and

$$\frac{n_0(\mathbf{r})}{n_0}=\left[1-\frac{v(\mathbf{r})}{\epsilon_F{}^0}\right]^{\frac{3}{2}}. \tag{A.9}$$

The resulting Poisson's equations can be solved simply under the additional assumption that $|v(\mathbf{r})/\epsilon_F|\ll 1$. For then Eqs. (A.1) and (A.5) become of the form

$$\nabla^2 v(\mathbf{r})=a^2 v(\mathbf{r}). \tag{A.10}$$

The solution of this equation with the appropriate boundary conditions

$$v(\mathbf{r})\underset{r\to 0}{\longrightarrow}\pm\frac{e^2}{\kappa}\left(\frac{1}{\mathbf{r}}\right),\quad v(\mathbf{r})\underset{r\to\infty}{\longrightarrow}0,$$

is

$$v(\mathbf{r})=\pm\frac{e^2}{\kappa}\left(\frac{e^{-ar}}{r}\right), \tag{A.11}$$

which is the screened Coulomb potential used in our calculations with $a=1/r_s$.

It is easily seen that

$$\frac{1}{(r_s{}^H)^2}=\frac{4\pi e^2}{\kappa}\left(\frac{n_H}{2\epsilon_F{}^H}\right)=\frac{e^2}{\pi\kappa}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}\left(\frac{\hbar\omega_0}{(\epsilon_F{}^H)^{\frac{1}{2}}}\right) \tag{A.12}$$

and

$$\frac{1}{(r_s{}^0)^2}=\frac{4\pi e^2}{\kappa}\left(\frac{n_0}{(2\epsilon_F{}^0/3)}\right)=\frac{2e^2}{\pi\kappa}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}(\epsilon_F{}^0)^{\frac{1}{2}}. \tag{A.13}$$

Classical statistics.—In this case it is clear that since

$$f(v+\epsilon_z)\sim e^{-v(\mathbf{r})/kT}e^{-\epsilon_z/kT}$$

we get

$$\frac{n(\mathbf{r})}{n_H}=\frac{n_0(\mathbf{r})}{n_0}=e^{-v(\mathbf{r})/kT}\cong 1-\frac{v(\mathbf{r})}{kT}$$

(for $|v(\mathbf{r})/kT|\ll 1$), and thus Poisson's equation for both cases is again of the form (A.10). Hence, the self-consistent potential energy is again of the form (A.11), with

$$\frac{1}{(r_s{}^H)^2}=\frac{4\pi e^2}{\kappa}\left(\frac{n_H}{kT}\right) \tag{A.14}$$

and

$$\frac{1}{(r_s{}^0)^2}=\frac{4\pi e^2}{\kappa}\left(\frac{n_0}{kT}\right). \tag{A.15}$$

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Variation of the Amplitude of Thermal Vibration on the Fusion Curve

J. J. Gilvarry*
The Rand Corporation, Santa Monica, California

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A differential relation given previously, which is equivalent to the Debye-Waller identification of the Debye and Lindemann frequencies at fusion, is generalized to take into account variation along the fusion curve of the critical ratio of the root-mean-square amplitude of thermal vibration to the nearest-neighbor distance of the atoms in the solid at fusion. Thus extended, the theory yields an expression for the Grüneisen parameter of a solid at fusion in terms of fusion parameters and the rate of change of the critical ratio with respect to volume, which is valid for elements whose fusion curves have either normal or abnormal slopes. Values of derivatives of the critical ratio with respect to volume, temperature, and pressure at fusion are obtained for 16 elements. The results yield evaluations of the change in the critical ratio along the experimentally determined fusion curves for three alkali metals, and permit estimates in other cases. It is concluded that the assumption of a fixed Lindemann constant along the fusion curve of a particular element represents an excellent approximation, in general, for elements with normal fusion curves (for the case of classical excitation of the lattice vibrations). The same conclusion is obtained, within certain approximations, from the order-disorder theory of Lennard-Jones and Devonshire for the melting process, and the theory of Fisher for stability of the liquid phase.

I. INTRODUCTION

IT has been pointed out by the author[1] and by Cartz[2] that the Lindemann law of melting can be derived under certain assumptions from the Debye-Waller theory of the thermal dependence of the intensity of Bragg reflection of x-rays from a solid. In a recent paper, the author obtained relatively accurate values of Lindemann constants, and thus of amplitudes of thermal vibration for the solid at melting, from the Debye-Waller theory for ten elements.[3] The results show that the Lindemann constant, and hence the critical ratio of the root-mean-square amplitude of thermal vibration to the nearest-neighbor distance of the

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* Now at Research Laboratories, Allis-Chalmers Manufacturing Company, Milwaukee, Wisconsin.

[1] J. J. Gilvarry, Phys. Rev. **102**, 308 (1956), referred to hereafter as I.

[2] L. Cartz, Proc. Phys. Soc. (London) **B68**, 951, 957 (1955).

[3] J. J. Gilvarry, Phys. Rev. **103**, 1700 (1956), referred to hereafter as II.

atoms in the solid at fusion, cannot be a strict constant over a lattice type. This fact leaves open the question of whether the Lindemann constant for a particular element is a strict constant along the fusion curve, as assumed in derivation of the Simon fusion equation from the Lindemann law.[4] The purpose of this paper is to answer the question, at least partially. The results have an obvious bearing on applications of the Lindemann law or the Simon equation to estimate melting temperatures in the interior of the earth[5–8] or planets.[9]

The derivation of the Simon equation in III is based on a theoretical evaluation, in terms of parameters of the fusion curve, of the Grüneisen parameter of the solid at melting. The comparison (Table V of I) of this quantity as obtained from Grüneisen's law with that obtained from fusion parameters shows that values by the former method consistently are slightly greater, when not equal within the accuracy of the data, except for the cases of Pb, Al, and Hg. However, the necessary bulk modulus is known only poorly for Hg. Further, results of II show some uncertainty in this parameter for Pb and Al at melting, and the volume change at fusion adopted for the latter element in I is questionable. If these three cases can be discounted, it seems reasonable to identify the difference in question with the rate of change along the fusion curve of the critical ratio (and thus of the Lindemann constant), which was neglected in I. With this extension of the theory, the sign found for the variation of critical ratio with volume or pressure is consistent with one's expectation, not only for elements which have a normal fusion curve, but also for those which do not. The latter class of elements is covered by the extended theory, but not by the theory of I.

The results are strictly valid on the Grüneisen and Debye-Waller theories, when it is assumed that the Poisson ratio of the solid along the fusion curve is a constant. It can be noted that this assumption is an essential element of the Grüneisen theory[10–12]; if the ratio varies significantly, one must take this fact into account by defining a Grüneisen parameter separately for the longitudinal and transverse waves.[13] The lattice vibrations will be assumed classically excited at fusion, so that the quantization parameters of I can be assigned their classical values.

II. THEORY

A parameter δ can be defined by

$$\delta = d\ln\rho/d\ln V_m, \tag{1}$$

in terms of the volume V_m of the solid at melting and the critical ratio ρ of the root-mean-square amplitude of thermal vibration to the nearest-neighbor distance of the atoms in the solid at fusion. When the Poisson ratio of the solid at fusion is constant, a procedure entirely analogous to that used in I yields

$$d\ln T_m/d\ln V_m = -2(\gamma_m - \delta - \tfrac{1}{3}) \tag{2}$$

as a differential relation equivalent to the Debye-Waller identification of the Debye and Lindemann frequencies, if T_m is the fusion temperature and γ_m is the Grüneisen parameter of the solid at fusion. The latter parameter enters Eq. (2) through the Lorentz-Slater expression[11,12]

$$\gamma_m = -\tfrac{1}{6} - \tfrac{1}{2} d\ln K_m/d\ln V_m, \tag{3}$$

where K_m is the bulk modulus of the solid at fusion. It can be proved directly[12] that γ_m is given also, from Grüneisen's law as applied to the solid at fusion, by

$$\gamma_m = K_m \alpha_m V_m / C_{V,m}, \tag{4}$$

where α_m is the volumetric coefficient of thermal expansion of the solid at fusion, and $C_{V,m}$ is the corresponding heat capacity at constant volume. By a method used in I, based on Clapeyron's equation, one obtains

$$\gamma_m = \Gamma + \delta, \tag{5}$$

where

$$\Gamma = \tfrac{1}{3} + \tfrac{1}{2} q K_m \Delta V/L, \tag{6}$$

in which q is defined in I, and ΔV and L are the volume change and latent heat of fusion, respectively. Equation (5) yields the corresponding result of I for δ vanishing, in which case Γ becomes a Grüneisen constant as evaluated from fusion parameters.

From Eqs. (1), (2), (5), and (6), one obtains

$$d\ln\rho/d\ln T_m = -\tfrac{1}{2}\delta(\Gamma - \tfrac{1}{3})^{-1} = -\delta L/qK_m\Delta V, \tag{7}$$

directly. Use of Clapeyron's equation yields

$$d\ln\rho/dP_m = -\tfrac{1}{2}\delta(\Gamma - \tfrac{1}{3})^{-1}\Delta V/L = -\delta/qK_m, \tag{8}$$

where P_m is the fusion pressure. Since the Lindemann constant c is defined in II by $c = (\sqrt{3}/2\pi)\lambda^{\frac{1}{3}}/\rho$, where λ is a function only of lattice type, the definition (1) yields $d\ln c/d\ln V_m = -\delta$ directly, with analogous derivatives as the negatives of the results of Eqs. (7) and (8).

One can expect the parameter δ to be positive, on intuitive grounds,[14] for either a normal fusion curve

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[8] J. J. Gilvarry (to be published).

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[10] E. Grüneisen, in *Handbuch der Physik* (Verlag Julius Springer, Berlin, 1926), Vol. 10, pp. 23, 25, 32.

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[12] J. J. Gilvarry, Phys. Rev. **102**, 331 (1956).

[13] D. Bijl and H. Pullan, Phil. Mag. **45**, 290 (1954).

[14] Dr. A. J. F. Siegert has pointed out to the author that the result follows directly if one assumes, instead of $[\langle u^2\rangle_{\text{Av}}]^{\frac{1}{2}} = \rho r_m$, the equation $[\langle u^2\rangle_{\text{Av}}]^{\frac{1}{2}} = \rho_0(r_m - a)$, where ρ_0 and a are constants. This assumption takes into account the possibility that the region (of linear extent a), over which the interatomic forces are markedly anharmonic, does not change with volume. One thus has $\rho = \rho_0(1 - a/r_m)$ and $\delta = \tfrac{1}{3}a/(r_m - a) > 0$.

(dT_m/dP_m positive) or an abnormal fusion curve (dT_m/dP_m negative). For the latter case, it follows from Eq. (5) that δ must be positive if the absolute value of the slope of the fusion curve is great enough to make Γ negative, since the Grüneisen parameter γ_m must be positive for the thermal pressure of the lattice to be positive. The slope of the fusion curve is given, from Eqs. (5) and (6), by

$$dT_m/dP_m = 2(\gamma_m - \delta - \tfrac{1}{3})T_m/qK_m, \tag{9}$$

so that a normal and an abnormal fusion curve correspond to $\delta < \gamma_m - \frac{1}{3}$ and $\delta > \gamma_m - \frac{1}{3}$, respectively. For δ vanishing, this criterion yields that given in I. From Eqs. (7), the sign of $d\ \ln\rho/d\ \ln T_m$ is negative or positive, according as the fusion curve is normal or abnormal. In either case, the sign of $d\ \ln\rho/dP_m$ follows as negative from Eq. (8). If $[\langle u^2\rangle_{\mathrm{Av}}]^{\frac{1}{2}}$ is the root-mean-square amplitude of thermal vibration at fusion, one has

$$d\ \ln[\langle u^2\rangle_{\mathrm{Av}}]^{\frac{1}{2}}/d\ \ln V_m = \delta + \tfrac{1}{3}. \tag{10}$$

Thus, this derivative is always positive; it is less than or greater than γ_m according as the fusion curve is normal or abnormal.

To obtain integrals expressing the change in ρ along a normal fusion curve, it will be assumed that the derivation of the Simon equation in III is valid to first order for δ vanishing, so that the variation of ρ can be calculated as a perturbation when δ is assumed constant and small relative to γ_m. From III, one can write

$$(\gamma_m - \tfrac{1}{3})/(\gamma_{m,0} - \tfrac{1}{3}) = (T_m/T_{m,0})^{-\beta}, \tag{11}$$

where $\gamma_{m,0}$ is the value of γ_m corresponding to the normal fusion temperature $T_{m,0}$, and β is defined by

$$\beta = \mu/(\eta - 1), \tag{12}$$

in which

$$\mu = d\ \ln(\gamma_m - \tfrac{1}{3})/d\ \ln V_m, \tag{13}$$

and η is fixed by

$$\eta = 2\gamma_{m,\mathrm{Av}} + \tfrac{1}{3} \tag{14}$$

in terms of an average Grüneisen parameter $\gamma_{m,\mathrm{Av}}$ over the range of interest on the fusion curve. Integration of Eqs. (7) with use of Eq. (11) yields

$$\ln(\rho/\rho_0) = -\tfrac{1}{2}\delta[\beta(\gamma_{m,0} - \tfrac{1}{3})]^{-1}[(T_m/T_{m,0})^{\beta} - 1], \tag{15}$$

for ρ at the fusion temperature T_m relative to its value ρ_0 at $T_{m,0}$. From this equation, the variation of ρ as a function of the fusion pressure P_m can be obtained by use of the Simon equation

$$P_m = (a/B)[(T_m/T_{m,0})^B - 1], \tag{16}$$

where

$$B = (\eta + \mu)/(\eta - 1), \tag{17}$$

and a is defined in III. One obtains

$$\ln(\rho/\rho_0) = -\tfrac{1}{2}\delta[\beta(\gamma_{m,0} - \tfrac{1}{3})]^{-1}[(BP_m/a + 1)^{\beta/B} - 1]. \tag{18}$$

Under the assumption $\delta \ll \gamma_m$ and the condition that osculating approximations at the origin of the fusion curve are valid, it has been pointed out in III that μ of Eq. (13) vanishes, γ_m becomes $\gamma_{m,0}$, η of Eq. (14) equals $2\gamma_{m,0} + \frac{1}{3}$, and the Simon exponent B of Eq. (17) reduces to the value

$$B = (6\gamma_{m,0} + 1)/2(3\gamma_{m,0} - 1), \tag{19}$$

obtained by Salter.[15] For this case, Taylor expansion of the Simon equation yields

$$P_m = a[(T_m/T_{m,0} - 1) + \tfrac{1}{4}(\gamma_{m,0} - \tfrac{1}{3})^{-1}(T_m/T_{m,0} - 1)^2] + O[(T_m/T_{m,0} - 1)^3], \tag{20}$$

where $O[x]$ designates terms of order x or higher. With use of the relation $T_m/T_{m,0} = (V_{m,0}/V_m)^{\eta-1}$ given in III, where $V_{m,0}$ is the initial value of V_m, one obtains

$$-(V_m - V_{m,0})/V_{m,0} = a_mP_m - b_mP_m^2 + O[P_m^3], \tag{21}$$

to the same order as Eq. (20), where

$$a_m = (q_0K_{m,0})^{-1}, \tag{22a}$$

$$b_m = (\gamma_{m,0} + \tfrac{2}{3})(q_0K_{m,0})^{-2}, \tag{22b}$$

are constants, in which q_0 and $K_{m,0}$ are the values of q and K_m, respectively, at the normal fusion temperature. The last two relations yield $\gamma_{m,0} = b_m/a_m^2 - \frac{2}{3}$. The parameter γ_m can be found directly from Eq. (21), by use of Eq. (3), when one notes that $K_m = -(V_m/q)dP_m/dV_m$ and one assumes q constant, as is done in the derivation of the Simon equation. The computation shows that $\gamma_m = b_m/a_m^2 - \frac{2}{3} = \gamma_{m,0}$ under this assumption, and thus that $\mu = 0$, only if the expansion of Eq. (21) is restricted to the terms shown explicitly, through second order.

The last result means that Salter's determination of the Simon exponent is valid only when the volume-pressure relation along the fusion curve is of the Bridgman form corresponding to the explicit terms of Eq. (21); thus, the evaluation can be applied in practice, for a large pressure range, only to relatively incompressible substances. In such a case, the Simon equation reduces to the terms shown explicity in Eq. (20). In contrast to the situation for the highly compressible alkali metals, one expects the range of pressure over which this approximation is valid to be large for the relatively incompressible metals, since the isothermal and isentropic equations of state of iron, for example, are of the Bridgman form up to at least $\frac{1}{3}$ megabar.[16]

In III, it is shown that K_m and $L/\Delta V$ obey a law of reduced states for $\delta \ll \gamma_m$, corresponding to

$$K_m/K_{m,0} = (V_{m,0}/V_m)^{\eta}, \tag{23a}$$

$$(L/\Delta V)/a = (V_{m,0}/V_m)^{\eta+\mu}. \tag{23b}$$

Use of these relations in Eq. (6) shows that Γ is constant when μ vanishes and q is constant. Since γ_m is constant in this case, one concludes immediately from the

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

[16] R. W. Goranson *et al.*, J. Appl. Phys. **26**, 1472 (1955).

connection (5) that δ is constant under the same conditions. Thus, one expects δ to be essentially constant for the relatively incompressible metals over the range of fusion pressure where the Bridgman relation of Eq. (21) is obeyed.

It follows that the correct forms of Eqs. (15) and (18) for the relatively incompressible elements are obtained by taking $\mu=0$, and thus $\beta=0$ from Eq. (12), and expanding both sides of the equations in question through terms of first order. Thus, one obtains

$$-(\rho-\rho_0)/\rho_0=\tfrac{1}{2}\delta(\gamma_{m,0}-\tfrac{1}{3})^{-1}(T_m/T_{m,0}-1), \quad (24)$$

for ρ as a function of T_m, and

$$-(\rho-\rho_0)/\rho_0=\delta a_m P_m, \quad (25)$$

for ρ as a function of P_m, where a_m is defined by Eq. (22a). These approximations should be valid over a pressure range comparable with that over which the Bridgman equation of state applies.

The fact that approximate constancy of δ can be shown only for the relatively incompressible elements suggests that this assumption for the alkali metals, which yields Eqs. (15) and (18), is not strictly valid in this case.

III. NUMERICAL RESULTS

In this paper, the Grüneisen parameter γ_m of the solid at fusion will be understood to be fixed by Grüneisen's law (4) applied to the solid at fusion (the identification of Γ as a Grüneisen constant will not be adopted). The values of γ_m and Γ shown in Table I are from I, except as otherwise noted in the cases of Pb and Al; the values of I for Hg are omitted. The table shows corresponding values of δ, $d\ln\rho/d\ln T_m$, and $d\ln\rho/dP_m$, as computed from Eqs. (5), (7), and (8), respectively, with use of data from I.

If Pb and Al are excluded, one notes that the signs appearing for the three derivatives are as specified in Sec. II for normal and abnormal fusion curves. For elements of the former class, the values of δ satisfy $\delta\ll\gamma_m$ reasonably (except for Sn), so that Eq. (5) implies the relation $\gamma_m\sim\Gamma$ of I to a good approximation, in general. For the three elements (Ga, Bi, and Sb) with abnormal fusion curves, δ is large and comparable with γ_m; in this case, the approximation $\gamma_m\sim\Gamma$ fails. The zero entries in Table I imply merely insufficient accuracy in γ_m and Γ to evaluate δ. These cases correspond (except for K) to relatively incompressible metals, and the accuracy of the data is not inconsistent with $\delta\leq 0.1$.

In Table I, the first lines corresponding to Pb and Al show values of γ_m and Γ from I; anomalously, δ is negative. It was noted in II that extrapolation to the melting point of data for these elements, determined ultrasonically for temperatures extending relatively close to the melting point, yielded bulk moduli significantly lower than those obtained by extrapolation of static compression data. The value of the relative volume change $\Delta V/V_m$ given in I for Al represents a mean given by Kubaschewski[17] from work of four investigators, and he noted that the value seems high. Futhermore, the entropy change given by Kubaschewski for Pb seems distinctly low relative to those for the other face-centered cubic elements, implying that the value of the latent heat L may be low. In Table I, the second lines for Pb and Al show determinations of γ_m by Eq. (4), from data of I but with values of K_m from II. The corresponding values of Γ from Eq. (6) were evaluated from data of I, except that values of K_m from II were used, values of L were taken from a compilation[18] of data for metals of high purity, and ΔV in the case of Al was obtained from one[19] of the four sources used in Kubaschewski's discussion. In both cases δ vanishes within the accuracy of the data. For the alkali metals, where the accuracy is relatively high, all values of γ_m and Γ satisfy $\Gamma\leq\gamma_m\leq\gamma$, where γ is the Grüneisen parameter at normal temperature and pressure. With the revision of Table I for Pb and Al, all values of Γ and γ_m satisfy this condition except those for Pb, where the discrepancy relative to γ is marginal, and those[20] for Mg, Sn, and Sb.

TABLE I. Values of derivatives corresponding to variation of the critical ratio ρ at fusion.

	γ_m	Γ	δ	$d\ln\rho/d\ln T_m$	$d\ln\rho/dP_m$ (megabar^{-1})
Cs	1.6	1.4	0.2	−0.09	−8
Rb	1.8	1.5	0.3	−0.1	−8
K	1.2	1.19	0	0	0
Na	1.2	1.1	0.1	−0.06	−1
Li	0.88	0.74	0.14	−0.17	−1.3
Ag	$2._0$	$1._7$	$0._3$	$-0._1$	$-0._4$
Cu	$1._3$	$1._3$	0	0	0
Fe	$1._1$	$1._1$	0	0	0
Zn	$1._8$	$1._8$	0	0	0
Mg	$2._1$	$1._9$	$0._2$	-0.0_5	$-0._4$
Sn	$2._8$	$2._1$	$(0._7)$	$(-0._2)$	$(-0._1\times 10)$
Ga	1.2	−1.2	2.4	0.80	−5.1
Bi	0.8_9	-0.6_0	1.4_9	0.8_0	$-5._3$
Sb	$1._1$	0.1_2	$1._0$	$2._4$	$-2._1$
Pb	3.4	3.7	(−0.3)	···	···
	2.8[a]	2.8[a]	0	0	0
Al	2.1	2.6	(−0.5)	···	···
	1.6[b]	1.6[b]	0	0	0

[a] From data of I, with use of the values $K_m=0.30$ megabar from II and $L=6.3$ cal/g from reference 18.

[b] From data of I, with use of the values $K_m=0.44$ megabar from II, $L=94.6$ cal/g from reference 18, and $\Delta V=0.019$ cm^3/g from reference 19.

In Table II, the normal centigrade fusion temperature $t_{m\,0}$ and the maximum value $t_{m\,\max}$ determined by Bridgman[21] at the maximum experimental pressure $P_{m,\max}$ are shown for three alkali metals. The fractional changes in the critical ratio ρ computed from Eqs. (15)

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[17] O. Kubaschewski, Trans. Faraday Soc. **45**, 931 (1949).

[18] *Metals Handbook* (American Society for Metals, Cleveland, 1948), p. 20.

[19] M. Töpler, Ann. Phys. u. Chem. **53**, 344 (1894). The value is the one cited in *Handbook of Chemistry and Physics* (Chemical Rubber Publishing Company, Cleveland, 1952), thirty-fourth eitidon, p. 1977.

[20] Both Γ and γ_m are almost certainly high for Mg, since the extrapolated bulk modulus at melting given in I is only slightly below the normal value.

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

Table II. Variation of the critical ratio ρ along the fusion curve for three alkali metals.

	$t_{m,0}$ °C	$t_{m,\max}$ °C	$-(\rho-\rho_0)/\rho_0$ Eq. (15)	$P_{m,\max}$ kg/cm^2	$-(\rho-\rho_0)/\rho_0$ Eq. (18)
Cs	29.7[a]	98.5[a]	0.03	4000[a]	0.03
Rb	38.7	95.9	0.02	3500	0.02
Na	97.6	177.2	0.01	12 000	0.01

[a] Bridgman, reference 21.

and (18) agree, as shown; values of δ from Table I were used with other data[22] from III. Values computed by means of the approximations (24) and (25) disagreed between themselves and from those of Table II by the order of 50–100%. The sign obtained for the change of ρ with fusion temperature in Table II is consistent with that observed by Dugdale and Simon[23] for the change in Lindemann constant for solid helium, but the magnitude of the change implied by their data is greater in spite of a smaller temperature range. Note, however, that the melting temperatures they observe are significantly below the Debye temperature, so that variation of the quantization parameter Q_m of I properly should be taken into account.

IV. DISCUSSION

The values of δ in Table I and of $(\rho_0-\rho)/\rho_0$ in Table II for the alkali metals are sufficiently small so that the derivation of the Simon equation given in III is virtually unaffected, for the pressure and temperature range covered by Bridgman's data. In general, the values of δ and γ_m justify the approximation $\delta \ll \gamma_m$ for elements with normal fusion curves.

From Eq. (18) and the values of δ in Table I, one obtains the result that ρ/ρ_0 decreases to about 0.8 for Cs and Rb, and to about 0.9 for Na, at a fusion pressure of 100 kilobars (roughly the limit of pressure measurement in Bridgman's experimental technique). If one assumes $\delta \sim 0.1$ for iron, consistently with the accuracy of the data in Table I, the ratio ρ/ρ_0 for this relatively incompressible element at the same pressure decreases by only about one percent, from Eq. (25) with use of data from I. Thus, the conclusion stands that the reformulation given of the Lindemann law yields an excellent approximation in general, when δ is assumed to vanish for elements with normal fusion curves. This fact is underscored by the success of the theory in predicting the complete inversion of the normal fusion order among the alkali metals at high pressure, as hypothesized from experimental data by Bridgman; aside from the Lindemann law, the prognostication required use only of the Thomas-Fermi equation of state and a common value of Poisson ratio for the alkali metals.[24] These considerations give some indication of the measure of confidence that can be attached to similar extrapolations in geophysical or astrophysical contexts.[5–9]

This theory characterizes an element having an abnormal fusion curve as one in which the rate of change with volume of the critical ratio ρ along the fusion curve is large enough to exceed $\gamma_m - \frac{1}{3}$, or $d \ln[\langle u^2\rangle_{\mathrm{Av}}]^{\frac{1}{2}}/d \ln V_m$ exceeds γ_m. The examples among the elements are all loosely-packed, with relatively low coordination numbers for Ga, Bi, and Sb, and the quite low value 4 for germanium[25] and silicon.[26] A correlation of low Grüneisen constant with loose packing for the elements is known. Druyvesteyn has pointed out that this constant for the body-centered cubic elements is less than 1.8, while the reverse is generally true for the face-centered cubic elements.[27] He explained the effect qualitatively on the basis of a Lennard-Jones intermolecular potential; a more detailed explanation has been given by Zener.[28] The correlation in question holds, in general, if the hexagonal close-packed elements and the rhombohedral elements As, Bi, and Sb are included in the comparison.[10,11] Thus, one can strongly suspect an abnormal fusion curve for As, which shows the very low value 0.19 for the Grüneisen constant[10] at normal pressure (where it sublimes on heating); in fact, the Grüneisen parameter at the triple point must rise to at least $\frac{1}{3}$ for this element, if a normal fusion curve is to be possible (since δ is non-negative). However, that an abnormal fusion curve for an element may not be simply a matter of loose packing is shown by the fact that graphite apparently has a normal fusion curve,[29] although the coordination number (3 in the plane of the benzene rings) is less than that of Ge and Si. Nevertheless, one can suspect an abnormal fusion curve for diamond (in its region of stability), since the lattice type is the same as for Ge and Si.

V. CONCLUSION

The results of this paper and of II permit one to assess tentatively the significance of the Lindemann law as reformulated from the Debye-Waller theory. It has been shown in II (on the basis of one counter-example) that the Lindemann constant is not strictly fixed over a lattice type. The results of this paper show that the variation of this parameter along the fusion curve does not vanish for the alkali metals, and is large for the elements with abnormal fusion curves. These facts mean that Lindemann's original idea, that instability

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[22] Values of $\gamma_{m,0}$ and B were taken from the first and fourth columns of Table I, respectively; values of β were taken which correspond to μ and η in the first two columns of Table II.

[23] J. S. Dugdale and F. Simon, Proc. Roy. Soc. (London) **A218**, 291 (1953).

[24] J. J. Gilvarry, Phys. Rev. **102**, 317 (1956).

[25] R. G. Shulman and D. M. Van Winkle, J. Appl. Phys. **24**, 224 (1953); H. T. Hall, J. Phys. Chem. **59**, 1144 (1955).

[26] C. H. L. Goodman, quoted in Trans. Faraday Soc. 52, 885 (1956).

[27] M. J. Druyvesteyn, Philips Research Repts. **1**, 77 (1946).

[28] C. Zener, *Elasticity and Anelasticity of Metals* (University of Chicago Press, Chicago, 1948), p. 30.

[29] H. Steinle and J. Basset, Z. angew. Mineral. **2**, 28 (1940); A. Neuhaus, Angew. Chem. **66**, 532 (1954).

of the lattice sets in when the amplitude of the thermal vibration reaches some definite critical size, can be true for a normal fusion curve only in an approximate sense (it is not clear that the same statement can be made on the assumption[30] of instability caused by appearance of an imaginary lattice frequency in the Born-von Kármán dynamics). However, the discussion of Sec. IV shows that the assumption of a fixed Lindemann constant along the fusion curve of a particular element represents an excellent approximation, in general, for elements with normal fusion curves when the lattice vibrations are classically excited.

The same conclusion can be shown directly, within certain approximations, from the order-disorder theory of fusion given by Lennard-Jones and Devonshire[31] (independently of their derivation of a relation of the Lindemann form). The Simon equation has been obtained by Domb[32] from a variant of the theory of these authors, and by de Boer[33] from an approximation on their theory. By use of Bethe's order-disorder approximation, Domb obtained the value $B=1+3/n$ for the Simon exponent on the assumption of a Lennard-Jones intermolecular potential in which n is the (negative) exponent of the replusive term and the attractive term is neglected. Grüneisen[10] has computed the Grüneisen constant directly for such a potential as[34] $(n+2)/6$ (corresponding to Domb's tacit neglect of coupling of the vibrational modes[12]). With this value of Grüneisen parameter, Eq. (19) from the Lindemann law yields *exactly* Domb's result. On the same approximation of neglect of the attractive term, de Boer obtained $B=5/4$ for $n=12$, which agrees with Domb's result and that of Eq. (19). Thus, these conclusions from approximations on an order-disorder theory are precisely those one obtains by assuming that the critical ratio ρ is constant along the fusion curve for a particular element. One expects the treatments of both Domb and de Boer to be valid at moderately high pressure, so that their discussions agree in principle with the method used by the author to obtain melting temperatures at high pressure from the Lindemann law (for $\delta=0$), by use of the Thomas-Fermi equation of state.[24]

Further, Fisher[35] has given a theory of the stability of a liquid phase, which yields a fusion equation identical in form with that of Simon. When the attractive term of a Lennard-Jones potential is ignored, he obtains Domb's result $B=1+3/n$ for the Simon exponent, in agreement with Eq. (19). In Fisher's derivation, the properties of the solid do not enter.

The view that fusion is due to instability of the lattice implies that prediction of fusion temperatures can be made from properties of the solid alone. However, the essential assumptions made by the author in developing the reformulation of the Lindemann law are the existence of harmonic lattice vibrations of the solid, and, for the differential forms (5) and (9), the validity of Clapeyron's equation; no assumption is made on the Gibbs free energy of the amorphous phase. Hence, certainly when the possibility of variable ρ is allowed, the theory should yield a general description of fusion, which is independent of the specific mechanism of the melting process.[15] In consonance with this view, the Lindemann assumption of a constant critical ratio of the solid at fusion, the order-disorder model of Lennard-Jones and Devonshire for the fusion process, and Fisher's theory of the stability of a liquid phase, all yield evaluations of the Simon exponent consistent with that obtained in III.

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[31] J. E. Lennard-Jones and A. F. Devonshire, Proc. Roy. Soc. (London) **A170**, 464 (1939).

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

[33] J. de Boer, Proc. Roy. Soc. (London) **A215**, 5 (1952).

[34] Consistency with Grüneisen's general result $(n+m+3)/6$ can be shown by noting that a term in the potential can be ignored in computation of the Grüneisen constant only if it is of the harmonic form $A(r-r_0)^2$, where A is a constant and r_0 is the normal value of the interatomic distance r (reference 12). An attractive term $-2Ar_0/r^m$ can be brought into this form only by taking $m=-1$ and including the constant Ar_0^2, which yields $A(r-r_0)^2$ when the second-order term Ar^2 is neglected, consistently with the fact that r must be small relative to r_0 for the repulsive term to be dominant.

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