

TABLE VII. p_c/p_w calculated from Eqs. (4), (5), and (6).
 $T_w = 3.0^\circ\text{K}$; $T_c = 0.5^\circ\text{K}$.

Rp_w cm μ	Eq. (4) (He ⁴)	Eq. (5) (He ³)	Eq. (6)
10	0.9999	0.9997	0.9999
3	0.999	0.997	0.999
1	0.994	0.973	0.987

down to Rp_c values of about 1 cm μ . Hence the entries below an Rp_w of 1, indicated by superscript a in Table III, should not be relied on very heavily.

CONCLUSION

Experimental measurements have shown that the thermomolecular ratios for He³ between room and

liquid helium temperatures do not differ within experimental error from values calculated from the Weber-Schmidt He⁴ equation, Eq. (1), for Rp_w values down to 5 cm μ . Theoretical considerations based on measured viscosities in the liquid hydrogen and helium regions indicate that deviations from these calculated ratios probably will exceed 1% for lower Rp_w values. When very low pressures are reached, the ratios for both gases should theoretically converge to the molecular-flow-region limiting value of $(T_c/T_w)^{1/2}$.

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The Lindemann and Grüneisen Laws*

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The Lindemann assumption of direct contact of neighboring atoms at fusion is replaced by the criterion that melting occurs when the root-mean-square amplitude of thermal vibration reaches a critical fraction ρ , presumed the same for all isotropic monatomic solids, of the distance of separation of nearest-neighbor atoms. The Debye-Waller theory of the temperature dependence of the intensity of Bragg reflection of x-rays is used, without further assumptions, to derive a generalized Lindemann law. In contrast to the Lindemann form, all physical quantities involved in this formulation are evaluated at the fusion point, and departure of the average energy of an atomic oscillation from the equipartition value is taken into account by the quantization factor of the Debye-Waller theory. If the Grüneisen constant γ_m of the solid at fusion is evaluated by its definition from the Debye frequency of the solid, use of the generalized Lindemann law and Clapeyron's equation permits one to express γ_m in terms of the bulk modulus of the solid at melting and the latent heat and volume change of fusion. By means of Grüneisen's law applied to the solid at fusion, γ_m can be expressed likewise in terms of the

corresponding bulk modulus, thermal expansion, volume, and heat capacity at constant volume; the two evaluations of γ_m connect the Lindemann and Grüneisen laws. These relations permit one to evaluate the slope and curvature of a fusion curve as functions of γ_m , and thus to express in terms of γ_m the conditions that a fusion curve be normal in the sense of Bridgman. Experimental fusion data on 13 cubic metals are used to evaluate the constant of proportionality (inversely proportional to ρ) in the Lindemann frequency; the values are reasonably constant. The corresponding values of ρ for Al and Cu show reasonable agreement with values deduced from x-ray intensity measurements. The average ρ seems significantly below values estimated by Grüneisen. Good agreement with the cubic metals is found for hexagonal close-packed elements, but not for elements with more complex lattices, in general. The two evaluations of the Grüneisen constant γ_m of the solid at fusion are shown to be in good agreement, experimentally, for 14 elements checked, but agreement fails for the elements Ga, Bi, and Sb, which show abnormal fusion curves.

THE order-disorder theory of fusion given by Lennard-Jones and Devonshire¹ yields excellent agreement with experiment.² The theory has the important consequence that it provides an approximate theoretical justification¹ for Lindemann's theory of fusion,^{3,4} beyond the elementary considerations on which the latter theory is based. Lindemann considers a solid composed of simple harmonic oscillators, as in the Grüneisen theory of solids.⁵ He assumes further

that the oscillators are arranged in a simple cubic lattice, and that any departure of the average energy of an oscillator from the equipartition value can be represented by the Einstein function appearing in the theory of heat capacity of solids. The basic assumption is made that fusion occurs when the amplitude of thermal vibration of the atoms reaches one-half the distance of separation of neighboring atoms less their diameter; that is, when direct contact of neighboring atoms occurs. A second assumption is made, that the Hooke constant of the thermal oscillation (with the mass of the atom) corresponds to the Einstein frequency of the solid as determined by the heat capacity. These hypotheses determine a characteristic frequency as a function of the melting temperature, which shows good numerical agreement with the characteristic frequencies

* Work sponsored by the U. S. Atomic Energy Commission.

¹ J. E. Lennard-Jones and A. F. Devonshire, *Proc. Roy. Soc. (London)* **A170**, 464 (1939).

² J. de Boer, *Proc. Roy. Soc. (London)* **A215**, 5 (1952).

³ F. A. Lindemann, *Physik. Z.* **11**, 609 (1910).

⁴ J. K. Roberts and A. R. Miller, *Heat and Thermodynamics* (Interscience Publishers, Inc., New York, 1951), p. 551.

⁵ E. Grüneisen, in *Handbuch der Physik* (Verlag Julius Springer, Berlin, 1926), pp. 1-59.

of Einstein and of the later theory of Debye, if a constant of proportionality is properly chosen.

Recently, the Lindemann law and the Debye equation of state have been used by Salter⁶ to derive theoretically Simon's melting-point formula.⁷ The empirical Simon relation can be justified² on the theory of Lennard-Jones and Devonshire; it fits experimental fusion curves reasonably well, by choice of two disposable coefficients. The fact that, when conjoined with the Debye equation of state, it implies the Simon law, and that it is implied by the theory of Lennard-Jones and Devonshire, suggests that the Lindemann relation may be more than a semiempirical rule.

The concept of direct contact of neighboring atoms at fusion is factitious. In this paper, the basic assumption is made that fusion occurs when the root-mean-square amplitude of thermal vibration reaches a critical fraction of the nearest neighbor distance of atoms at fusion; the fraction is presumed the same for all isotropic monatomic solids. The theory of Debye⁸ and Waller⁹ for the temperature dependence of the intensity of Bragg reflection of x-rays is used to derive the corresponding form of Lindemann's law without further assumptions. As usually formulated,⁴ the Lindemann relation equates a frequency determined in terms of fusion parameters with a frequency (the Einstein or Debye frequency) corresponding to normal temperature. In the formulation given here, all thermodynamic variables entering the relation are evaluated at the fusion point. As a consequence, a connection between fusion parameters and the Grüneisen constant of a solid at melting emerges. Thus, a direct relationship between the Lindemann and Grüneisen theories is established.

The basic Debye-Waller theory corresponds to the assumption of linear thermal oscillation of the atoms. Hence, the reformulation of the Lindemann law, as given, ignores anharmonic terms in the potential energy of an atom, such as have been introduced into the theory of the heat capacity of solids by Born and Brody,¹⁰ and have been included in the theory of the temperature dependence of x-ray reflection intensity by Waller.¹¹ The possible effect of lattice defects¹² near the melting point has been neglected; the sharp increase in heat capacities of the alkali metals near the fusion point has been attributed to such a cause.¹³ Further, the restriction of the theoretical discussion to isotropic monatomic solids ignores Zener's extension of the Debye-Waller theory to anisotropic crystals.¹⁴ For these

reasons (and others), one can hope at best only for approximate agreement of the theory with experiment.

I. GENERALIZED LINDEMANN LAW

In the Debye-Waller formula $I_T = I_0 e^{-2M}$ for the intensity I_T at absolute temperature T relative to the intensity I_0 at zero temperature, of x-rays reflected by a crystal, the parameter M is given by⁹

$$M = 8\pi^2 (\sin\theta/\lambda)^2 \langle u^2 \rangle_{\text{av}}, \quad (1)$$

where λ is the wavelength of the radiation and θ is the Bragg angle, and $\langle u^2 \rangle_{\text{av}}$ is the mean-square amplitude, normal to the plane of reflection, of the thermal vibration of the atoms. For an isotropic, monatomic crystal,¹⁵ the Debye continuum model yields

$$M = (6h^2 T / mk\Theta^2) (\sin\theta/\lambda)^2 Q(x), \quad (2)$$

where m is the mass of an atom, h and k are the Planck and Boltzmann constants, respectively, and Θ is the Debye temperature of the lattice. The quantization factor Q is defined by

$$Q(x) = \Phi(x) + \frac{1}{4}x, \quad (3)$$

where $\Phi(x)$ is the Debye function

$$\Phi(x) = x^{-1} \int_0^x y(e^y - 1)^{-1} dy, \quad (4)$$

in which

$$x = h\nu/kT, \quad (5)$$

if ν is the Debye frequency. The term $x/4$ in Q takes account of the zero-point energy. Comparison of Eqs. (1) and (2) yields

$$\langle u^2 \rangle_{\text{av}} = (3kT/4\pi^2 m \nu^2) Q(x). \quad (6)$$

For x small, the expansion of Q is

$$Q = 1 + x^2/36 - x^4/3600 + \dots, \quad (7)$$

so that Q is approximately unity for $x \ll 1$ or $x \sim 1$.

Lindemann's basic assumption will be reformulated to state that the root-mean-square amplitude of atomic vibration at fusion is a critical fraction ρ of the distance r_m of separation of nearest neighbor atoms; that is,

$$\langle u^2 \rangle_{\text{av}} = \rho^2 r_m^2. \quad (8)$$

For close-packed lattices (face-centered cubic or hexagonal), the volume v_m per atom of the solid at melting is connected with the nearest neighbor distance r_m by

$$v_m = r_m^3/\sqrt{2}. \quad (9)$$

For other lattice types, the variation of v_m/r_m^3 from the close-packed value is too small to consider here. With this expression, Eqs. (6) and (8) yield

$$\nu_m = \nu_L Q_m^{\frac{1}{2}}, \quad (10)$$

where ν_m is the Debye frequency of the solid at fusion, $Q_m = Q(x_m)$ in terms of the corresponding value x_m of x at fusion, and ν_L is defined by

$$\nu_L = cm^{-\frac{1}{2}} v_m^{-\frac{1}{3}} (kT_m)^{\frac{1}{2}}, \quad (11)$$

¹⁵ C. Zener and G. E. M. Jauncey, Phys. Rev. 49, 17 (1936).

⁶ L. Salter, Phil. Mag. 45, 369 (1954).

⁷ F. Simon, Z. Electrochem. 35, 618 (1929); Trans. Faraday Soc. 33, 65 (1937).

⁸ P. Debye, Ann. Physik 42, 49 (1914).

⁹ I. Waller, Z. Physik 51, 213 (1923).

¹⁰ M. Born and E. Brody, Z. Physik 6, 132 (1921).

¹¹ I. Waller, Ann. Physik 83, 153 (1927).

¹² K. F. Stripp and J. G. Kirkwood, J. Chem. Phys. 22, 1579 (1954).

¹³ L. G. Carpenter, J. Chem. Phys. 21, 2245 (1953).

¹⁴ C. Zener, Phys. Rev. 49, 122 (1936).

where T_m is the absolute melting temperature and the dimensionless constant c is given by

$$c = 3^{1/2} (27^{1/6} \pi \rho)^{-1}. \quad (12)$$

The frequency ν_L can be written likewise as

$$\nu_L = CM^{-1/2} V_m^{-1/3} T_m, \quad (13)$$

where M is the atomic weight and V_m is the atomic volume of the solid at fusion, if

$$C = N^{1/2} R^{1/2} c, \quad (14)$$

in which N is Avogadro's number and R is the gas constant. Equation (13) represents the Lindemann frequency, with V_m substituted for the normal volume and a different choice of the constant C ; Eq. (10) is the generalized Lindemann law with the Debye frequency evaluated at fusion and with the quantization factor Q_m in place of the Einstein function.

The Debye frequency ν_m of the solid at melting is given by

$$\nu_m = s_m \eta M^{-1/2} \kappa_m^{1/2} v_m^{1/6}, \quad (15)$$

where κ_m is the bulk modulus (incompressibility)¹⁶ of the solid at melting and s_m , from the expressions for the wave velocities in an isotropic elastic solid, is defined in terms of the value σ_m of Poisson's ratio¹⁶ of the solid at fusion by

$$s_m = \left[\frac{3}{2(1+\sigma_m)} \right]^{1/2} \left[\frac{9/4\pi}{[2(1-\sigma_m)]^{-3/2} + 2[1-2\sigma_m]^{-3/2}} \right]^{1/2}. \quad (16)$$

Use of Eq. (15) in Eq. (10) yields

$$Q_m k T_m = \Omega \kappa_m v_m, \quad (17)$$

where $\Omega(\sigma_m)$ is defined by

$$\Omega = (s_m/c)^2. \quad (18)$$

Equation (17) can be written likewise as

$$Q_m R T_m = \Omega \kappa_m V_m, \quad (19)$$

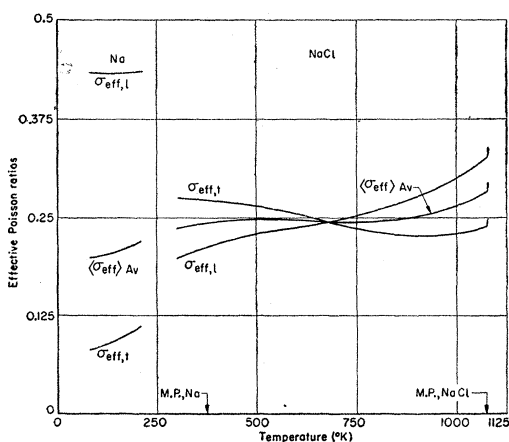


FIG. 1. Effective Poisson ratios for NaCl and for Na as a function of temperature (M.P. designates melting point).

¹⁶ The value can be taken indifferently as isothermal or adiabatic for a solid [H. Jeffreys, Proc. Cambridge Phil. Soc. 26, 101 (1930)].

which reduces to

$$R T_m = \Omega \kappa_m V_m, \quad (20)$$

for $x_m \ll 1$ or $x_m \sim 1$. The analogy of the last equation to the equation of state of an ideal gas can be noted.

Conjunction with Eq. (19) of the equation of state $P = f(V, T)$ of the solid (P is the pressure and V is the atomic volume) yields two simultaneous equations for the fusion temperature T_m in terms of the fusion pressure or fusion volume of the solid. Salter's derivation⁶ of Simon's melting-point formula⁷ from Lindemann's law corresponds, for example, to choice of the Debye equation of state for $P = f(V, T)$. To use Eq. (19), however, one must know the value of Poisson's ratio σ_m of the solid at fusion.

Detailed information on elastic constants up to a high melting temperature (1077°K) is available from results of Hunter and Siegel¹⁷ on NaCl, obtained by an ultrasonic pulse technique. Sodium chloride is a cubic crystal with three independent elastic constants, so that the expressions for wave velocities on which Eq. (15) is based, which correspond to an isotropic solid with two elastic constants, are not strictly valid. However, the anisotropy factor $[2c_{44}/(c_{11} - c_{12})]$ in terms of the elastic stiffness constants has a value of about 0.7 at room temperature and thus is near unity. Hence, by comparing the expressions for the velocity of a longitudinal and a shear wave along a cube axis, $(c_{11}/d)^{1/2}$ and $(c_{44}/d)^{1/2}$, respectively, if d is the density, with the corresponding expressions for an isotropic solid, one can obtain effective Poisson ratios in the two cases, $\sigma_{\text{eff}, l}$ and $\sigma_{\text{eff}, t}$, respectively, defined by

$$\sigma_{\text{eff}, l} = (3 - c_{11}/\kappa)/(3 + c_{11}/\kappa), \quad (21a)$$

$$\sigma_{\text{eff}, t} = \frac{1}{2}(3 - 2c_{44}/\kappa)/(3 + c_{44}/\kappa), \quad (21b)$$

if κ is the bulk modulus. These effective Poisson ratios are shown for NaCl in Fig. 1 as a function of T up to the melting temperature. One notes that the velocity of the shear wave in the solid does not vanish at the fusion point, and that the average of the two Poisson ratios of Eqs. (21), defined by

$$\langle \sigma_{\text{eff}} \rangle_{\text{Av}} = \frac{1}{3}(\sigma_{\text{eff}, l} + 2\sigma_{\text{eff}, t}), \quad (22)$$

is roughly constant at the Cauchy value $\frac{1}{4}$ appropriate to an ionic crystal.

The figure illustrates the basic result established by Hunter and Siegel, that a crystalline solid behaves as such right up to the melting point, as far as the transmission of elastic waves is concerned. Hence, it is reasonable to assume that Poisson's ratio is approximately independent of temperature up to fusion. Experimental data as detailed and to as high a melting temperature as that for NaCl do not exist for metals, but the effective Poisson ratios shown in Fig. 1 for Na (of low-melting temperature)¹⁸ are not in contradiction with the assumption. The value of s_m defined by Eq.

¹⁷ L. Hunter and S. Siegel, Phys. Rev. 61, 84 (1942).

¹⁸ S. L. Quimby and S. Siegel, Phys. Rev. 54, 293 (1938).

(16) is shown in Fig. 2 as a function of σ_m . It should be emphasized that the hypothesis that Poisson's ratio is constant up to fusion is not essential to the theory, and is made only in default of experimental information on σ_m . With values of σ_m available, Eq. (19) or (20) permits empirical evaluation, which will be carried out in Sec. III, of the constant c of the Lindemann frequency.

The form of Eq. (20) with values under normal conditions substituted for κ_m and V_m (and with $Q_m=1$) is ascribed by Grüneisen⁵ to Einstein and Lindemann; a variant determined empirically has been given by Richards.¹⁹ Explicit introduction of the fusion volume V_m in the Lindemann frequency has been made by Grüneisen.²⁰ These formulations correspond to replacing the factor s_m in Eq. (15) by an average over different solids.

II. THE GRÜNEISEN CONSTANT

The Grüneisen constant γ of a solid can be defined^{5,20} by

$$\gamma = -d \ln \nu / d \ln V, \quad (23)$$

on the assumption that the Debye frequency ν is a function only of the volume. The value γ_m of the constant for a solid at fusion is

$$\gamma_m = -\frac{1}{6} - \frac{1}{2} d \ln \kappa_m / d \ln V_m, \quad (24)$$

from Eq. (15), on the further assumption that the Poisson ratio σ_m of the solid at fusion is independent of the volume. A similar hypothesis is made in the derivation of the analog of Eq. (24) for normal temperature^{21,22}; grounds for extending the approximation to the case at hand are provided by the conclusion of Hunter and Siegel, that the elastic properties of a solid at melting are essentially similar to those of a solid under normal conditions. On the basis of Grüneisen's law,^{5,20} the value of γ_m should be given likewise by

$$\gamma_m = \kappa_m \alpha_m V_m / C_{V,m}, \quad (25)$$

where α_m is the volumetric coefficient of thermal expansion of the solid at the fusion point, and $C_{V,m}$ is the corresponding heat capacity at constant volume.

Differentiation of Eq. (19) with respect to V_m , with use of Eq. (24), yields

$$(1 - O_m/Q_m) d \ln T_m / d \ln V_m = \frac{2}{3} - (2 - O_m/Q_m) \gamma_m, \quad (26)$$

where $O_m(x_m) = x_m dQ_m/dx_m$ is given by

$$O_m = -\Phi(x_m) + x_m(\exp x_m - 1)^{-1} + \frac{1}{4} x_m. \quad (27)$$

From the fact that

$$dP_m/dT_m = (\partial P/\partial T)_V + (\partial P/\partial V)_T dV_m/dT_m, \quad (28)$$

where the total derivatives are evaluated along the fusion curve and the partial derivatives (and V_m)

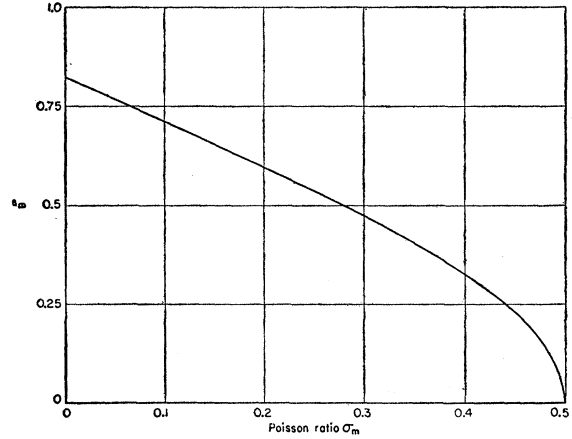


FIG. 2. The parameter s_m as a function of the fusion value σ_m of Poisson's ratio.

correspond to the solid at fusion, one can show that

$$dT_m/dV_m = -(\kappa_m/V_m)(dT_m/dP_m)(1 - \kappa_m \alpha_m dT_m/dP_m)^{-1}. \quad (29)$$

Use of this expression and of Clapeyron's equation in Eq. (26) yields

$$\gamma_m = \frac{2}{3} \left[2 - \frac{O_m}{Q_m} \right]^{-1} + \left[\frac{1 - O_m/Q_m}{2 - O_m/Q_m} \right] \frac{q \kappa_m \Delta V}{L}, \quad (30)$$

in which

$$q = (1 - \kappa_m \alpha_m T_m \Delta V / L)^{-1}, \quad (31)$$

where L is the latent heat of fusion and ΔV is the change in volume (from solid to liquid) in fusion.

The expansion of O_m for x_m small is

$$O_m = x_m^2/18 - x_m^4/900 + \dots, \quad (32)$$

so that O_m is approximately zero for $x_m \ll 1$ or $x_m \sim 1$. Under these conditions, Eq. (30) yields

$$\gamma_m = \frac{1}{3} + \frac{1}{2} q \kappa_m \Delta V / L, \quad (33)$$

which can be written alternatively as

$$\gamma_m = \frac{1}{3} + \frac{1}{2} (qR/\Omega) (T_m \Delta V / LV_m), \quad (34)$$

from Eq. (20). The parameter q of Eq. (31) is equal to the reciprocal factor in the right-hand side of Eq. (29); since $(\partial P/\partial V)_T$ for the solid at fusion does not differ greatly from dP_m/dV_m , q correspondingly does not differ greatly from unity, and can be written

$$q = 1 + \kappa_m \alpha_m T_m \Delta V / L, \quad (35)$$

in general, or alternatively, as

$$q = 1 + \gamma_m C_{V,m} T_m \Delta V / LV_m, \quad (36)$$

from Eq. (25). These relations for γ_m , which are algebraic in fusion parameters, yield a direct connection via Eq. (25) between the Lindemann and Grüneisen theories. The connection is susceptible to an experimental verification, which will be carried out in Sec. III.

¹⁹ T. W. Richards, J. Am. Chem. Soc. 37, 1643 (1915).

²⁰ E. Grüneisen, Ann. Physik 39, 258 (1912).

²¹ J. C. Slater, Phys. Rev. 57, 744 (1940).

²² J. C. Slater, *Introduction to Chemical Physics* (McGraw-Hill Book Company, Inc., New York, 1939), pp. 238, 259, 261, 451.

From Eq. (26) with the use of Eq. (29), one obtains

$$\left\{1 - \frac{O_m}{Q_m} + \alpha_m T_m \left[\left(2 - \frac{O_m}{Q_m}\right) \gamma_m - \frac{2}{3} \right] \right\} \frac{dT_m}{dP_m} = \left[\left(2 - \frac{O_m}{Q_m}\right) \gamma_m - \frac{2}{3} \right] \frac{T_m}{\kappa_m}. \quad (37)$$

For x_m small, this equation yields

$$dT_m/dP_m = 2(\gamma_m - \frac{1}{3})T_m/q\kappa_m. \quad (38)$$

If $\gamma_m > \frac{1}{3}$, this equation states that the fusion temperature T_m is a monotone-increasing function of the fusion pressure P_m , so that, in this respect, the fusion curve predicted by the generalized Lindemann relation is normal in the sense of Bridgman.^{23,24} Only if $\gamma_m = \frac{1}{3}$ at finite pressure can the predicted fusion curve be in accord with the hypothesis of Tammann,²⁵ that the fusion temperature rises to a maximum and then falls, and only if $\gamma_m \rightarrow \frac{1}{3}$ for P_m large can it be in accord with the alternative hypothesis of Schames,²⁶ that an asymptotic fusion temperature exists. Equation (33) can be rewritten as

$$L/\Delta V = \frac{1}{2}(\gamma_m - \frac{1}{3})^{-1}q\kappa_m. \quad (39)$$

Since this equation specifies only the ratio $L/\Delta V$, it yields no direct information on the existence or non-existence of a critical point (where L and ΔV must vanish simultaneously so that dT_m/dP_m remains finite), but it is consistent with the latter possibility, since the ratio is specified as always positive if $\gamma_m - \frac{1}{3}$ is positive.

The preceding results show that the theory yields correctly the sign of the slope of the normal fusion curve if $\gamma_m > \frac{1}{3}$. Equation (38) yields the approximation

$$d^2T_m/dP_m^2 = -2(\gamma_m - \frac{1}{3} + d\gamma_m/d \ln V_m)T_m/q^2\kappa_m^2, \quad (40)$$

corresponding to $Q_m = 1$, $O_m = 0$, and q a constant of the order of unity. The fusion curve for all substances, according to Bridgman,^{23,24} shows a negative value of d^2T_m/dP_m^2 ; that is, the curve of T_m vs P_m is concave to the pressure axis. Hence, the fusion curve predicted by the generalized Lindemann law is completely normal in the sense of Bridgman only if $\gamma_m > \frac{1}{3}$ and the inequality

$$\gamma_m - \frac{1}{3} + d\gamma_m/d \ln V_m > 0 \quad (41)$$

is satisfied.

The necessity for evaluating at the fusion point the Debye frequency appearing in Eq. (10) is underwritten by the experimental results of Owen and Williams.²⁷ These authors found that values of Θ deduced, by means of Eq. (2), from measurement of the intensity of Bragg reflection of x-rays, are not constant for Al, Cu,

and Au over the temperature range from 293 to 900°K. The observed values of Θ at temperature T relative to the value Θ_0 at temperature T_0 are represented well by²⁸

$$\Theta = \Theta_0[1 - \gamma\alpha(T - T_0)], \quad (42)$$

where α is the volumetric coefficient of thermal expansion. This relation is precisely what the Grüneisen theory demands on the basis of Eqs. (15) and (23), if the temperature dependence of Θ exists only by virtue of the change in volume.

A relation for γ_m in terms of fusion parameters (but depending also on the average coefficient of thermal expansion from absolute zero to the melting temperature), somewhat similar to Eq. (33), has been given by Grüneisen.²⁰ The result depends on Grüneisen's hypothesis that the fractional change in volume from absolute zero to the melting temperature is a constant for all solids, and like Eq. (33), it is derived by use of Clapeyron's equation to convert a differential into an algebraic function of fusion parameters.

III. COMPARISON WITH EXPERIMENT

Values of thermodynamic variables at the fusion point are assembled in Table I to check Eq. (20) for the elements which show the same cubic lattice (body-centered or face-centered) at both normal temperature and fusion, and for which sufficient data can be obtained. For Pb and Al, the temperature variation of the bulk modulus can be obtained from measurements of Birch and Law,²⁹ extending to temperatures fairly close to the melting temperature. In other cases, the tabulated values of κ_m were obtained from the (approximate) formula

$$\kappa_m = \kappa_0[1 - \eta\alpha(t_m - t_0)], \quad (43)$$

where t_m is the centigrade fusion temperature and the normal bulk modulus κ_0 corresponds to temperature t_0 ; the parameter

$$\eta = -(\kappa\alpha)^{-1}(\partial\kappa/\partial T)_P = \kappa\alpha^{-1}(\partial\alpha/\partial P)_T \quad (44)$$

is a dimensionless constant varying from about 3 to perhaps 10 for most solids. The values of η shown are averages for each element obtained from a survey of data given by Birch,³⁰ or from a tabulation of Grüneisen⁵ based on results of Bridgman. From the corresponding temperature ranges indicated for η and for the thermal expansion α , the correction of Eq. (43) (unnecessary

²³ P. W. Bridgman, *The Physics of High Pressure* (G. Bell and Sons, Ltd., London, 1949), pp. 160, 189.

²⁴ P. W. Bridgman, *Revs. Modern Phys.* 7, 1 (1935).

²⁵ G. Tammann, *Kristallisieren und Schmelzen* (Verlag von J. A. Barth, Leipzig, 1903), p. 90; *Aggregatzustände* (Verlag von L. Voss, Leipzig, 1922), p. 94.

²⁶ L. Schames, *Ann. Physik* 38, 830 (1912); 39, 887 (1912).

²⁷ E. O. Owen and R. W. Williams, *Proc. Roy. Soc. (London)* A188, 509 (1947).

²⁸ For Al, Eq. (42) is valid up to only 600°K, since the values of Θ show nonlinearity as a function of T near the melting temperature. For such a case, C. Zener and S. Bilinsky [*Phys. Rev.* 50, 101 (1936)] have given a modification of the Debye-Waller theory in terms of a variable Θ of form more general than corresponds to Eq. (42). One can show, with use of Grüneisen's law, that their expression for Θ reduces to the linear form (42) if the heat capacity C_P is constant. The limitations on the simple Debye-Waller theory (in terms of a constant Θ) at high temperature are discussed by R. W. James [*The Optical Principles of the Diffraction of X-Rays* (G. Bell and Sons, Ltd., London, 1948), p. 231].

²⁹ F. Birch and R. R. Law, *Bull. Geol. Soc. Am.* 46, 1219 (1935).

³⁰ F. Birch, *J. Geophys. Research* 57, 227 (1952).

TABLE I. Values of the ratio $s_m^2\kappa_m V_m/RT_m$ and of the Lindemann constant c for elements with cubic lattices.

	t_m °C	$10^{-6}\kappa_0$ bars	η	$10^4\alpha$ (°C) ⁻¹	$10^{-6}\kappa_m$ bars	V_m cm ³ /mole	σ_m	$\frac{s_m^2\kappa_0 V_0}{RT_m}$	$\frac{s_m^2\kappa_m V_m}{RT_m}$	c	Weight
Cs	29.7 ^a	0.0203 ^b	0.0203	71.0 ^a	(0.30) ^e	12.7	12.7	3.6	1
Rb	38.7	0.031 ₄	0.031 ₄	56.0	(0.30) ^e	15.0	15.1	3.9	9/10
K	62.5	0.0318	3.2 (0-95°C)	255. (0-50°C)	0.0308	45.7	0.30 ^e	11.4	11.2	3.3	1
Na	97.6	0.0691	4.3 ₅ (0-95°C)	213. (0-95°C)	0.0643	24.0	0.24 ^a	15.8	14.8	3.8	1
Li	186. ^d	0.116 ^b	4.6 ^e (0-95°C)	168. ^d (0-95°C)	0.10 ₁	13.4 ^f	(0.24) ^e	11.7	10.5	3.2	9/10
Pb	327.4 ^d	0.42 ^a	0.35 ^h	18.8 ⁱ	0.42 ₅ ^j	12.	10.	3.2	9/10
Al	660.1	0.757	0.56 ₆	10.3	0.33	18.0	14.0	3.7	9/10
Ag	960.8 ^d	1.00 ^k	6.7 ^l (30-75°C)	67.2 ^d (0-900°C)	0.5 ₈	11.2 ⁱ	0.37 ^j	13.9	8.7	3.0	3/4
Cu	1083.	1.37	7.8 (30-75°C)	60.9 (0-1000°C)	0.6 ₈	7.60	0.33	16.0	9.8	3.1	3/4
Fe	1532. ^m	1.68 ^k	7.6 ^e (0-100°C)	45.0 ^d (20-900°C)	0.8 ₁	7.68 ^m	0.28 ^j	19.5	10.	3.2	1/2
Ni	1453. ^d	1.87 ^k	6.0 ^l (30-75°C)	48.9 ^d (25-900°C)	1. ₁	7.2 ^f	0.36 ^j	13.1	8.4	2.9	1/4
Pd	1552.	1.90	3.4 (30-75°C)	41.4 (16-1000°C)	1. ₆	9.4	0.39	12.9	1. ₁	3.3	1/4
Pt	1769.	2.76	9.2 (30-75°C)	30.6 (0-1000°C)	1. ₄	9.7	0.39	17.4	9.0	3.0	1/4

^a Kubaschewski (reference 32).^b Gilvarry (reference 38).^c Birch (reference 30).^d From *Smithsonian Physical Tables* (Smithsonian Institute, Washington, D. C., 1954).^e Value for K computed by Eq. (22) from elastic constants given by C. Kittell [*Introduction to Solid State Physics* (John Wiley and Sons, Inc., New York, 1953), p. 50]; value for Na computed similarly (for normal temperature) from data of Quimby and Siegel (reference 18). Values for Cs and Rb taken equal to that of K; value for Li taken equal to that of Na.^f Computed from thermal expansion to the melting point.^g Slater (reference 22).^h Computed from temperature corrections of Birch and Law (reference 29).ⁱ Determined (or extrapolated) from data in *Landolt-Börnstein physikalisch-chemische Tabellen* (Verlag Julius Springer, Berlin, 1923), fifth edition.^j Values (or averages) from *Metals Handbook* (American Society for Metals, Cleveland, 1948), or from *Mechanical Properties of Metals and Alloys*, National Bureau of Standards Circular C447 (United States Government Printing Office, Washington, D. C., 1943).^k Slater (reference 21).^l Grüneisen (reference 5).^m Stott and Rendall (reference 33).

for Cs and Rb) should be accurate for K and Na, and should be reasonably accurate for Li. For elements below Al in Table I, the listed values of κ_m are merely estimates, of an accuracy which is uncertain but which decreases for the elements of higher melting temperature.³¹ Values of the fusion volume V_m were obtained from a critical survey of fusion data given by

³¹ Birch and Law (reference 29) represent their measurements of compressibility on Al up to 435°C by a linear relation in the temperature, and their measurements on Pb up to 259°C by an expression containing a small quadratic term, which corresponds to only six percent of the total change observed in compressibility with temperature, or only one percent of the compressibility itself. The observed temperature coefficients are in close agreement with those obtained by Bridgman over the restricted range 30-75°C. The data of Hunter and Siegel (reference 17) show that some curvature exists in the graph of κ vs T . To compensate for any curvature, values of the average thermal expansion over as large a temperature range possible were taken, so that Eq. (43) should be valid at least as a zero-order approximation. These considerations yield some justification for assumption of this linear relation over the temperature ranges in question. Iron undergoes phase transitions below its melting temperature, but this fact does not invalidate use of Eq. (43), since the δ -phase stable near fusion is merely a reappearance of the normal α phase. For both Fe and Ni, any "ΔE-effect" [C. Zener, *Elasticity and Anelasticity of Metals* (University of Chicago Press, Chicago, 1948), p. 105] has been ignored.

Kubaschewski,³² from work of Stott and Rendall,³³ or from data in standard tables. The tabulated values (in some cases estimated from single-crystal constants) of Poisson's ratio σ_m refer to normal temperature. Table I shows the value of $s_m^2\kappa_m V_m/RT_m$ for each element, assigned a weight to correspond to the presumptive accuracy in κ_m and V_m ; the corresponding value of c defined by Eqs. (17) and (18) is shown likewise. Throughout this section, $Q_m=1$ and $O_m=0$ will be taken; these assumptions cause negligible error.

On the assumption (8), the tabulated values of the ratio $s_m^2\kappa_m V_m/RT_m$ should be constant, from Eq. (20), as is true approximately. The listed values of $s_m^2\kappa_0 V_0/RT_m$ (V_0 is the normal volume) corresponding to the Lindemann assumption are roughly constant likewise, which indicates that the two assumptions are approximately equivalent, empirically. However, there is less tendency for the values of $s_m^2\kappa_m V_m/RT_m$ to increase at the higher fusion temperatures relative to the values for the alkali metals, than is the case for

³² O. Kubaschewski, *Trans. Faraday Soc.* 45, 931 (1949).³³ V. H. Stott and J. H. Rendall, *J. Iron Steel Inst.* 175, 374 (1953).

TABLE II. Comparison of critical ratios ρ of vibration amplitude to nearest neighbor distance at fusion, from x-ray and fusion data.

	Θ_m °K	$[\langle u^2 \rangle_{Av}]^{\frac{1}{2}}$ Å	r_m Å	ρ	ρ (Table I)
Al	300 ^a	0.24	2.9	0.08 ₂	0.066
Cu	280	0.20	2.6	0.07 ₆	0.07 ₆
Au	180	0.21	2.9	0.07 ₁	...

^a Extrapolated from data of Owen and Williams (reference 27); the quadratic temperature correction in the case of Al was made from an average curve drawn to the data of Fig. 4.

$s_m^2 \kappa_0 V_0 / RT_m$. It is essential to retain the factor s_m^2 in $s_m^2 \kappa_m V_m / RT_m$, without averaging over the elements; otherwise the values of the ratio show wide deviations from the average for Pb and for Li (to a less extent). The presumption is strong that values of σ_m actually corresponding to the fusion temperature and accurate values of κ_m would reduce the variance shown by the table for the constant c of the Lindemann frequency. Aside from such uncertainties, possible effects of anharmonicity,¹¹ and, particularly in the case of the alkali metals, lattice imperfections,¹⁸ part of the variance shown may be due to deviations of the Debye continuum model from the more accurate models of Born and von Kármán³⁴ or Blackman,³⁵ or from Bhatia's extension³⁶ of the model of Born and von Kármán to cubic metals.

In Table II are shown the values of Θ_m , the Debye temperature of the solid at fusion from the x-ray intensity measurements of Owen and Williams,²⁷ as extrapolated linearly for Cu and Au but quadratically²⁸ for Al. The corresponding root-mean-square amplitude $[\langle u^2 \rangle_{Av}]^{\frac{1}{2}}$ of thermal vibration at fusion, as computed from Eq. (6), is shown likewise, with the values of r_m determined by Eq. (9) from the values of V_m in Table I. For Al and Cu, the critical ratios $\rho = [\langle u^2 \rangle_{Av}]^{\frac{1}{2}} / r_m$ show reasonable agreement with the values, given for comparison, deduced from the corresponding values of c in Table I by means of Eq. (12).

An average value over the elements (with their assigned weights) in Table I is shown in Table III for the constant c of the Lindemann frequency, with its weighted standard deviation Σ and the ratio Σ/c . The corresponding value of C from Eq. (14), and of ρ from Eq. (12), are shown likewise. The average value of ρ from the data of Table II is given also, with the corresponding values of c and C . One notes that the over-all agreement is quite satisfactory. Both values of ρ appearing are significantly below the average values of²⁰ 0.085, and of somewhat less than⁵ 0.10₆, estimated by Grüneisen. Weighted averages of c computed separately for the body-centered (alkali elements and Fe) and face-centered elements in Table I agree with each other within less than ten percent, so that no evidence exists,

within the significance of the data, for a systematic difference in c between the two classes of elements. The ratio of the standard deviation to the average, computed with equal weight for each element, of the Lindemann analog of c obtained by replacing $\kappa_m V_m$ by $\kappa_0 V_0$, exceeds the corresponding ratio in Table III by a factor of about three.

In Table IV, values of the ratio $s_m^2 \kappa_m V_m / RT_m$, and of the constant c defined by Eqs. (17) and (18), are shown for a number of elements with noncubic lattices. In the cases where experimental results for these anisotropic crystals show a significant difference in the linear compressibilities a_{11} and a_{\perp} , parallel and perpendicular to the crystal axis, respectively, extrapolated bulk moduli were determined from the relation

$$\kappa^{-1} = a_{11} + 2a_{\perp}. \quad (45)$$

From the fact³⁷ that the mean-square thermal displacement in a hexagonal crystal is given in terms of the corresponding values, $\langle u_{11}^2 \rangle_{Av}$ and $\langle u_{\perp}^2 \rangle_{Av}$, parallel and perpendicular to the crystal axis, respectively, by

$$\langle u^2 \rangle_{Av} = \frac{1}{3} [\langle u_{11}^2 \rangle_{Av} + 2\langle u_{\perp}^2 \rangle_{Av}], \quad (46)$$

and the fact that the average Debye temperature $\langle \Theta \rangle_{Av}$ is given in terms of values Θ_{11} and Θ_{\perp} , associated with directions parallel and perpendicular to the crystal axis, respectively, by

$$[\langle \Theta \rangle_{Av}]^{-2} = \frac{1}{3} (\Theta_{11}^{-2} + 2\Theta_{\perp}^{-2}), \quad (47)$$

it follows that Eq. (45) represents a proper average in this case. One notes that the values of $s_m^2 \kappa_m V_m / RT_m$ and of c for the hexagonal close-packed elements Zn and Mg are consonant with those in Table I, in agreement with one's expectation.

The other elements in Table IV with more complex lattices and of generally lower-melting point (excluding Te but including Sb) seem to form a distinct group with a value of the Lindemann constant higher than corresponds to Table III. It should be emphasized that because of the limitation of Eq. (2) to isotropic solids, the theory as formulated is not directly applicable to elements with complex lattices. For such elements, the mean-square amplitude of thermal vibration, as averaged over different directions in the crystal, should be connected with the average Debye temperature from expressions for wave velocities in an isotropic solid, by a function differing in a constant of proportionality from that corresponding to Eq. (6). For complex crystals, Eq. (9) also requires modification, and the

TABLE III. Values of empirical constants, from averages.

	c	Standard deviation Σ	Σ/c	$10^{-12}C$ (erg/°K) ^{1/2} mole ^{-1/2}	ρ
Table I	3.4	0.09	0.03	2.6	0.072
Table II	3.2			2.8	0.07 ₆

³⁴ M. Born and T. von Kármán, *Physik. Z.* **13**, 297 (1912).

³⁵ M. Blackman, *Proc. Roy. Soc. (London)* **A159**, 416 (1937).

³⁶ A. B. Bhatia, *Phys. Rev.* **97**, 363 (1955).

³⁷ G. W. Brindley and P. Ridley, *Proc. Phys. Soc. (London)* **51**, 69 (1939).

TABLE IV. Values of the ratio $\kappa_m^2 V_m / RT_m$ and of the Lindemann constant c for elements with noncubic lattices.

	Lattice	T_m °C	$10^{-6}\kappa_m$ bars	V_m cm ³ /mole	σ_m	$\kappa_m^2 V_m / RT_m$	c
Zn	h.c.p.	419.5 ^a	0.43 ^b	9.56 ^c	(1/3) ^d	1 ₃	3.6
Mg	h.c.p.	651	0.34	14.8	0.35	1 ₁	3.3
Hg	rhomb.	-38.9 ^a	0.23 ^e	14.14 ^c	(1/3) ^d	3 ₁	5.5
Ga	complex	29.7 ^a	0.49 ^f	11.8 ^c	(1/3) ^d	41	6.4
Sn	tetra.	231.9 ^a	0.47 ^b	16.5 ^c	0.33 ^d	3 ₄	5.9
Bi	rhomb.	271.3	0.29	21.6	0.33	2 ₆	5.1
Te	Se type	452	0.21	20.9	(1/3)	1 ₃	3.6
Sb	rhomb.	630.5	0.47	18.8	(1/3)	2 ₁	4.6

^a From *Smithsonian Physical Tables* (Smithsonian Institute, Washington, D. C., 1954).

^b Extrapolated from data of Bridgman (reference 23) for 30 and 75°C, corrected according to Slater (reference 21). For all elements except Bi, Eq. (45) was used.

^c From *Smithsonian Physical Tables* (Smithsonian Institute, Washington, D. C., 1954) or *Landolt-Börnstein physikalisch-chemische Tabellen* (Verlag Julius Springer, Berlin, 1923), fifth edition.

^d Parenthetic values are average over metals [C. Zwikker, *Physical Properties of Solid Materials* (Interscience Publishers, Inc., New York, 1954), p. 90]; other values from *Mechanical Properties of Metals and Alloys*, National Bureau of Standards Circular C447 (United States Government Printing Office, Washington, D. C., 1943).

^e From value for liquid at melting point quoted by J. F. Kincaid and H. Eyring [J. Chem. Phys. 5, 587 (1937)], combined with rough value for difference in compressibility of liquid and solid at fusion given by P. W. Bridgman [Proc. Am. Acad. Arts Sci. 47, 347 (1912)].

^f Value for solid at 20°C given by Bridgman (reference 23) corrected according to Slater (reference 21).

possibility cannot be ignored that ρ of Eq. (8) is a function of lattice type.

To compare the Grüneisen constants γ_m as determined from fusion parameters and from Grüneisen's law, thermodynamic variables at fusion are tabulated in Table V for those elements in Tables I and IV for which data are available. These data, in conjunction with those of Table I or IV, are sufficient to determine γ_m from Eq. (25) and from Eq. (33). Values of $C_{V,m}$ were computed from values of $C_{P,m}$, the fusion heat capacity of the solid at constant pressure, by means of the thermodynamic identity $C_{V,m} = C_{P,m} - \kappa_m \alpha_m^2 V_m T_m$. The value of γ , the Grüneisen constant under normal conditions, is shown likewise for comparison. One notes that agreement of the values of γ_m is very good, in general, for the elements with cubic lattices and with hexagonal close-packed lattices (Zn and Mg); any disparities do not exceed those common in comparisons of γ from Grüneisen's law with values deduced from the analog of Eq. (24) under normal conditions.^{21,22,38} The agreement holds in spite of the fact that the values of κ_m and L range in magnitude by a factor of about 40 and 7, respectively. For Hg and Sn, the agreement is fair, in spite of the deviation of c from the average of Table III in these cases.

For all the elements in Table V except Ga, Bi, and Sb, γ_m exceeds $\frac{1}{3}$ and the fusion curve is normal as regards sign of slope. For the latter three elements, the slope dT_m/dP_m is negative for the phases which are stable at ordinary pressures.³⁹ It is known that Ga and

Bi undergo a phase transition at high pressure to a polymorphic form showing a normal fusion curve; the behavior of ice is similar. One notes from Table V that identity of the Grüneisen constants from fusion parameters and from Grüneisen's law fails outright for the three elements in question. A similar anomaly arises in connection with Mott's theory of liquids.⁴⁰ Mott treats the liquid state essentially as an amorphous solid on the Debye theory, by assigning a characteristic frequency to the liquid which is lower than the corresponding frequency of the solid. This assumption permits evaluation of the ratio of characteristic frequencies in the solid and the liquid, and thus the corresponding ratio of electrical conductivities, in terms of the latent heat of fusion and the melting temperature. Mott's expression for the ratio of the conductivities is in good accord with experimental values, in general, but it fails in the cases of Ga, Bi, and Sb, by yielding the wrong sense (relative to unity) of the ratio.

Kubaschewski³² has pointed out that the quantity

$$\delta = LV_m / T\Delta V \quad (48)$$

is nearly a constant for a considerable number of

TABLE V. Comparison of Grüneisen constants.

	$\Delta V/V_m$	L cal/ mole	$C_{P,m}$ cal/ °C mole	$10^3 \alpha_m$ (°C) ⁻¹	γ_m Eq. (33)	γ_m Eq. (25)	γ
Cs	0.026 ^a	500 ^a	7.39 ^a	0.29 ^a	1.4	1.6	1.60 ^b
Rb	0.025	524	7.17	0.27	1.5	1.8	1.86
K	0.0255 ^a	571 ^a	7.98 ^c	0.25 ^a	1.19	1.2	1.41 ^b
Na	0.025	630	7.55	0.22	1.1	1.2	1.37
Li	0.0165	703	7.08	0.18	0.74	0.88	1.17
Pb	0.035 ^a	1190 ^a	6.97 ^a	0.12 ^a	3.7	3.4	2.73 ^d
Al	0.060	2520	7.8	0.099	2.6	2.1	2.17
Ag	0.038	2740	7.47	0.081	1.7	2.0	2.40
Cu	0.0415	3110	7.5	0.070	1.3	1.3	1.96
Fe	0.03 ^e (±0.005)	3600 ^f	10.3 ^g	0.064 ^h	1.1	1.1	1.60 ^d
Zn	0.042 ^a	1720 ^a	7.07 ^a	0.113 ^a	1.8	1.8	2.01 ^d
Mg	0.041	2080	7.6	0.110	1.9	2.1	1.51
Hg	0.037	602	6.79	0.171	3.2	2.1	...
Sn	0.028	1690	7.17	0.095	2.1	2.8	2.14
Ga	-0.032 ⁱ	1340 ^a	6.39 ^a	0.054 ^a	(-1.2)	1.2	...
Bi	-0.0335	2600	6.86	0.040	(-0.60)	0.8 ₉	1.14
Sb	-0.0095	4740	6.4	0.033	(0.12)	1.1	0.92

^a Kubaschewski (reference 32).

^b From Grüneisen (reference 5), corrected to correspond to values of κ in Table I.

^c Carpenter, Harle, and Steward, *Nature* 141, 1015 (1938).

^d Grüneisen (reference 5).

^e Stott and Rendall (reference 33).

^f J. H. Averbary, quoted by F. E. Simon [Nature 172, 746 (1953)].

^g Value recommended in survey of data by J. B. Austin [Indust. and Engr. Chem. 24, 1225 (1932)].

^h Value (from empirical formula of Kubaschewski) given by Stott and Rendall (reference 33).

ⁱ Kubaschewski (reference 32). Value for Sb is from Matuyama (reference 40).

Matuyama [Science Repts Tôhoku Imp. Univ. 27, 1 (1928)] show a definite negative value of ΔV , in contradiction of the positive value of M. Toeppler [Ann. Physik und Chemie 53, 344 (1894)], which is reproduced in the *International Critical Tables* (McGraw-Hill Book Company, Inc., New York, 1929).

⁴⁰ N. F. Mott, *Proc. Roy. Soc. (London)* A146, 465 (1934).

³⁸ J. J. Gilvarry, *J. Chem. Phys.* 23, 1925 (1955).

³⁹ Antimony is not listed by Bridgman (references 23 and 24) as showing an abnormal fusion curve. However, results of Y.

metals, with the average value 60 cal/deg mole, which yields the empirical relation $dP_m/dT_m = \delta/V_m$ from Clapeyron's equation. In terms of this constant one obtains

$$\gamma_m = \frac{1}{3} + \frac{1}{2}qR/\Omega\delta, \quad q = 1 + \gamma_m C_{V,m}/\delta, \quad (49)$$

from Eqs. (34) and (36), respectively, which yield $\gamma_m = 1.6$ and $q = 1.2$ as average values over the metals, if $C_{V,m}$ is given the Dulong and Petit value and if Ω is evaluated (with $\sigma_m = \frac{1}{3}$) from the value $c = 3.4$ of Table III. The average values of γ_m from the data of Table V (exclusive of values for Ga, Bi, and Sb) are 1.8 from both Eq. (25) and Eq. (33); the corresponding value of q is 1.2. The validity of Kubaschewski's relations is a consequence of the fact that γ_m is nearly a constant over most solids; in a similar manner, the validity of an empirical relation antedating the formulation of Grüneisen's law by many years is justified by the law of Dulong and Petit and by the constancy of γ over most solids.²⁰

IV. CONCLUSION

The excellent agreement shown by Table V between the two evaluations of the Grüneisen constant at fusion is a strong indication of the validity of the reformulation of Lindemann's law, for monatomic elements. The agreement implies that the relation $\nu_m = \nu_L$ yields not only the right magnitude, approximately, of the fusion temperature, but likewise the correct slope of the fusion curve. As one notes, no attempt has been made to check the theory against experiment for the ionic or

molecular crystals. Direct extension of the theory to ionic crystals is complicated by the limitation of the Debye-Waller theory to monatomic solids.

One notes that Eq. (10) differs from the corresponding Lindemann form, in the essential respect that quantum effects are included on the basis of the Debye, rather than the Einstein theory. Similarly, the form (24) taken for the Grüneisen constant corresponds to that derived first by Lorentz⁴¹ and later by Slater²¹ for the Debye model. Dugdale and MacDonald⁴² have suggested a form for the Grüneisen constant as evaluated from the equation of state, which implies that this value for γ_m should be reduced by $\frac{1}{3}$. In a further paper,⁴³ however, the author shows that the result (for zero pressure) of Dugdale and MacDonald is appropriate to an Einstein solid of independent atoms. Hence, the considerations of this paper, and of the following two papers, are fully consistent with the Debye theory.

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⁴¹ H. A. Lorentz, *Proc. Roy. Acad. Amsterdam* **19**, 1324 (1916).

⁴² J. S. Dugdale and D. K. C. MacDonald, *Phys. Rev.* **89**, 832 (1953).

⁴³ J. J. Gilvarry, this issue [*Phys. Rev.* **102**, 331 (1956)].