mathcal{U} and \mathcal{K} can be noted. From Eq. (27) and the definition of α_0 , it follows that $\mathcal{U}(T)$ is simply the volume of the solid at temperature T and at zero pressure. Equations (20) and (21) yield

$$\eta \alpha = -K^{-1}(\partial K / \partial T)_P, \quad (35)$$

and hence $\mathcal{K}(T)$ of Eq. (32) is the bulk modulus of the solid at temperature T and at zero pressure.

To this point, it has been assumed tacitly that states of the solid at zero pressure are observable at arbitrary temperature, since the coefficient α_0 of volume expansion must be determined experimentally. This condition is not met for a solid with a normal fusion curve, when the temperature exceeds the normal melting temperature. In this case, Birch's relation (25) must be replaced by

$$\alpha = \alpha_m \{1 - \eta_m [(P/K) - (P_m/K_m)]\}, \quad (36)$$

where $P_m(T)$ is the pressure, $K_m(T)$ is the bulk modulus, and $\alpha_m(T)$ and $\eta_m(T)$ represent values of α and η , respectively, all of which are measured for the

solid on the fusion curve at a given temperature T (and thus can be regarded as functions only of temperature). With this value of α , Eqs. (24) and (28) yield

$$\mathcal{U} = V_{m,0} \exp \int_{T_{m,0}}^T \left(1 + \eta_m \frac{P_m}{K_m}\right) \alpha_m dT, \quad (37a)$$

$$\mathcal{K} = K_{m,0} \exp \left[-\int_{T_{m,0}}^T \left(1 + \eta_m \frac{P_m}{K_m}\right) \eta_m \alpha_m dT\right], \quad (37b)$$

respectively, where $V_{m,0}$ and $K_{m,0}$ are the values of V and K , respectively, for the solid at the temperature $T_{m,0}$ for fusion under zero pressure; the paths of integration are along the fusion curve. The corresponding generalized equation of state is to be applied only for $P(T) \geq P_m(T)$. These forms for \mathcal{U} and \mathcal{K} can be reduced to those of Eqs. (27) and (32) by writing

$$\alpha = \alpha_m (1 + \eta_m P_m / K_m), \quad \eta_0 = \eta_m, \quad (38)$$

from Eq. (36), so that $\alpha_0(T)$ is the hypothetical value of α possessed by the solid if metastable below its fusion temperature at $P=0$. Substituting into Eqs. (37) the values of α_m and η_m implied by Eqs. (38), one can write

$$\mathcal{U} = V_{m,0} \exp \int_{T_{m,0}}^T \alpha_0 dT, \quad (39a)$$

$$\mathcal{K} = K_{m,0} \exp \left[-\int_{T_{m,0}}^T \eta_0 \alpha_0 dT\right], \quad (39b)$$

where the paths of integration correspond to zero pressure. Hence, \mathcal{U} and \mathcal{K} retain their physical interpretations as the volume and bulk modulus, respectively, of the solid at zero pressure for temperature T .

In the preceding, the parameters \mathcal{U} and \mathcal{K} have been written in exponential form for mathematical convenience. Only rarely does the accuracy with which α_0 and η_0 are experimentally known justify retention of terms beyond the first in the expansion of the exponential. To first order, $P(T)$ of Eq. (33) can be written as the sum of a temperature-dependent correction and the pressure $P(T_0)$ corresponding to the isothermal equation as

$$P = P(T_0) + \frac{K_0}{n-m} [n y^n - m y^m - \eta_0 (y^n - y^m)] \times \int_{T_0}^T \alpha_0 dT, \quad (40)$$

where $y = V_0/V$ (η_0 has been taken as a constant). At nonvanishing pressure, the first two terms in the brackets in this equation are dominant over the terms in parentheses with η_0 as coefficient, since the latter terms cancel for $V = V_0$. The relative smallness of the terms involving η_0 is advantageous, since this parameter is difficult to determine experimentally and

relatively accurate values are available in few cases. Grüneisen²⁴ and Birch⁸ provide tables of η for elements and some compounds.

As noted, the parameter ξ of the multiplicative correction (5) to the Birch equation as expressed in the form (4), has a value quite close to zero for very many (if not most) elements and compounds. When ξ does not vanish but is independent of temperature, it is clear from the derivation that the generalized relation (15) is valid within the approximations made, when multiplied by the correction factor (5). However, the experimental results of Swenson⁹ for the alkali metals at low temperature show that ξ depends on temperature when it does not vanish for these elements. But whether ξ depends on temperature or not, one notes that the generalized relation (15), when multiplied by the correction factor (5), reduces at any fixed temperature precisely to the general form of the isothermal Birch equation, because of the physical significance of the parameters \mathcal{U} and \mathcal{K} . Thus, no reason seems to exist why the generalized Birch equation should not be reliable for arbitrary temperature when the factor (5) is included and ξ depends on temperature. This statement should be true within the approximations entailed in Birch's derivation of the isothermal form, and implies that the difficulty raised by Eq. (31) in representing correctly the temperature dependence of K is a shortcoming of Birch's equation in the form (4), and not of the analysis employed here.

IV. THERMAL PROPERTIES OF THE SOLID

In this section, the salient thermal properties of the solid will be examined, as implied by the generalized equation of state. Inasmuch as $\xi=0$ for the majority of solids, the discussion will be restricted to this case for simplicity.

In the Mie-Grüneisen theory of the thermal pressure of a lattice, the total pressure P is expressed in terms of a volume-dependent pressure p and a thermal component P_T of pressure, by^{15,16}

$$P = p + P_T. \tag{41}$$

If the volume variation of all lattice frequencies ν_i is the same, so that the Grüneisen parameter γ can be defined by

$$\gamma = -(\partial \ln \nu_i / \partial \ln V)_T, \tag{42}$$

the basic result of the theory is

$$P_T = \gamma E_T / V, \tag{43}$$

where E_T is the thermal energy of the lattice.^{15,16} One obtains

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial P_T}{\partial T}\right)_V = \gamma \frac{C_V}{V} + \left(\frac{\partial \gamma}{\partial T}\right)_V \frac{E_T}{V} \tag{44}$$

directly, where C_V is the heat capacity of the solid at constant volume. The generalization (15) has been

required to meet Eq. (17) through terms of first order in P/K . To this order, therefore, for a solid to which the Mie-Grüneisen theory is applicable, the generalized equation of state satisfies

$$K\alpha = \gamma C_V / V + (\partial \gamma / \partial T)_V E_T / V, \tag{45}$$

which represents Grüneisen's law.

The usual statement of Grüneisen's law differs from Eq. (45) by omission of the term involving $(\partial \gamma / \partial T)_V$, in conformity with Grüneisen's postulate that the lattice frequencies are a function only of the volume.^{15,24} When this hypothesis is not satisfied, the general form (45) follows from the fundamental result (43). By use of the Lorentz-Slater formula (12), one obtains

$$\gamma = \frac{1}{2} \frac{n^2(\mathcal{U}/V)^n - m^2(\mathcal{U}/V)^m}{n(\mathcal{U}/V)^n - m(\mathcal{U}/V)^m} \frac{1}{6} \tag{46}$$

as the Grüneisen parameter corresponding to the generalization (15) of the isothermal equation of state. In general, this expression for γ depends on the temperature through the parameter \mathcal{U} (although it does not involve \mathcal{K}). However, it has been noted that $V = \mathcal{U}$ for zero pressure. Hence, Eq. (46) yields the result that γ at any temperature has the strictly constant value given by Eq. (14), if the pressure is zero. In this case, the last term in the form (45) of Grüneisen's law vanishes. Therefore, Grüneisen's postulate is satisfied for zero pressure.

To discuss the temperature dependence of γ for nonvanishing pressure, it is convenient to make use of the volume v possessed by the solid at zero temperature, rather than the actual volume V . These two quantities are related to each other at the same pressure by

$$V = v \exp \int_0^T \alpha dT. \tag{47}$$

The bulk modulus K will be written in a form corresponding to Eq. (41), as

$$K = k + K_T, \tag{48}$$

where k (like p in this case) depends only on v , and K_T (like P_T) is a temperature-dependent component. If the exponentials in Eqs. (27) and (32) are expanded to first order, and Birch's approximation (25) is used, γ of Eq. (46) can be written to first order as

$$\gamma = \gamma_0 - \left[\frac{d\gamma_0}{d \ln v} \int_0^T \eta_0 \alpha_0 dT \right] \frac{p}{k}, \tag{49}$$

where

$$\gamma_0 = \frac{1}{2} \frac{n^2(v_0/v)^n - m^2(v_0/v)^m}{n(v_0/v)^n - m(v_0/v)^m} \frac{1}{6} \tag{50}$$

and

$$\frac{d\gamma_0}{d \ln v} = \frac{1}{2} \frac{nm(n-m)^2(v_0/v)^{n+m}}{[n(v_0/v)^n - m(v_0/v)^m]^2} \tag{51}$$

depend on pressure. only of v term in p/k , can Eq. (15) pressure in practice who use the usual function approximations for P small

The equation and temperature of solid objects at temperature last term the usual temperature dependence becomes when one of the volume Eqs. (4) expressions

where R in the lattice for the Debye temperature.¹⁵ C

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$\mathcal{K} = k_0 [$

where K tively, derivative is given follows

depend only on the ratio of v to its value v_0 at zero pressure. It follows that γ at low pressure is a function only of v to the extent that the temperature-dependent term in Eq. (49), which is proportional to the ratio p/k , can be neglected. Accordingly, the prescription of Eq. (15) for including the effect of temperature on the pressure should yield approximately the same results in practice as the method of Walsh and associates,^{18,19} who use the Mie-Grüneisen relation (43) directly, on the assumption that the Grüneisen parameter is a function only of the volume v . It follows also that the approximate constancy assumed for the Murnaghan exponent n of Eq. (8) represents a consistent assumption for P small.

The equation of state as an explicit function of volume and temperature can be found from Eq. (15) for a solid obeying the Debye theory at sufficiently low temperature. In this case, C_V and E_T vary with temperature as T^3 and T^4 , respectively, and thus the last term can be ignored in Eq. (45), which reduces to the usual form of Grüneisen's law. Hence, the temperature dependence of the coefficient α of thermal expansion becomes the same as that of the heat capacity C_V , when one neglects the small temperature dependence of the Grüneisen parameter, the bulk modulus, and the volume (under isobaric conditions) specified by Eqs. (49), (48), and (47), respectively. The Debye expression for the heat capacity is

$$C_V = (12\pi^4/5)NR(T/\Theta)^3, \quad (52)$$

where R is the gas constant, N is the number of moles in the solid, and Θ (proportional to the maximum lattice frequency and thus a function of volume) is the Debye temperature in the limit of zero temperature.¹⁵ Grüneisen's law yields

$$\alpha = (12\pi^4/5)NR(\gamma_0/kv)(T/\Theta)^3, \quad (53)$$

where γ_0 is given by Eq. (50). Expressing the pressure differentiation in the definition (20) of η in terms of one with respect to the volume v , one obtains

$$\eta = 5\gamma_0 - \frac{2}{3} + d \ln \gamma_0 / d \ln v \quad (54)$$

by using Eqs. (42) and (53); the derivative appearing corresponds to that of Eq. (51). Hence, for a Debye solid at low temperature, the parameters \mathcal{U} and \mathcal{K} can be written through first-order terms in the exponentials involved, as

$$\mathcal{U} = v_0 [1 + (3\pi^4/5)NR(\gamma_0/k_0v_0)T^4/\Theta_0^3], \quad (55a)$$

$$\mathcal{K} = k_0 \left[1 - \pi^4 NR \left(3\gamma_0 - \frac{2}{3} + \frac{d \ln \gamma_0}{d \ln v} \right) \left(\frac{\gamma_0}{k_0 v_0} \right) \frac{T^4}{\Theta_0^3} \right], \quad (55b)$$

where k_0 and Θ_0 represent values of k and Θ , respectively, evaluated at $v=v_0$, to which point γ_0 and the derivative appearing also correspond. The value of γ_0 is given by Eq. (14), and the value of the derivative follows as

$$d \ln \gamma_0 / d \ln v = nm(n+m-\frac{1}{3})^{-1}, \quad (56)$$

from Eq. (51). Substitution of the results of Eqs. (55) into Eq. (15) yields the explicitly temperature-dependent equation of state. It is seen that the thermal component P_T of pressure varies as T^4 in this limit.

The results obtained can be applied to the case of an ideal harmonic solid which, because of the absence of anharmonicity of the lattice vibrations, shows no thermal pressure and no thermal expansion. In this case, the lattice frequencies are strict constants, so that the Grüneisen constant γ vanishes. It is clear from Eq. (46) or Eq. (51) that γ can be constant only if at least one of the exponents n and m vanishes. Selecting $m=0$, one obtains $\gamma = \frac{1}{2}(n - \frac{1}{3})$, which vanishes only for $n = \frac{1}{3}$. In the general case, \mathcal{U} and \mathcal{K} of Eqs. (27) and (32) can be independent of the temperature only for α_0 equal to zero, and this value of α_0 follows from Grüneisen's law (45) when γ vanishes. For the Debye model, Eqs. (55) show that \mathcal{U} and \mathcal{K} reduce to v_0 and k_0 , respectively, for γ_0 equal to zero. Hence, the entire development is consistent with the expression

$$P = 3k_0[(v_0/v)^{\frac{1}{3}} - 1] \quad (57)$$

for the equation of state of an ideal harmonic solid, as established previously by the author for this case.²² This equation corresponds to Eq. (9), derived by Murnaghan from the linear theory of finite strain.

As noted, the generalized equation of state predicts that the Grüneisen parameter should be independent of temperature at zero pressure. On this point, direct evidence from experimental data for temperatures higher than normal is available from values of γ computed by Birch for compounds⁸ and by the author for elements.³⁰ The results of the author show no more than a small or moderate decrease, in general, of the parameter over the range of temperature from normal to the fusion point; the decrease might be interpreted as a consequence of anharmonicity, since the temperatures involved exceed the Debye temperature, in general. For low temperature, the experimental evidence is conflicting. In this case, Bijl and Pullan found an anomalously large decrease relative to its normal value in the parameter for copper,³¹ but Figgins *et al.* observed an increase for aluminum.³² However, Baluffi and Simmons recently have reported measurements of the thermal expansion of copper from 102° down to 8°K, and have concluded that no evidence exists for a real variation of γ in this temperature range.³³ Their results are in agreement with those of Rubin *et al.*³⁴ for temperatures down to about 110°K. These considerations tend to justify the assumption that the exponent n of Murnaghan's Eq. (7) with n evaluated

³⁰ J. J. Gilvarry, Phys. Rev. 102, 308 (1956).

³¹ D. Bijl and H. Pullan, Physica 21, 285 (1955).

³² Figgins, Jones, and Riley, Phil. Mag. 1, 747 (1956).

³³ R. W. Baluffi and R. O. Simmons, Bull. Am. Phys. Soc. Ser. II, 2, 137 (1957).

³⁴ Rubin, Altman, and Johnston, J. Am. Chem. Soc. 76, 5289 (1954).

from Eq. (8) in terms of γ_w or γ , is at least approximately independent of volume and temperature.

One notes that Eq. (51) predicts a positive value of $d\gamma_0/d \ln v$. On the basis of the Lindemann law, the author has shown that the curvature of the fusion curve can be normal in the sense of Bridgman only if $\gamma - \frac{1}{3} + d\gamma/d \ln V$ is positive for the solid at fusion³⁰; the sign of the derivative implied by Eq. (51) thus is consistent with this result. In a comparison with experiment of a form of Simon's semiempirical fusion equation obtained theoretically, the author has determined values of $d \ln(\gamma - \frac{1}{3})/d \ln V$ for the alkali metals.²⁰ The values are positive, consistently with Eq. (51), and are of the order implied by Eq. (56) for n and m chosen to correspond to the Birch equation.

It can be noted that the generalized equation of state obtained is concordant with, but is not restricted by, the validity of Grüneisen's law. This conclusion follows from the fact that the basic relation (17), to which the generalized equation of state conforms, is a thermodynamic identity independent of a model. For a metal at sufficiently low temperature, Grüneisen's law fails in the sense that the Grüneisen parameter requires a correction for the contribution of the electrons to the thermal pressure³⁵; for a similar reason, the law is generally not valid for a superconductor. In neither case should the generalization to arbitrary temperature involved in Eq. (15) fail to be applicable within the approximations made, if the form (4) is valid under isothermal conditions.

V. COMPARISON WITH EXPERIMENTAL DATA

Results of Swenson⁹ for the compression of the alkali metals at two temperatures (77 and 4.2°K) can be used to compare predictions of the generalized Birch equation with experiment. The element potassium will be chosen for the check, since the corresponding values of the parameter ξ of the correction factor (5) vanish at both temperatures.

Swenson expresses his results for the pressure as a function of compression by tabulating values of the density and the compressibility K_0^{-1} at zero pressure for the two temperatures in question, which fix the constants V_0 (for unit mass) and K_0 of the isothermal Birch equation as fitted to his data. The values of the latter pair of constants corresponding to the former are shown in the first two columns of Table I, for

TABLE I. Parameters of the generalized Birch equation of state for potassium, from data of Swenson.

T °K	V_0 cm ³ /g	K_0 10 ⁴ atmos	α_0 (°C) ⁻¹	$\eta_0 \alpha_0$ (°C) ⁻¹	η_0
77	1.09 ₂	3.38	0.0001 ₆	0.0003 ₇	2.4
4.2	1.08 ₁	3.47			

³⁵ S. Visvanathan, Phys. Rev. 81, 626 (1951); J. J. Gilvarry, Phys. Rev. 102, 317 (1956).

potassium at the two temperatures. On Swenson's definitions, V_0 and K_0 depend on the temperature; hence V_0 and K_0 represent values of \mathcal{V} and \mathcal{K} , respectively, in the notation of this paper. The pressure for potassium is shown in Fig. 1 as a function of the relative compression $(\mathcal{V}-V)/\mathcal{V}$ for the two temperatures, as computed from the isothermal Birch equation with constants from Table I.

The values of the parameters α_0 , $\eta_0 \alpha_0$, and η_0 for potassium are shown in the last three columns of Table I, as implied by the constants in the first two columns. Since these determinations correspond directly to the data of Swenson, it is clear that values at the two temperatures of \mathcal{V} and \mathcal{K} from Eqs. (27) and (32), respectively, merely reproduce the values of V_0 and K_0 in the first two columns of Table I. Thus, a substantive check of the generalized Birch equation cannot

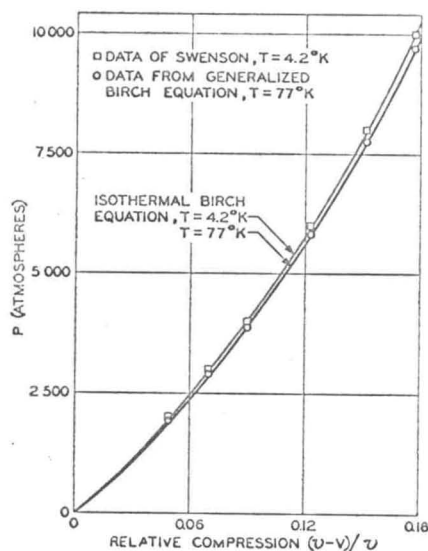


FIG. 1. Pressure as a function of the relative compression for potassium, as computed from the isothermal Birch equation with data from Table I, for comparison with data points at 77°K predicted by the generalized Birch equation from values at 4.2°K.

be obtained directly, since its form with parameters evaluated numerically for one of the two temperatures is simply the isothermal form with constants equal to those of Swenson.

However, Swenson tabulates smoothed experimental data for potassium at one temperature, 4.2°K. An independent check of the generalized Birch equation can be obtained by using it to predict pressures at 77°K from the tabular values for 4.2°K, given as a function of $(V_0 - V)/V_0 = (\mathcal{V} - V)/\mathcal{V}$. For a fixed value of the last quantity, Eq. (15) states that $P(T)$ is given in terms of $P(T_0)$ by

$$P(T) = [1 - \eta_0 \alpha_0 (T - T_0)] P(T_0). \tag{38}$$

Use of this equation with values of parameters from Table I to predict pressures at 77°K from those at 4.2°K yields excellent agreement with results from the

isothermal Birch equation shown in Fig. 1. The degree of agreement is shown in Fig. 2, where the difference between the two pressures is plotted as a function of relative compression. The difference is small, indicating excellent agreement between the two equations.

The degree of agreement is clearly by Fig. 2, where the difference between the two pressures is plotted as a function of relative compression. The difference is small, indicating excellent agreement between the two equations.

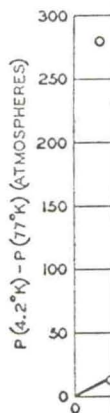


FIG. 2. Difference in pressure between 4.2 and 77°K as a function of relative compression, from Swenson's data and the generalized Birch equation. The difference is small, indicating excellent agreement between the two equations.

comparison of the results with Swenson's data and the generalized Birch equation.

It is clear that the results can be used directly to predict pressures at 77°K from those at 4.2°K, given as a function of relative compression. The difference is small, indicating excellent agreement between the two equations.

isothermal Birch equation at the higher pressures, as shown in Fig. 1. At the intermediate pressures, data points from Swenson's tabulation are high (by amounts up to 3%) with respect to the associated Birch curve; correspondingly, values from Eq. (58) are high also. Agreement improves for data points (not shown) at the lower pressures. Consistently with Eq. (58), the curve in Fig. 1 for 77°K lies below that for 4.2°K; this order reverses when P is plotted against V directly.

The degree of agreement obtained is exhibited more clearly by Fig. 2, which shows, for a given value of $(V-V_0)/V_0$, the difference $P(4.2^\circ\text{K}) - P(77^\circ\text{K})$ of the pressures at 4.2 and 77°K as computed from Swenson's data for 4.2°K by use of Eq. (58), and as determined from the isothermal Birch equation with Swenson's values of parameters. The difference found vanishes for two values of the abscissa, and is less than three percent at the highest datum point shown. This

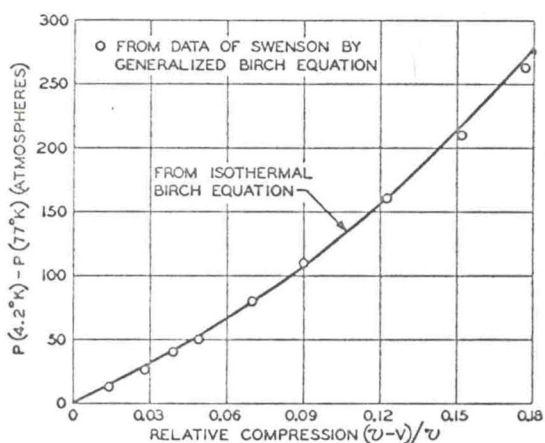


FIG. 2. Difference $P(4.2^\circ\text{K}) - P(77^\circ\text{K})$ of the pressures at 4.2 and at 77°K for a given relative compression, as computed from Swenson's data for 4.2°K by means of the generalized Birch equation, for comparison with values determined from the isothermal Birch equation with parameter values from Table I.

comparison is unaffected by the degree to which Swenson's data for 4.2°K are fitted by the isothermal Birch equation.

VI. CONCLUSION

It is clear from the comparison with Swenson's results that the generalized Birch equation can be used directly to fit experimental pressure-volume data corresponding to a range of temperature, as the isothermal equation has been used in the past for the case of fixed temperature.

For the range of high pressures greater than a limit in the order of megabars, the effect of shock waves on solids has been treated theoretically on the basis of a temperature-dependent equation of state from the statistical atom model.³⁶ This equation of state loses validity for the lower pressures, where it must be supplemented by a relation appropriate to this pressure range.¹² Use of the generalized Birch equation for this purpose permits an analysis at the lower pressures on lines analogous to those followed in the case of the Thomas-Fermi equation of state.³⁷ The problem in question is of interest in connection with the explosive impact of meteorites and the associated crater production.

The generalized Birch equation has an obvious application in studies of the earth's internal constitution, since it should be applicable at the pressures of the mantle, where one cannot use reliably an equation of state from the statistical atom model, as is possible (within an approximation) for the higher pressures of the core. Birch has used his equation of state to estimate the density in the earth's core, by extrapolation of experimental data of Bridgman, on the assumption that the core is iron.⁸ His result for the central density is about 20% higher than Bullen's value deduced from seismological data.³⁸ Of this discrepancy, Birch estimates that perhaps half may be due to the neglected effect of temperature. The generalized Birch equation may be of use in further study of this point.

ACKNOWLEDGMENTS

Thanks are due Mr. J. F. Britt for computational work. Critical discussions of the manuscript with Dr. W. S. Rothwell and Dr. C. W. Little, Jr., are acknowledged. Thanks are tendered to Dr. J. M. Walsh of Los Alamos Scientific Laboratory for the privilege of referring to manuscripts prior to publication.

Note added in proof.—It has been verified that the generalized relation (15), with the multiplicative correction factor (5) included for a given temperature, fits the data of Swenson⁹ for the alkali metals other than potassium. In this reference, the values of $\Delta V/V_0$ tabulated for cesium are incorrect because of a transcription error, although the corresponding contents given for the isothermal Birch equation are correct, as the author has been informed by Dr. Swenson.

³⁶ J. J. Gilvarry and J. E. Hill, *Publ. Astron. Soc. Pacific* 68, 223 (1956); *Astrophys. J.* 124, 610 (1956).

³⁷ J. J. Gilvarry, *J. Appl. Phys.* 27, 1467 (1956).

³⁸ K. E. Bullen, *Monthly Notices Roy. Astron. Soc. Geophys. Suppl.* 6, 50 (1950).

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