V. CONCLUSION

The results of this paper yield a practical method of determining the lattice corrections to thermodynamic functions computed on the Thomas-Fermi model. No attempt has been made to take account of the long-range order which may be present in the amorphous phase above the fusion temperature. Presumably, the existence of such order must introduce corrections to thermodynamic functions computed on the Thomas-Fermi model, analogous to the lattice corrections. Mott's theory of liquids[34] may provide an approach to such questions.

ACKNOWLEDGMENTS

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Equation of the Fusion Curve*

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A generalization of the Lindemann law given previously is used in conjunction with the Murnaghan equation of state for a solid to derive a law of reduced states for fusion, valid for the case of classical excitation of the lattice vibrations at melting. If the bulk modulus and volume of the solid at fusion and the melting temperature are reduced by dividing the quantity in question by its corresponding value at the origin of the fusion curve, any reduced variable of this set can be expressed as a power of any other, with an exponent involving a constant appearing in the Murnaghan equation. It is shown that the ratio of the latent heat to the volume change of fusion obeys a similar law of reduced states, on the basis of an assumed form of the volume dependence of the Grüneisen parameter of the solid along the fusion curve. The constant appearing in the Murnaghan equation of state is interpreted physically in terms of an average Grüneisen parameter of the solid. The law of reduced states yields an immediate derivation of the empirical Simon equation for the fusion curve. For the alkali metals, it is shown that experimental values of the temperature exponent in the Simon equation are quantitatively compatible with the theoretical evaluation given, and, furthermore, that the theory can predict approximate values of the exponent, in practice.

THE empirical equation[1]

$$\log(P_m+A)=B\log T_m+C, \tag{1}$$

where P_m and T_m are the fusion pressure and absolute temperature, respectively, and A, B, and C are disposable coefficients, has been proposed by Simon to represent the fusion curve. By evaluating the constant C at the triple point of temperature T_t (and negligible pressure), he has put the equation in the form

$$P_m=A[(T_m/T_t)^B-1] \tag{2}$$

for elements of low melting point; this form will be referred to as the Simon equation. If a reduced pressure P_m' and temperature T_m' are defined by P_m/A and T_m/T_t, respectively, Eq. (2) yields the Simon law,

$$P_m'=T_m'^B-1, \tag{3}$$

of corresponding states for fusion. This law is analogous to the law of corresponding states for a van der Waals gas, with the constant A and the triple-point temperature as reducing parameters corresponding to the critical pressure and temperature, respectively.

If the constants A and B are selected by trial, Eq. (2) yields a good fit to the observed melting curves of solids of low melting point. Values of the constants for various elements, as derived from experimental work prior to 1937, are tabulated (except for D_2)[2] by Ruhemann and Ruhemann.[3] Later work[4] has extended the pressure range over which the equation is applicable. The Simon exponent B is roughly 2 for most of the substances (He, H_2, Ne, N_2) of low melting point, except for A, for which it is somewhat over unity. For the alkali metals, T_t in Eq. (2) must be replaced by the normal melting temperature; reported values[5] of the exponent B are approximately 4. Values quoted for the Simon exponent by different authors frequently are fairly discrepant for the same element. Part of the variance is presumably due to the fact that a requirement merely of fit to the data does not necessarily

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[2] K. Clusius and E. Bartholomé, Z. physik. Chem. B30, 237 (1935).

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fix the parameters of a two-parameter curve uniquely, although Simon[6,7] has indicated the use of the initial slope of the fusion curve (or of Clapeyron's equation) to reduce Eq. (2) to a one-parameter curve.

Domb[8] has derived the Simon equation theoretically from the order-disorder fusion theory of Lennard-Jones and Devonshire,[9] for the range of moderately high pressure where a Lennard-Jones intermolecular potential is a sufficient approximation. His expression for the Simon exponent is $B=1+3/n$, where n (about 9 to 12) is the (negative) exponent of the repulsive term in the potential. A derivation from the same model has been given by de Boer[10]; he obtains the constant value 1.25 for the Simon exponent. Both these evaluations of the Simon exponent are somewhat too low to correspond to reported values for the elements of low melting point (except for argon), and they are definitely too low to correspond to published values for the alkali metals. Salter[11] has used the Lindemann law and the Debye equation of state to obtain a fusion equation identical in form with Simon's equation, with the exponent evaluated in terms of Grüneisen's constant for the solid. He notes that use of normal values of the Grüneisen constant in his expression yields values of the Simon exponent considerably below reported values for the alkali metals, but in reasonable accord for argon.

Recently, the author has given a generalized Lindemann law which may represent a basic criterion of fusion, at least for isotropic monatomic solids.[12] The generalization yields an experimentally verified relation connecting the Grüneisen constant of the solid at melting with fusion parameters, and explains the validity of an empirical relation of Kubaschewski.[13] The theory yields the conclusion that the fusion curve is determined by conjunction of the equation of state of the solid with the generalized Lindemann law. In this paper, it will be shown that, by selection of the Murnaghan equation of state[14] for the solid, the theory of I yields a fusion equation identical in form with Simon's equation and providing quantitative agreement with experiment for the alkali metals. The discussion presupposes that the normal vibrations of the solid at melting are classically excited, so that the quantization parameters Q_m and O_m of I are equal to unity and zero respectively. This limitation excludes cases (such as H_2, D_2, and He at low temperature) in which the zero-point energy at fusion is relatively large.

I. LAW OF REDUCED STATES

The equation of state of the solid will be taken as that derived by Murnaghan[14] from his "integrated linear theory" of finite strain. If P is the pressure corresponding to the volume V of the solid, this equation of state is

$$P=(\kappa_0/\eta)[(V_0/V)^\eta-1], \tag{4}$$

where κ_0 is the normal bulk modulus (incompressibility) corresponding to the normal volume V_0, and η is a constant. The bulk modulus κ of the solid follows as

$$\kappa=\kappa_0(V_0/V)^\eta. \tag{5}$$

By determining η empirically, Murnaghan has obtained an excellent fit of Bridgman's pressure-volume data on Na, for pressures up to 100 kilobars. The value obtained for η (and the corresponding κ_0) varies somewhat with the pressure range selected for direct fit. The largest relative deviations are found for the lowest pressures, which corresponds to the fact that Eq. (4) represents an approximation in the large (rather than an osculating approximation at the origin).

The bulk modulus κ_m of the solid at melting can be regarded as a function only of the corresponding volume V_m of the solid. Since the Murnaghan equation specifies κ, by Eq. (5), as a function only of the volume, application of this equation of state to the solid along the fusion curve is a legitimate approximation. Hence, Eq. (5) yields

$$\kappa_m/\kappa_{m,0}=(V_{m,0}/V_m)^\eta, \tag{6}$$

where $\kappa_{m,0}$ and $V_{m,0}$ are the values of κ_m and V_m, respectively, corresponding to the origin of the fusion curve. In principle, the parameter η should be determined from the pressure-volume relationship for the solid along the fusion curve; unfortunately, such data are not usually available from experiment for the elements of higher melting temperature (such as the alkali metals). Physical validity can be claimed for use of the Murnaghan equation of state for the solid at fusion only if values of η inferred from fusion curves are reasonably consonant with those obtained from experimental equations of state.

The Lindemann law for the case of classical excitation of the lattice vibrations at melting of a monatomic solid can be written

$$RT_m=\Omega\kappa_m V_m, \tag{7}$$

where R is the gas constant, T_m is the absolute melting temperature corresponding to the molar volume V_m, and Ω, defined in I, is a function of Poisson's ratio at fusion and of the Lindemann constant. Under the assumption of I that the fusion value of Poisson's ratio is a constant, use of Eq. (6) in Eq. (7) yields

$$T_m/T_{m,0}=(V_{m,0}/V_m)^{\eta-1}, \tag{8}$$

where $T_{m,0}$ is the temperature corresponding to the origin of the fusion curve. From this equation and

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[6] F. E. Simon, in *L. Farkas Memorial Volume* (Research Council of Israel, Jerusalen, 1952), p. 37.

[7] F. Simon, Nature **172**, 746 (1953).

[8] C. Domb, Phil. Mag. **42**, 1316 (1951).

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[11] L. Salter, Phil. Mag. **45**, 369 (1954).

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[14] F. D. Murnaghan, *Finite Deformation of an Elastic Solid* (John Wiley and Sons, Inc., New York, 1951), p. 70.

Eq. (6), one obtains

$$\kappa_m/\kappa_{m,0}=(T_m/T_{m,0})^b, \tag{9}$$

where

$$b=\eta/(\eta-1). \tag{10}$$

Equations (6), (8), and (9) yield a law of reduced states for fusion, in which the reducing parameter for κ_m, T_m, or V_m is the corresponding value at the origin of the fusion curve; any reduced variable can be expressed as a power of any other, with an exponent in terms of the Murnaghan parameter η. The law is referred to as one of reduced (rather than corresponding) states in accordance with Simon's nomenclature,[6] since the reducing parameters are not constant as in the law of corresponding states for a van der Waals gas. The relations are consistent with the Lindemann law (7) in the form

$$T_m/T_{m,0}=(\kappa_m/\kappa_{m,0})(V_m/V_{m,0}), \tag{11}$$

which presupposes that the Poisson ratio of the solid is constant along the fusion curve.

It is shown in I that the ratio of the latent heat L to the volume change ΔV of fusion is given by

$$L/\Delta V=q\kappa_m/2(\gamma_m-\tfrac{1}{3}), \tag{12}$$

where γ_m is the value of the Grüneisen parameter of the solid at the point (T_m,P_m) of the fusion curve, and q is a parameter defined in I. The quantity $\gamma_m-\frac{1}{3}$ can be regarded as a function only of the volume V_m of the solid at fusion. Its analytic dependence on V_m will be taken as

$$(\gamma_m-\tfrac{1}{3})/(\gamma_{m,0}-\tfrac{1}{3})=(V_m/V_{m,0})^\mu, \tag{13}$$

where $\gamma_{m,0}$ is the value of γ_m corresponding to the origin of the fusion curve, and μ is defined by

$$\mu=d\ln(\gamma_m-\tfrac{1}{3})/d\ln V_m, \tag{14}$$

analogously to the definition of γ_m in terms of the fusion value of the Debye frequency. On the assumption that μ is constant, its value can be inferred from the equation

$$d^2T_m/dP_m{}^2=-2(1+\mu)(\gamma_m-\tfrac{1}{3})T_m/q^2\kappa_m{}^2 \tag{15}$$

of I, as applied at the origin. The parameter q is of the order of unity, with the average value 1.2 over the elements discussed in I; it can be presumed for purposes of the present discussion that q shows only small variation over the fusion curve and can be assigned the constant value q_0 corresponding to the origin. Under these assumptions, use of Eqs. (6) and (13) in Eq. (12) yields the law

$$(L/\Delta V)/a=(V_{m,0}/V_m)^{\eta+\mu} \tag{16}$$

of reduced states for $L/\Delta V$, where the parameter a is defined by

$$a=q_0\kappa_{m,0}/2(\gamma_{m,0}-\tfrac{1}{3}). \tag{17}$$

By Eq. (12), the parameter a appearing as the reducing parameter for $L/\Delta V$ is equal to the value of the latter quantity at the origin. Bridgman has expressed opposition to the idea of a law of corresponding states for fusion,[15] since L and ΔV separately do not exhibit definite signs of such a law (except possibly for the alkali metals)[16]; note, however, that it is the ratio $L/\Delta V$ which obeys the law (16) of reduced states.

By means of Eq. (8), one can write Eq. (13) as

$$(\gamma_m-\tfrac{1}{3})/(\gamma_{m,0}-\tfrac{1}{3})=(T_{m,0}/T_m)^\beta, \tag{18}$$

where

$$\beta=\mu/(\eta-1). \tag{19}$$

Similarly, the law (16) of reduced states for $L/\Delta V$ can be written

$$(L/\Delta V)/a=(T_m/T_{m,0})^B, \tag{20}$$

in which

$$B=b+\beta=(\eta+\mu)/(\eta-1), \tag{21}$$

where b is defined by Eq. (10). It is clear that any reduced variable corresponding to the set κ_m, V_m, T_m, $\gamma_m-\frac{1}{3}$, and $L/\Delta V$ can be expressed as a power of any other.

Equation (13) demands that the Grüneisen parameter γ_m of the solid be a variable along the fusion curve. The Murnaghan parameter η appearing in Eq. (6) can be interpreted in terms of an average value $\gamma_{m,\mathrm{Av}}$ of the Grüneisen parameter γ_m over the fusion curve, by means of the equation

$$\gamma_m=-\tfrac{1}{6}-\tfrac{1}{2}d\ln\kappa_m/d\ln V_m, \tag{22}$$

given in I. Application of this equation to Eq. (6) corresponding to the Murnaghan equation yields

$$\gamma_{m,\mathrm{Av}}=\tfrac{1}{2}(\eta-\tfrac{1}{3}). \tag{23}$$

Note that this identification in terms of an average Grüneisen constant yields a physical interpretation of the Murnaghan parameter η (introduced as an empirical constant in the integrated linear theory of finite strain) which applies in general and not merely at fusion.

It has been emphasized that the Murnaghan equation of state represents an approximation in the large for the equation of state along the fusion curve. If the Murnaghan parameter η is chosen by fitting the pressure-volume curve over a small range of pressure near the origin of the fusion curve, one must obtain

$$\eta_0=2\gamma_{m,0}+\tfrac{1}{3} \tag{24}$$

for η in terms of the Grüneisen parameter at the origin, as follows from Eq. (22) or Eq. (23). In this case, Eqs. (6) and (8) can be written

$$\kappa_m=\kappa_{m,0}(V_{m,0}/V_m)^{2\gamma_{m,0}+1/3}, \tag{25a}$$

$$T_m=T_{m,0}(V_{m,0}/V_m)^{2(\gamma_{m,0}-1/3)}, \tag{25b}$$

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[15] P. W. Bridgman, Revs. Modern Phys. 7, 1 (1935).

[16] P. W. Bridgman, *The Physics of High Pressure* (G. Bell and Sons, Ltd., London, 1949), p. 211.

respectively, and Eq. (9) becomes

$$\kappa_m = \kappa_{m,0}(T_m/T_{m,0})^{b'}, \tag{26}$$

where

$$b' = (6\gamma_{m,0}+1)/[2(3\gamma_{m,0}-1)]. \tag{27}$$

The three equations (25a) (25b), and (26) are valid only as osculating approximations at the origin; by means of Eq. (23), one can show that they differ only in the substitution of $\gamma_{m,0}$ for $\gamma_{m,\mathrm{Av}}$ from their correspondents in the large, Eqs. (6), (8), and (9), respectively.

These osculating approximations are derivable directly from the Grüneisen postulate that the Debye frequency, in general, is a power-law function only of the volume; if ν_m is the Debye frequency of the solid at melting, this assumption yields the expression

$$\nu_m = G/V_m^{\gamma_{m,0}}, \tag{28}$$

where G is a constant, for ν_m in the neighborhood of the origin of the fusion curve. The Debye frequency of a monatomic solid at melting is given likewise by

$$\nu_m = s_m N^{1/3} M^{-1/2} \kappa_m^{1/2} V_m^{1/6}, \tag{29}$$

where M is the atomic weight, N is Avogadro's number, and s_m is a function, defined in I, of the value of Poisson's ratio of the solid at melting. On the assumption of I that the Poisson ratio at fusion is constant, comparison of Eqs. (28) and (29) yields Eq. (25a). Equation (25b) and thus Eq. (26) then follow directly from Eq. (7), or from the identification $\nu_m = \nu_L$, where ν_L is the Lindemann frequency defined in I.

II. SIMON EQUATION

The general result,

$$dP_m/dT_m = q\kappa_m/2(\gamma_m - \tfrac{1}{3})T_m, \tag{30}$$

for the slope of the fusion curve has been obtained in I. If q is given the constant value q_0 corresponding to the origin, integration of this equation with use of Eqs. (9) and (18) yields

$$P_m - P_{m,0} = (a/B)[(T_m/T_{m,0})^B - 1], \tag{31}$$

where $P_{m,0}$ is the pressure corresponding to the origin of the fusion curve, a is given by Eq. (17), and B is defined by Eq. (21). Equation (31) has precisely the form, with $A = a/B$, of the Simon equation (2) (except for the introduction of the constant $P_{m,0}$ of integration to make both sides of the equation vanish together at the origin). The equation assumes a reduced form, analogous to Eq. (20) for $L/\Delta V$, if the left-hand side is rewritten as $(P_m - P_{m,0})/a$.

Equation (31) of the fusion curve yields the correct initial slope demanded by Eq. (30), and the correct initial value a of the ratio $L/\Delta V$ required by Eq. (12); thus Clapeyron's equation is satisfied at the origin, independently of the value of the Simon exponent B. As has been pointed out, the parameter μ of Eq. (14), which corresponds to the volume variation of $\gamma_m - \frac{1}{3}$ and enters B through β of Eq. (19), can be evaluated by application at the origin of Eq. (15) for d^2T_m/dP_m^2. In this case, it follows that Eq. (31) yields the correct curvature of the fusion curve at the origin corresponding to Eq. (15); note, however, that this equation has been derived in I on the assumption that q is constant.

The derivation of Simon's equation given by Salter,[11] based on the Debye equation of state, assumes that the Grüneisen parameter has a constant value. His result is essentially

$$P_m - P_{m,0} = A[(T_m/T_{m,0})^{b'} - 1], \tag{32}$$

where A is specified only as a constant and b' is defined by Eq. (27). Since the exponent b of Eq. (10) can be written in terms of the average Grüneisen parameter of Eq. (23) as

$$b = (6\gamma_{m,\mathrm{Av}}+1)/[2(\gamma_{m,\mathrm{Av}}-1)], \tag{33}$$

it follows that Salter's evaluation of the Simon exponent corresponds to substituting $\gamma_{m,0}$ for $\gamma_{m,\mathrm{Av}}$ in b and taking $\beta = 0$ (corresponding to $\mu = 0$) in Eqs. (21) for B.

Equation (30) for dP_m/dT_m is susceptible to a physical interpretation. If one writes the parameter q, in a form deducible from results of I, as

$$q = (1 - \kappa_m\alpha_m dT_m/dP_m)^{-1}, \tag{34}$$

in which α_m is the coefficient of volume expansion of the solid at fusion, substitution of this expression into Eq. (30) yields

$$dP_m/dT_m = \kappa_m/2(\gamma_m - \tfrac{1}{3})T_m + \kappa_m\alpha_m. \tag{35}$$

The second term on the right-hand side of this equation is given by Grüneisen's law as

$$\kappa_m\alpha_m = \gamma_m C_{V,m}/V_m = [(\partial P/\partial T)_V]_m, \tag{36}$$

where $C_{V,m}$ is the heat capacity of the solid at fusion, and the subscript m on the last term designates evaluation of the partial derivative for the solid on the fusion curve. Hence, the second term in Eq. (35) for dP_m/dT_m corresponds to the increment in thermal pressure of the lattice as T_m is increased. Thus, the assumption $q = q_0$ made in deriving Eqs. (20) and (31) corresponds to the postulate that $[(\partial P/\partial T)_V]_m$ bear a constant ratio to the total derivative dP_m/dT_m along the melting curve. From the fact that

$$dP_m/dT_m = [(\partial P/\partial V)_T]_m dV_m/dT_m + [(\partial P/\partial T)_V]_m, \tag{37}$$

it follows that

$$[(\partial P/\partial V)_T]_m dV_m/dT_m = \kappa_m/2(\gamma_m - \tfrac{1}{3})T_m. \tag{38}$$

Hence, the first term in Eq. (35) for dP_m/dT_m corresponds to the increment, as T_m and thus V_m is changed, of that part of the pressure which depends directly on the volume, that is, the pressure corresponding (for low or moderate compression) to the potential energy of an atom in the interatomic force field. Salter's derivation of the Simon equation assumes that this term is constant; thus he obtains the correct form of the exponent b' of Eq. (27) in terms of $\gamma_{m,0}$ but fails to obtain the analog of the expression a/B corresponding to the Simon coefficient.

Simon[1] has shown that the coefficient A of Eq. (2) is of the order of the internal pressure of the solid. Approximate numerical consistency of this result with the evaluation of the Simon coefficient given here can be shown by means of Grüneisen's law and an expression[7] for the internal pressure from the Grüneisen theory of solids.

III. COMPARISON WITH EXPERIMENT

In this section, the preceding theory will be compared with Bridgman's experimental results[17] on the fusion curves of the alkali metals Cs, Rb, K, and Na, extending over pressure ranges up to 12 kilobars; the element Li will be ignored, since Bridgman's measurements were made on a somewhat impure sample.[18] To make a comparison of Eq. (20) and of Eq. (31) with the data, values of $\kappa_{m,0}$ entering the reducing parameter a are available from Table I of I. Values of $\gamma_{m,0}$ from Eq. (12), and of q_0 from Eq. (31) of I, are shown in Table I, as evaluated to correspond to Bridgman's experimental values of L and ΔV at the normal melting point; the values of $\gamma_{m,0}$ given for the alkali metals in Table V of I correspond to data for L and ΔV from other sources. The third entry of Table I is the parameter a of Eq. (17).

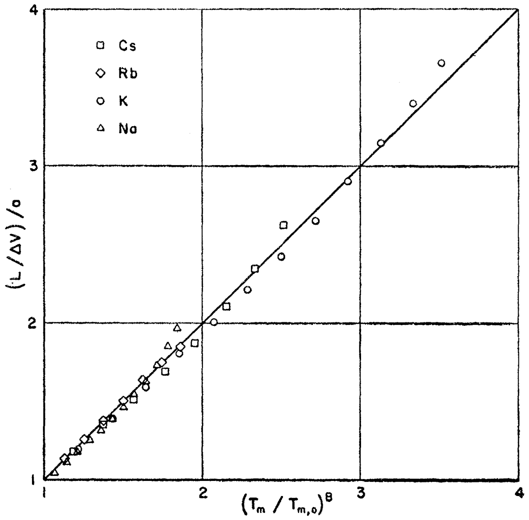

FIG. 1. Comparison of the law of reduced states (straight line) for the ratio $L/\Delta V$ in terms of the fusion temperature, against Bridgman's experimental data for four alkali metals. Values of the Simon exponent B (tabulated in the fourth column of Table I) selected in each case for best over-all fit to the data.

Equation (20) states that the ordinate $(L/\Delta V)/a$, when plotted against $(T_m/T_{m,0})^B$, should yield a straight line of inclination 45°. In Fig. 1, this ordinate from Bridgman's experimental values of L and ΔV and values of a from Table I is shown as a function of $(T_m/T_{m,0})^B$ for the alkali metals, where the Simon exponent B has been selected by trial in each case to yield the best over-all fit to the data. For the same value of B in each case, the values of $(P_m-P_{m,0})/a$ corresponding to Bridgman's pressure-temperature data at fusion are shown in Fig. 2 as a function of $B^{-1}[(T_m/T_{m,0})^B-1]$; the data yield closely the straight line of inclination 45° demanded by Eq. (31). The maximum error indicated at the highest ordinate on Fig. 2 for any element does not exceed 3%, which may be within the experimental error. The values of the Simon exponent B obtained for each element are shown in Table I, with values, for comparison, as determined by others from essentially the same data. The disparities are explainable on two counts: the election in this paper to obtain the Simon exponent by a best fit corresponding to Eq. (20), rather than to the Simon equation (31) directly, and the requirement of this theory that the Simon coefficient A be a/B, with a given by Eq. (17), which insures that Clapeyron's equation is satisfied at the origin of the fusion curve.

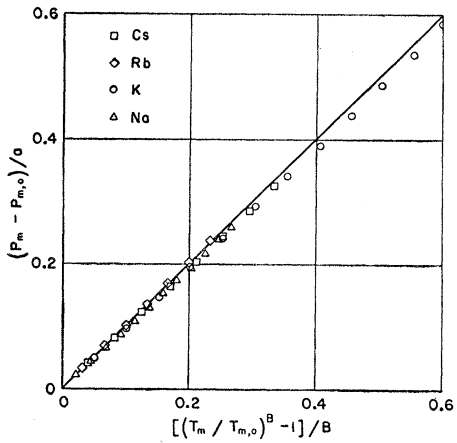

FIG. 2. Comparison of the Simon equation (straight line), with values of B tabulated in the fourth column of Table I, against Bridgman's experimental data for four alkali metals.

The question at issue is to show that the values of the Simon exponent obtained are compatible with the theory given. Since experimental data on the volumes of the alkali metals along the fusion curve are not available, the values of the Murnaghan parameter η,

TABLE I. Parameters of the Simon equation.

	$\gamma_{m,0}$	q_0	$10^{-6}a$ bars	B Eq. (20)	B
Cs	1.34	1.18	0.0119	4.50	4.75[a]
Rb	1.6_4	1.22	0.0146	3.70	4.2
K	1.20	1.15	0.0202	4.21	4.53
Na	1.13	1.13	0.0454	3.15	3.56

[a] Value for Cs from Simon and Glatzel (reference 5); values for Rb, K, Na from J. A. W. Huggill, as quoted by Salter (reference 11).

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[17] P. W. Bridgman, Phys. Rev. 3, 153 (1914); 27, 68 (1926).

[18] P. W. Bridgman, Proc. Am. Acad. Arts. Sci. 56, 59 (1921).

Table II. Parameters of fusion curves.

	μ Eq. (15)	η Eq. (21)	η	$\gamma_{m,\mathrm{Av}}$ Eq. (23)	$\gamma_{m,\mathrm{Av}}$ Eq. (39)	η Eq. (40)	B Eq. (21)
Cs	3.5[a]	2.3	...	1.0	1.1_0	2.6	3.8
Rb	4.7	3.1	...	1.4	1.4_2	3.2	3.6
K	$2._8$	$2._2$	...	0.9_5	0.9_5	$2._3$	$3._9$
Na	$(2._6)$	$(2._7)$	3.79[b] (50–60 kilobars) 2.86 (90–100 kilobars)	$(1._2)$	$(1._0)$	$(2._3)$	$(3._8)$

[a] Values at the origin of d^2T_m/dP_m^2 in Eq. (15) were computed from second differences of T_m *vs* P_m from Bridgman's data (reference 17). It was necessary to smooth the values of Δ^2T_m near the origin for K. For Na, the values of Δ^2T_m were too erratic to permit smoothing, and the value at the origin was taken as the average of values corresponding to the first four intervals of P_m.

[b] See reference 14. Parenthetic pressure ranges correspond to direct fit.

which enters B, must be obtained indirectly. Values of the parameter μ corresponding to the volume variation of $\gamma_m-\frac{1}{3}$ are shown in Table II, as determined by Eq. (15) from quantities evaluated at the origin; values of d^2T_m/dP_m^2 were computed by numerical differentiation of the fusion temperature with respect to pressure. As noted, the value for Na is somewhat doubtful, as is that for K to a less extent. These values of μ and the values of the fourth column of Table I for B yield the tabulated values of η in the second column of Table II, from Eqs. (21). It is seen that the values of η are reasonably concordant with the listed values obtained by Murnaghan from direct fit, over ten-kilobar intervals of pressure, of the pressure-volume curve for Na at normal temperature.

A severer test of the assumptions underlying the theory can be obtained by noting that the average value $\gamma_{m,\mathrm{Av}}$ of the Grüneisen parameter along the fusion curve, defined by Eq. (23) in terms of η, should be approximately equal to the average value defined implicitly by Eq. (18) for the variation of $\gamma_m-\frac{1}{3}$ with fusion temperature. The latter average is given by

$$\frac{\gamma_{m,\mathrm{Av}}-\frac{1}{3}}{\gamma_{m,0}-\frac{1}{3}}=\frac{1-(T_{m,0}/T_{m,\max})^{\beta-1}}{(\beta-1)(T_{m,\max}/T_{m,0}-1)},\tag{39}$$

where $T_{m,\max}$ is the maximum temperature on an observed fusion curve. It is seen that agreement is reasonable for tabulated values of $\gamma_{m,\mathrm{Av}}$ in Table II, as obtained by means of Eq. (23) from the values of η in the second column, and as obtained by means of Eq. (39) from the values of μ and η in the first and second columns, respectively. One should not expect identity necessarily, since the two evaluations of $\gamma_{m,\mathrm{Av}}$ correspond to different methods of averaging. Finally, one notes that $d\gamma_m/dT_m$ is negative, from Eq. (18); the sign of the derivative agrees with the relation $\gamma_{m,\mathrm{Av}}<\gamma_{m,0}$, which holds for the values of $\gamma_{m,\mathrm{Av}}$ in Table II except for one instance in the doubtful case of Na.

The approximate equality of these two evaluations of $\gamma_{m,\mathrm{Av}}$ yields a method of inferring the value of η from knowledge of the values of $\gamma_{m,0}$ and μ. If Eq. (39) is rewritten, by means of Eqs. (23) and (24), as

$$\frac{\eta-1}{\eta_0-1}=\frac{1-(T_{m,0}/T_{m,\max})^{\beta-1}}{(\beta-1)(T_{m,\max}/T_{m,0}-1)},\tag{40}$$

the definition $\beta=\mu/(\eta-1)$ permits one to solve the equation for η by trial, if η_0 and μ are known. Values of η obtained in this manner, with use of values of $\gamma_{m,0}$ and μ from Tables I and II, respectively, are shown in the sixth column of Table II; the agreement with the values of the second column is satisfactory. Values of B from Eq. (21) corresponding to values of μ and η from the first and sixth columns, respectively, are tabulated in the last column of Table II; the agreement with the values of the fourth column of Table I is good for Rb and K, but the differences in the cases of Cs and Na reflect the sensitivity of $B=(\eta+\mu)/(\eta-1)$ to the value of $\eta-1$ in the denominator. Thus, the theory given is able to predict an approximate value of the Simon exponent for the alkali metals; by way of contrast with the values of the last column of Table II, note that Salter's evaluation (27) of the Simon exponent yields numbers of the order of 1.5.

By use of a Taylor expansion of Eq. (18) to obtain an evaluation of $\gamma_{m,\mathrm{Av}}$, one finds the explicit expression

$$\eta\sim\tfrac{1}{2}\{\eta_0+1+[(\eta_0-1)^2-4\mu(T_{m,\max}/T_{m,0}-1)]^{1/2}\},\tag{41}$$

valid as an approximation provided $T_{m,\max}/T_{m,0}$ is sufficiently small. This equation yields values of η differing from those corresponding to Eq. (40) by about 6% on the average for Cs, Rb, and Na; it fails for K, where the large value of $T_{m,\max}/T_{m,0}-1$ (in this case about $\frac{1}{3}$) makes the radical imaginary.

On the assumption that the heat capacity of the solid at fusion has the Dulong and Petit value, Eqs. (36) and (34) of I yield the approximation

$$q=1+2\gamma_m(3\gamma_m-1)\Omega,\tag{42}$$

in which Ω is the parameter appearing in Eq. (7). Use of Eq. (18) in this expression for q with values of μ and η from Table II, permits one to evaluate the minimum value $q_{\min}$ of q corresponding to the temperature $T_{m,\max}$ on a fusion curve. The relative difference $(q_0-q_{\min})/q_0$ is largest for the elements K and Cs showing the largest ordinates in Fig. 2, in which cases it amounts to about 10%. Since this value probably exceeds the experimental error in the fusion data, Eqs. (20) and (31) are valid only as first-order approximations; a more refined analysis should take the variation of q into account.

IV. CONCLUSION

The successful comparison of theory with experiment for the alkali metals permits one to assess tentatively the significance of the Simon equation for elements of relatively high melting point. For elements of low melting point, such as the molecular crystals, applicability of the Murnaghan equation of state has not been verified; hence the conclusions are not necessarily valid for elements of this class, for which the Simon equation was originally devised.

The fundamental fusion criterion on this theory is Eq. (7) corresponding to the Lindemann law, from which the Simon equation follows through choice of the Murnaghan equation (or one of similar analytic form) as the equation of state of the solid. However, a treatment analogous to that given here, based on a Birch equation[19] (also derived from the theory of finite strain) or other justifiable equation of state, will not necessarily yield the analytic form of Eq. (31), but should be capable of representing the experimental facts as well, if Eq. (7) is accepted. Further, the evaluation (21) of the Simon exponent implies some dependence on the pressure range covered by the fusion curve, and the evaluation of the Simon coefficient shows a dependence on the arbitrary position of the origin of the fusion curve. These considerations suggest that the Simon equation has more the character of an interpolation formula than a basic fusion equation, at least for the elements of higher melting temperature.

The fact that the Simon equation can be derived so directly from the generalized Lindemann law of I, for low pressure, justifies to some extent the step of extrapolating the law, for high pressure, to obtain the fusion curve on the basis of the Thomas-Fermi equation of state.[20]

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Grüneisen Parameter for a Solid under Finite Strain*

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An evaluation of the Grünesisen parameter (or constant) from the equation of state of a solid has been obtained by Druyvesteyn and Meyering on the basis of the theory of finite strain. The result differs (by $-\frac{1}{3}$) from the corresponding evaluation on the Debye theory, as given by Lorentz and by Slater. The value of Druyvesteyn and Meyering is derived here without use of the formal theory of finite strain, and shown to correspond physically to a model of independent pairs of nearest neighbor atoms, rather than to the Debye model of coupled atomic vibrations. This fact resolves a paradox raised by Dugdale and MacDonald in connection with an ideal harmonic solid, and ascribed by them to neglect of finite strain. The presence of a state of finite hydrostatic pressure, upon which elastic waves or pressure changes of infinitesimal amplitude are impressed, is taken into account explicitly by means of Murnaghan's theory of finite strain, to obtain the Grüneisen parameter, as evaluated from the equation of state, on the Debye model and for a Druyvesteyn-Meyering solid. The results are identical in the two cases with the corresponding values obtained without use of the formal theory of finite strain. Hence, no basis exists for the modification at finite pressure in the Grüneisen parameter from the Debye theory, as proposed by Dugdale and MacDonald. A comparison of average values over a relatively large number of elements, of Grüneisen constants as evaluated from Grüneisen's law and from the equation of state on the Debye model, shows excellent agreement at normal and at melting temperature.

I. INTRODUCTION

FROM results of Lorentz[1] and Slater,[2,3] the Grüneisen parameter (or constant) γ_D of an isotropic solid can be evaluated from its equation of state as

$$\gamma_D = -\tfrac{2}{3} - \tfrac{1}{2}(\partial P/\partial V)^{-1}(V\partial^2 P/\partial V^2), \qquad (1)$$

where P is the pressure corresponding to the volume V. As indicated by the subscript D, this result is based on the Debye theory; it presupposes that the Poisson ratio of the solid is constant. In a number of papers[4–6] concerned with the fusion curve and the behavior of solids under pressure, the author has assumed that the evaluation (1) of the Grüneisen parameter is valid at high pressure, for the Debye theory.

The question can be raised whether the theory of

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