Grüneisen's Law and the Fusion Curve at High Pressure*

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The correction to Grüneisen's law corresponding to the effect of the electrons at high pressure is determined, on the assumption that the lattice contribution to the pressure is small, and that the equation of state of the solid can be approximated by results of the statistical Thomas-Fermi atom model for the electron pressure. The effect of a first-order temperature perturbation, for temperatures low in the sense of the model, is included in the Thomas-Fermi theory, but exchange is neglected. For temperatures subject to the restriction noted, but high enough so that the electronic contribution to the heat capacity dominates the lattice contribution, Grüneisen's law is valid as a formal relation on the Thomas-Fermi theory, with a physical reinterpretation of the proportionality constant which enters. The fusion curve under high compression is determined from a reformulation of the Lindemann law given previously, on the similarity assumption that the ratio of the amplitude of thermal vibration to nearest neighbor distance has the same value at high pressure as at low. The fusion temperature as a function of pressure is determined to zero order from results of the zero-temperature Thomas-Fermi theory, on the

assumption that Poisson's ratio is independent of temperature and pressure. It is shown that the general temperature-perturbed Thomas-Fermi theory is adequate to determine the fusion curve on this model, except for the domain of large atomic number near the Fermi-Dirac limit of high pressure, for values of Poisson's ratio which are not relatively high. Exclusive of this domain, it is proved that the predicted fusion curve is normal in the sense of Bridgman, and is not in accord with the hypotheses of Tammann or of Schames. Fusion curves predicted for the alkali elements at high pressure are in accord with experimental results of Bridgman for low pressure, in the sense that the high-pressure curves show a reversal of normal order with respect to atomic number of melting temperature in the alkali metal family, as postulated by Bridgman from extrapolation of the low-pressure curves. The theory presented yields a general method of determining the corrections, corresponding to the lattice contributions, in thermodynamic functions determined from the Thomas-Fermi model (the method is subject to a limitation on physical validity in the Fermi-Dirac limit of high pressure).

O UTSIDE the region of normal pressure and temperature, Grüneisen's law has been discussed by various authors for a number of metals[1] and for solid hydrogen and deuterium[2] on the basis of experimental data, for low temperature and for low or moderate pressure. The validity of the law for the temperatures and moderate pressures corresponding to conditions in the earth's mantle has been discussed by Birch.[3] Visvanathan[4] has considered the modification in the law at very low temperature due to the electrons. A similar modification corresponding to the effect of the electrons is necessary at high pressure. In this paper, the extension of the law to high pressures is considered, on the assumption that the equation of state of the solid is given by results of the statistical Thomas-Fermi atom model and that the lattice contribution to the pressure is small.

By assuming the identity of the Lindemann and Debye characteristic frequencies at moderately high pressures, Uffen[5] has estimated the melting point gradient in the earth's mantle. He evaluated the Debye frequency from the known values of the speeds of elastic waves at various depths in the mantle (obtained by analysis of travel times of seismic waves), obtaining the density at each depth from Bullen's determination of the density distribution in the earth.[6] This procedure yields a maximum temperature in the earth's mantle at the core boundary which is in agreement with an

independent estimate made by Daly,[7] and is concordant with an upper limit given by Jeffreys.[8]

In this paper, Uffen's method, which amounts to a similarity assumption, is generalized to obtain the fusion curve at high compression. The explicit development will be based on a reformulation of Lindemann's law given by this author in a previous paper.[9] In that paper it is shown that adjunction of an equation of state of the solid to the reformulated Lindemann rule yields the fusion curve; the equation of state corresponding to the Thomas-Fermi atom model will be taken here. Final justification of the method must be based on a fundamental theory of fusion, such as that of Lennard-Jones and Devonshire[10] (which implies the Lindemann rule at low pressure). These authors considered their original model too crude to be applied reliably at high pressure but Domb[11] has applied the model (with modifications) to the range of moderate pressure where a Lennard-Jones intermolecular potential is a sufficient approximation, to derive theoretically Simon's empirical melting formula.[12] It will be shown that the generalized Lindemann law, in conjunction with the Thomas-Fermi model, yields a dependence of fusion pressure on temperature which is consonant with the results of Domb for the range of moderate pressure.

Thermodynamic functions of the Thomas-Fermi

[1] D. Bijl and H. Pullan, Phil. Mag. 45, 290 (1954).
[2] H. D. Megaw, Phil. Mag. 28, 129 (1939).
[3] F. Birch, J. Geophys. Research 57, 227 (1952).
[4] S. Visvanathan, Phys. Rev. 81, 626 (1951).
[5] R. J. Uffen, Trans. Am. Geophys. Union 33, 893 (1952).
[6] W. M. Elsasser, Revs. Modern Phys. 22, 1 (1950).

[7] R. A. Daly, Bull. Geol. Soc. Amer. 54, 401 (1943).
[8] H. Jeffreys, Monthly Notices Roy. Astron. Soc., Geophys. Suppl. 3, 6 (1932).
[9] J. J. Gilvarry, preceding paper [Phys. Rev. 102, 308 (1956)] (referred to hereafter as I).
[10] J. E. Lennard-Jones and A. F. Devonshire, Proc. Roy. Soc. (London) A170, 464 (1939).
[11] C. Domb, Phil. Mag. 42, 1316 (1951).
[12] F. Simon, Z. Electrochem. 35, 618 (1929); Trans. Faraday Soc. 33, 65 (1937).

atom are available from work[13,14] of this and another author, for temperatures which are low in the sense of the model (small relative to the maximum energy of an electron at the atom boundary). It will be shown that Grüneisen's law and the fusion curve from Lindemann's rule can be discussed adequately (with some reservations) to zero order under this temperature restriction. The fact that the Thomas-Fermi atom model loses much of its physical validity at pressures below a limit in the order of megabars[15] restricts the results to high pressure, and the statistical nature of the model limits its strict applicability to elements of large atomic number. The effect of exchange in the Thomas-Fermi model[16] will not be included explicitly, but the necessary modifications are fairly direct.

As an incidental result, the theory presented provides a general method on the Debye theory of determining the corrections, corresponding to the lattice contributions, in thermodynamic functions determined from the Thomas-Fermi model; the method generalizes results of others.[17]

The Debye and Grüneisen theories presuppose that an atom (nucleus and electron cloud) oscillates thermally as a rigid unit. Reitz[18] has shown that for the limit of a degenerate Fermi-Dirac gas and for the temperatures in question, differential oscillation of the nucleus relative to the electron cloud becomes important. As a consequence, the (nonelectronic) thermal pressure in this limit is determined less by the compressibility of the lattice than by the polarizability of the atom[19]; an analogous factor must be taken into account in the theory of the long optical vibrations of an ionic crystal.[20] For this reason, the validity of the results on the lattice term in Grüneisen's law and on the thermodynamic functions of the lattice is restricted to pressures below the limit of very high compression corresponding to a degenerate Fermi-Dirac gas.

I. INTRODUCTION

The equation of state of the solid (assumed to be a pure element) will be approximated by results of the Thomas-Fermi atom model, on the assumption that the lattice pressure is negligible relative to the electronic pressure P_e. The latter assumption will be justified in Sec. IV. On this model, P_e is approximately equal to its zero-temperature value, designated by p for convenience, provided that the absolute temperature T is sufficiently less than a limiting temperature T_0. In

[13] J. J. Gilvarry, Phys. Rev. 96, 934 (1954), referred to hereafter as II; Phys. Rev. 96, 944 (1954), referred to hereafter as III.
[14] J. J. Gilvarry and G. H. Peebles, Phys. Rev. 99, 550 (1955), referred to hereafter as IV.
[15] H. Jensen, Z. Physik 111, 373 (1938).
[16] Feynman, Metropolis, and Teller, Phys. Rev. 75, 1561 (1949).
[17] Fermi, Teller, and Ulam (unpublished report).
[18] J. Reitz (unpublished report).
[19] W. G. McMillan (unpublished report).
[20] M. Born and K. Huang, Dynamical Theory of Crystal Lattices (Clarendon Press, Oxford, 1954), p. 100.

terms of two dimensionless variables, ϕ_b and x_b, obtained by solution of the zero-temperature Thomas-Fermi equation, the zero-temperature pressure p and the corresponding volume v of the atom are given by

$$p = (Z^2 e^2 / 10\pi\mu^4)(\phi_b/x_b)^{5/2}, \tag{1a}$$

$$v = (4\pi/3)(\mu x_b)^3, \tag{1b}$$

where Z is the atomic number, e is the electronic charge, and $\mu = a_0(9\pi^2/128Z)^{\frac{1}{3}}$ in terms of the first Bohr radius a_0 of the hydrogen atom. In II, computational results were used to determine a fitted function for ϕ_b in terms of x_b; this fitted function makes the equation of state [parametrically from Eqs. (1)] and thermodynamic functions directly available for the case of zero temperature. For validity of the zero-temperature Thomas-Fermi model, one must have $T \ll T_0$, where the limiting temperature T_0 is defined by

$$Z^{-4/3}kT_0/\mathcal{E} = 4(2/9\pi^2)^{\frac{1}{3}}\phi_b/x_b, \tag{2}$$

in terms of the atomic unit $\mathcal{E} = e^2/a_0$ of energy. Note that, in the zero-temperature approximation, all thermodynamic functions scale with atomic number Z for fixed x_b; from Eqs. (1), the scaling factor for pressure is $Z^{10/3}$ and the scaling factor for volume is Z^{-1}.

Through terms in T^2 corresponding to a first-order temperature perturbation in the Thomas-Fermi model, the electronic pressure P_e is given by

$$P_e = p[1 + (5/2)(\sigma + 2\tau)\zeta(kT)^2], \tag{3}$$

where k is Boltzmann's constant and $\zeta = \pi^2\mu^2/8Z^2e^4$ or $\zeta = (1.017Z^{4/3}\mathcal{E})^{-2}$ if $\mathcal{E}$ is a Hartree unit of energy. The perturbation paramenters σ and τ depend on the solutions of the first-order temperature-perturbed and the zero-temperature Thomas-Fermi equations, and they can be evaluated in terms of x_b (and thus of v or p) from fitted functions given in II and IV. In terms of the parameter ϵ_T defined by

$$\epsilon_T = -(\partial \ln P_e/\partial \ln v)_T, \tag{4}$$

the isothermal and adiabatic bulk moduli corresponding to the electronic pressure can both be evaluated as $\epsilon_T P_e$. The value of ϵ_T is given by

$$\epsilon_T = \epsilon_0 - [4\epsilon_0\tau + (5/6)d\sigma/d \ln x_b]\zeta(kT)^2, \tag{5}$$

in which the corresponding zero-temperature value $\epsilon_0 = -d \ln p/d \ln v$ is determined by

$$\epsilon_0 = (5/6)(1 - d \ln\phi_b/d \ln x_b). \tag{6}$$

The electronic heat capacity $C_{v,e}$ at constant volume and the electronic entropy S_e, per atom, are given by

$$C_{v,e} = S_e = 15pv(\sigma + 2\tau + 3\omega)\zeta k^2 T, \tag{7}$$

in which ω, like σ and τ, is a perturbation parameter available from fitted functions given in II and IV. The Thomas-Fermi coefficient of volume expansion α_e can

be evaluated as

$$\alpha_e = 5\epsilon_0^{-1}(\sigma+2\tau)\zeta k^2 T. \tag{8}$$

The temperature-perturbation terms given here correspond to use of the volume v of the atom as an independent (and thus unperturbed) parameter. Perturbation terms of higher order can be included by means of the general perturbation method given in II and III, to permit corresponding relaxation of the condition $T \ll T_0$.

The total pressure P is the sum

$$P = P_e + P_l \tag{9}$$

of the electronic pressure P_e and the pressure P_l due to the lattice. On the Debye model, a monatomic lattice can be represented dynamically by an isotropic continuum in which elastic waves of longitudinal and transverse type propagate. Thermodynamic functions of the lattice are obtainable in terms of the Debye frequency, or corresponding Debye temperature, by standard results of statistical mechanics.[21] Since the normal frequencies of vibration of the lattice all vary with volume in the same manner as the maximum or Debye frequency, results of the Grüneisen theory of solids are directly applicable.[22,23]

The pressure P_l is determined by $P_l = -(\partial F_l/\partial v)_T$, where the Helmholtz function F_l per atom of the monatomic lattice is given (with omission of a zero-point term) by

$$F_l = 3kT[\ln(1-e^{-x}) - \tfrac{1}{3}D(x)], \tag{10}$$

in which $x = h\nu/kT$ if h is Planck's constant and ν is the Debye frequency, and $D(x)$ is the Debye function defined by

$$D(x) = 3x^{-3}\int_0^x y^3(e^y-1)^{-1}dy. \tag{11}$$

With use of the Gibbs-Helmholtz equation, one obtains[24]

$$P_l = \gamma_l E_l/v, \tag{12}$$

where the thermal energy E_l per atom of the lattice is determined (with omission of the zero-point term) by

$$E_l = 3kTD(x) \tag{13}$$

and the lattice Grüneisen parameter γ_l is given by

$$\gamma_l = -(\partial \ln\nu/\partial \ln v)_T. \tag{14}$$

The lattice contribution $C_{v,l} = (\partial E_l/\partial T)_v$ per atom to the heat capacity at constant volume is

$$C_{v,l} = 3k[4D(x) - 3x(e^x-1)^{-1}]. \tag{15}$$

[21] J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley and Sons, Inc., New York, 1940), pp. 251, 386.
[22] E. Grüneisen, in *Handbuch der Physik* (Verlag von Julius Springer, Berlin, 1926), pp. 1–59.
[23] J. C. Slater, *Introduction to Chemical Physics* (McGraw-Hill Book Company, Inc., New York, 1939), pp. 219, 239.
[24] C. Kittel, *Introduction to Solid State Physics* (John Wiley and Sons, Inc., New York, 1953), p. 80.

The normal frequencies of vibration all vary with volume as $v^{-\gamma_l}$; note that a similarity assumption is entailed.[17]

II. THE GRÜNEISEN LAW

The derivation of the usual form of Grüneisen's law presupposes that the electronic contributions to the heat capacity and to the quantity $(\partial P/\partial T)_v$ are negligible relative to the corresponding lattice contributions. This condition can be (and in fact generally is) violated at high pressure; the appropriate generalization of Grüneisen's law for this case will be considered.

The Debye frequency ν of a monatomic lattice is defined by

$$\nu = sm^{-1/2}\kappa^{1/2}v^{1/6}, \tag{16}$$

where m is the mass of an atom, κ is the bulk modulus $-v(\partial P/\partial v)_T$ corresponding to the total pressure, and s is a function of Poisson's ratio σ which is defined by Eq. (16) of I if s_m is replaced by s and σ_m by σ. With use of the assumption $P_l \ll P_e$ and of Eqs. (3) and (4), one obtains

$$\nu = sm^{-1/2}\epsilon_0^{1/2}p^{1/2}v^{1/6} + O(T^2), \tag{17}$$

where the presence of terms arising from the temperature-perturbation terms in P_e and ϵ_T has been indicated by the common notation $O(T^2)$. The relative smallness of the latter terms in general (for $T \ll T_0$) indicates that the assumption that ν is a function only of the volume, made as an approximation in application of the Grüneisen theory under normal conditions,[22,23] is closely fulfilled at high pressure for sufficiently low temperature.

In general, the value of Poisson's ratio must be known to obtain the thermodynamic functions of the lattice. In I, it has been assumed that the ratio is independent of temperature. In Fig. 1, values of $\sigma_{\text{eff},l}$, $\sigma_{\text{eff},t}$, and $\langle\sigma_{\text{eff}}\rangle_{\text{Av}}$, as defined in I, are shown for Al and Cu as a function of pressure up to about 10 kilobars, from data of Lazarus.[25] One notes that both values of $\langle\sigma_{\text{eff}}\rangle_{\text{Av}}$ are closely constant. On the basis, in part, of these experimental data, it will be assumed that Poisson's ratio is approximately independent of pressure as well as temperature.
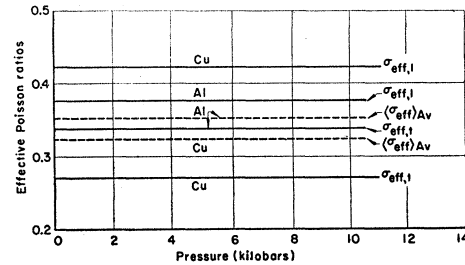

FIG. 1. Effective Poisson ratios as a function of pressure from experimental results of Lazarus, for Al and Cu.

[25] D. Lazarus, Phys. Rev. 76, 545 (1949).

The assumption that Poisson's ratio is approximately constant with pressure is not contradicted by geophysical information[3,6] on the earth's mantle obtained by analysis of seismic data. Throughout the mantle [possibly of olivine $(Mg,Fe)_2SiO_4$, or a similar material], the value of the ratio is about 0.3, up to pressures of the order of 1.4 megabars. Jeffreys' hypothesis[8] that the material of the mantle is just below the point of fusion is some justification for assuming that a solid retains an approximately constant value of Poisson's ratio at high pressure up to the melting point. Support for Jeffreys' hypothesis comes from the fair agreement of the melting temperature in the mantle at the boundary of the core, computed on this basis, with Uffen's value.[5] In any event, the assumption that Poisson's ratio is constant with pressure and temperature implies that $\frac{1}{2}\lambda/(\lambda+\mu)$, where λ and μ are the Lamé parameters, is constant, and thus is a similarity assumption in the same sense as the extrapolation of the generalized Lindemann rule, to be made later.

At high pressure, one expects that the lattice of a pure element will be one of the close-packed forms, face-centered cubic or hexagonal, and that pressure will induce a lattice transformation to one of these forms in elements whose normal lattices are not of these types.[26] Values of Poisson's ratio for elements with close-packed lattices are given in I for a number of cases. For elements with other than close-packed lattices under normal conditions, it is necessary to adopt at high pressure an average value of Poisson's ratio over the close-packed elements; from the data of I, this average is 0.37. Note that the last assumption is not essential to the theory, but is made in default of experimental (or theoretical) information.

On the assumption that Poisson's ratio is constant and that $P_l \ll P_e$, the lattice Grüneisen parameter of Eq. (14) becomes

$$\gamma_l = \frac{1}{6}(3\epsilon_0 - 1 - 3d\,\ln\epsilon_0/d\,\ln v) + O(T^2), \qquad (18)$$

from Eqs. (4) and (16); it can be seen from Fig. 3 of II that the logarithmic derivative which appears is small relative to ϵ_0. Values of γ_l from this equation are shown in Fig. 2 as a function of the scaled pressure $Z^{-10/3}p$, as computed with use of Eq. (6) from the fitted function of II for ϕ_b. In the Fermi-Dirac limit corresponding to $p \to \infty$, one has $\epsilon_0 \to 5/3$ and thus $\gamma_l \to 2/3$, and, in the opposite limit $p \to 0$ corresponding to an infinite atom, one has $\epsilon_0 \to 10/3$ and thus $\gamma_l \to 3/2$ (in both cases, $d\,\ln\epsilon_0/d\,\ln v$ vanishes). Hence, the limits of variation of γ_l are relatively small. The range of abscissas in Fig. 2 corresponds approximately to the range of computed data directly fitted by the fitted functions of II and IV; the highest values of pressure approach those corresponding to a degenerate Fermi-Dirac gas.

[26] Support for this assumption in the case of the alkali metals (normally body-centered cubic) is given by J. Bardeen [J. Chem. Phys. 6, 372 (1938)]; at a pressure of about 22 kilobars, Cs transforms to a lattice which is probably face-centered cubic.

With use of the identity $(\partial P/\partial T)_v = \kappa\alpha$, in which α is the volumetric coefficient of thermal expansion and the product $\kappa\alpha$ involves both electronic and lattice contributions, differentiation of Eq. (9) with respect to temperature at constant volume yields

$$\kappa\alpha = (\gamma_e C_{v,\,e} + \gamma_l C_{v,\,l})/v, \qquad (19)$$

from Eqs. (3), (7), and (12), if the electronic Grüneisen parameter γ_e is defined by

$$\gamma_e = \frac{1}{3} - \omega/(\sigma + 2\tau + 3\omega). \qquad (20)$$

Terms of higher order arising from the Thomas-Fermi temperature perturbation have been neglected in Eq. (19); thus, this equation is the generalization of Grüneisen's law to high pressure for temperatures small in the sense of the Thomas-Fermi model. The usual form of the law is recovered for $C_{v,\,e}/C_{v,\,l} \to 0$. The fitted functions given in II and IV have been used to plot γ_e as a function of the scaled pressure $Z^{-10/3}p$ in Fig. 2. It is shown in III that $-\sigma$, τ, and $-\omega$ are monotonic-decreasing functions of p, so that γ_e is a monotonic function between its limiting values, given from results of II as $\frac{2}{3}$ in the Fermi-Dirac limit, and $\frac{1}{3}$ for the limit of an infinite atom. With the former limit $\gamma_e = \frac{2}{3}$ corresponding to the free-electron theory of metals, the electronic term in Eq. (19) is that given by Visvanathan.[4] One notes that both Grüneisen parameters γ_l and γ_e are of approximately the same order of magnitude.

As noted, validity of the temperature-perturbed Thomas-Fermi model in this application requires that the temperature involved be significantly less than the temperature T_0 defined by Eq. (2). For temperatures less than T_0 but sufficiently high that the electronic heat capacity dominates the lattice heat capacity, the lattice terms can be neglected in the generalized Grüneisen law (since $\gamma_e \sim \gamma_l$). The lattice heat capacity cannot exceed the Dulong and Petit value, $3k$ per atom of a monatomic lattice, so that the equality $C_{v,\,e} = 3k$ defines a limiting temperature T_1 such that $T > T_1$ is an approximate criterion that $C_{v,\,e}$ dominate $C_{v,\,l}$. The value of T_1 is given from Eqs. (1) and (7) by

$$Z^{-1/3}kT_1/\mathcal{E} = (48/\pi^2)(2/9\pi^2)^{1/3}$$
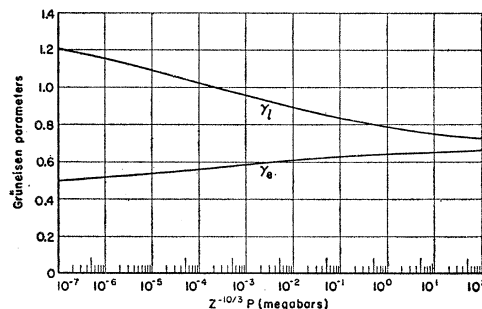$$\times [(\sigma + 2\tau + 3\omega)x_b^{1/2}\phi_b^{5/2}]^{-1}. \qquad (21)$$

FIG. 2. The lattice Grüneisen parameter γ_l and the electronic Grüneisen parameter γ_e, as a function of scaled pressure on the Thomas-Fermi model.
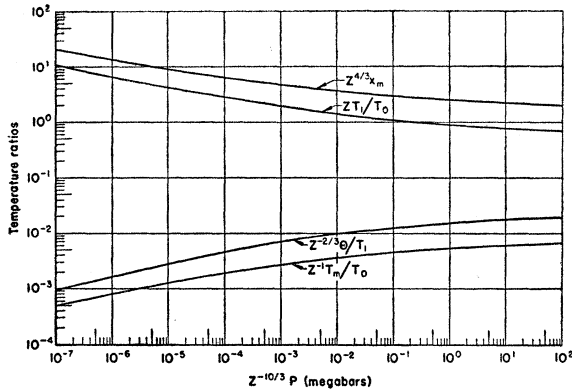
FIG. 3. Scaled ratios of significant temperatures as a function of scaled pressure on the Thomas-Fermi model.

The ratio of T_1 to T_0 is shown, in the scaled form ZT_1/T_0, as a function of the scaled pressure $Z^{-10/3}p$ in Fig. 3. One notes that T_1 is significantly below the limiting temperature T_0 for moderate or large Z, but the condition fails to hold for the lower Z-values, particularly for the lowest values of scaled pressure. Hence, for $T_1 \ll T \ll T_0$, the extended Grüneisen law reduces to

$$\kappa\alpha = \epsilon_0 p\alpha_e = \gamma_e C_{v,\,e}, \qquad (22)$$

where α_e is the Thomas-Fermi value of α defined by Eq. (8). This equation yields the result that Grüneisen's law is valid, under the temperature restriction stated, as a formal relation on the Thomas-Fermi model, with a physical re-interpretation of the proportionality constant which enters. The result follows because the first-order temperature-perturbed Thomas-Fermi theory satisfies a general criterion given by Davies[27] that a law of Grüneisen form apply.

The Debye temperature Θ defined by $k\Theta = h\nu$ can be determined to zero order from Eq. (17), by means of Eqs. (1) and (6), as

$$Z^{-1}k\Theta/\mathcal{E} = (8/9)(6/\pi)^{1/3}(s/\beta^{1/2})$$
$$\times (1 - d\,\ln\phi_b/d\,\ln x_b)^{1/2}(\phi_b{}^5/x_b{}^3)^{1/4}, \qquad (23)$$

where β is the ratio of the mass of a hydrogen atom to that of an electron, and the approximation $m = 2\beta Z m_e$, wher m_e is the electron mass, has been used for the mass m of the atom. The ratio of Θ to T_1, in the scaled form $Z^{-2/3}\Theta/T_1$, is shown as a function of the scaled pressure $Z^{-10/3}p$ in Fig. 3; the fitted function of II for ϕ_b has been used, and the value $s = 0.37$, corresponding to the average value 0.37 of Poisson's ratio over the close-packed elements of I, has been taken. One notes that Θ is less than T_1 for any physical value of Z and for any pressure shown, so that the lattice heat capacity has actually reached (at least approximately) the equipartition value at the temperature T_1.

The foregoing results apply only to the solid, in general, and thus are subject to the reservation that

[27] R. O. Davies, Phil. Mag. 43, 473 (1952).

the temperature in question be lower than the fusion temperature (to be evaluated in the next section). However, the limiting form (22) of Grüneisen's law can be valid above the fusion temperature, since it does not contain a lattice term. Omission of the Reitz frequency changes somewhat the limit of the lattice Grüneisen parameter in the Fermi-Dirac limit.[18]

III. THE FUSION CURVE

The generalized Lindemann law can be written, from results of I, as

$$kT_m = Q_m{}^{-1}\Omega\kappa_m v_m, \qquad (24)$$

where T_m is the absolute melting temperature, and κ_m and v_m are the bulk modulus and volume of the atom for the solid, respectively, as evaluated at fusion. The quantization factor Q_m, which takes account of departure from equipartition, is defined in I as a function of the ratio

$$x_m = \Theta_m/T_m, \qquad (25)$$

where Θ_m is the Debye temperature at fusion; Ω is defined by

$$\Omega = [2^{7/6}\pi s_m(\sigma_m)\rho/3^{1/2}]^2, \qquad (26)$$

where s_m is given in I as a function of the fusion value σ_m of Poisson's ratio, and ρ is the critical ratio of the root-mean-square amplitude of thermal vibration to nearest neighbor distance at fusion. In general, conjunction with Eq. (24) of the equation of state $P = f(v,T)$ of the solid yields two simultaneous equations for the fusion temperature in terms of the fusion pressure P_m; the Thomas-Fermi equation of state will be adopted for the solid at high pressure, under the assumption $P_l \ll P_e$. The fusion criterion is that the ratio, at temperature T_m and pressure P_m, of thermal vibration amplitude to nearest neighbor distance, equal the corresponding ratio at normal pressure, where the latter is assumed the same for all isotropic monatomic solids; possible effects of differential motion of the nucleus relative to the electron cloud are ignored.[18] Thus a similarity assumption is entailed in this extrapolation of the generalized Lindemann law to high pressure. The value σ_m of Poisson's ratio at fusion will be taken in accordance with the previous assumption that Poisson's ratio is independent of temperature and pressure.

Since the temperature perturbation method used in connection with the Thomas-Fermi model corresponds to use of the atom volume v as independent variable, one has $v_m = v$. From Eqs. (3) and (4), the value of κ_m is $\epsilon_0 p + O(T_m{}^2)$. Hence, use of the Thomas-Fermi model under the approximation $P_l \ll P_e$ yields

$$kT_m = \Omega\epsilon_0 pv + O(T_m{}^2), \qquad (27)$$

which is valid as a zero-order approximation for the melting temperature, provided $x_m \ll 1$ or $x_m \sim 1$, and provided $T_m \ll T_0$, where T_0 is defined by Eq. (2).
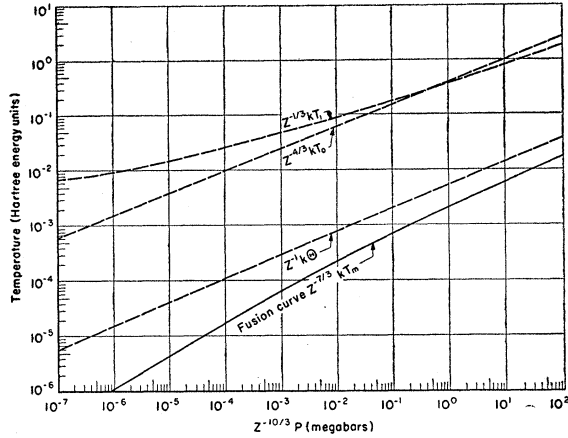
Fig. 4. The scaled fusion temperature from the extrapolated Lindemann law as a function of scaled pressure on the Thomas-Fermi model, for a Poisson ratio of 0.37 corresponding to an average over the close-packed elements. The Debye temperature Θ, and the limiting temperatures T_0 and T_1, are likewise shown (dashed). Temperatures are in Hartree energy units (27.2 ev or 3.16×10^5 °K).

Alternatively, Eq. (27) can be written

$$kT_m = \Omega\epsilon_0(\gamma_0-1)u + O(T_m^2), \qquad (28)$$

where u is the zero-temperature Thomas-Fermi energy given in II, and γ_0 (not to be confused with a Grüneisen parameter) is defined by $u = pv/(\gamma_0-1)$ and is evaluated in II. The fusion pressure P_m is $p+O(T_m^2)$, from Eq. (3). From Eqs. (1) and (6), the zero-order approximation to T_m can be expressed as

$$Z^{-7/3}kT_m/\mathcal{E} = (4/9)(2/9\pi^2)^{1/3}$$
$$\times\Omega(1-d\ln\phi_b/d\ln x_b)x_b^{1/2}\phi_b^{5/2}. \qquad (29)$$

This fusion curve is shown as a function of the scaled fusion pressure $Z^{-10/3}p$ in Fig. 4, as evaluated from the fitted function of II for ϕ_b; the value $s_m=0.37$ has been taken, corresponding to the average Poisson ratio 0.37 over the close-packed elements, which yields $\Omega=0.012$ from the value $\rho=0.072$ of Table III in I. Scaled values of the limiting temperatures T_0 and T_1, and of the Debye temperature Θ corresponding to a Poisson ratio of 0.37, are shown (dashed) on the same graph.

In terms of Θ defined by Eq. (23), one has $\Theta_m=\Theta$ $+O(T_m^2)$. The value of the ratio x_m of Eq. (25), corresponding to this value of Θ_m for $\sigma_m=0.37$ and to T_m of Eq. (29), is shown in the scaled form $Z^{4/3}x_m$ as a function of the scaled pressure $Z^{-10/3}p$ in Fig. 3. One notes that the condition $x_m\ll1$ or $x_m\sim1$ is met in general but can be violated for the lowest values of Z at the lowest scaled pressure shown. For the latter domain, higher order terms in Q_m^{-1} can be taken into account by expanding the parameter as

$$Q_m^{-1} = 1 - x_m'^2/36 - x_m'^4/2025 + \cdots, \qquad (30)$$

in terms of the variable,

$$x_m' = k\Theta_m/\Omega\kappa_m v_m, \qquad (31)$$

which reduces to x_m when $Q_m\sim1$.

The ratio of T_m (corresponding to the average Poisson ratio 0.37) from Eq. (29) to T_0 of Eq. (2), expressed in the scaled form $Z^{-1}T_m/T_0$, is shown as a function of the scaled fusion presure $Z^{-10/3}p$ in Fig. 3. One notes that the condition $T_m\ll T_0$ is met reasonably for any Z at the lower scaled pressures. In the Fermi-Dirac limit, however, T_m can become comparable to T_0 for large Z, since $T_m/T_0\rightarrow(2/3)\Omega Z$ (numerically, 0.74 for $Z=92$ and for Ω corresponding to the average Poisson ratio). Hence, for the larger values of Z at the higher pressures, a sufficient number (depending on the value of Poisson's ratio) of perturbation orders must be included in the general perturbation method given in II and III, or the electronic pressure should be determined from the Thomas-Fermi equation as generalized to arbitrary temperature.[16]

The neglected perturbation terms are easily evaluated in the Fermi-Dirac limit, from the expression[21]

$$P_e = \frac{2}{3}\frac{Z\eta'}{v}\left[1+\frac{5\pi^2}{12}\left(\frac{kT}{\eta'}\right)^2 - \frac{\pi^4}{16}\left(\frac{kT}{\eta'}\right)^4 + \cdots\right], \qquad (32)$$

for the pressure of a degenerate gas of Z-electrons in the volume v of the atom. The chemical potential η' [equal to kT_0 of Eq. (2)] at zero temperature can be evaluated from results of II as

$$\eta' = \tfrac{1}{2}(9\pi^4)^{1/3}Z^{2/3}\mathcal{E}a_0^2/v^{2/3}, \qquad (33)$$

in this case, where a_0 is the first Bohr radius for hydrogen. From Eq. (24), the melting temperature in the Fermi-Dirac limit can be expanded as

$$kT_m = \tfrac{2}{3}\Omega Z\eta'\left[1+\frac{\pi^2}{27}(\Omega Z)^2 + \frac{37\pi^4}{3645}(\Omega Z)^4 + \cdots\right]. \qquad (34)$$

Numerically, ΩZ is 1.1 for $Z=92$ and for the average value 0.37 of Poisson's ratio over the close-packed elements, but it is only 0.52 for $Z=82$ and for a Poisson ratio of 0.43, which is the normal value[28] of the ratio for Pb; thus, the series of Eq. (34) is rapidly convergent for Pb. Hence, results of the general temperature-perturbed Thomas-Fermi model from II and III are sufficient to determine the fusion curve, in general, except for the domain of large Z near the Fermi-Dirac limit of pressure when the Poisson ratio is not relatively large. Since the purely formal extrapolation made of the generalized Lindemann rule takes no account of the possible effect of differential motion of the nucleus relative to the electron cloud,[18] these results for the Fermi-Dirac limit are subject to some doubt as regards physical validity.

[28] C. Zwikker, Physical Properties of Solid Materials (Interscience Publishers, Inc., New York, 1954), p. 90.

The Grüneisen constant γ_m of the solid at fusion, as defined in I, is $\gamma_l + O(T_m^2)$, where γ_l is given by Eq. (18). The parameter q of I is $1 + O(T_m^2)$, and, since the condition $x_m \ll 1$ or $x_m \sim 1$ is fulfilled in general, the parameters Q_m and O_m of I will be given the values unity and zero, respectively. Hence, results of I yield

$$k dT_m/dP_m = (\epsilon_0 - 1 - d \ln\epsilon_0/d \ln v)\Omega v + O(T_m^2) \quad (35)$$

for the slope of the fusion curve. It is easily shown from numerical results of II that the parenthetic coefficient of Ωv is always positive, so that the fusion curve on this model has normal sign of slope when the temperature-perturbed Thomas-Fermi model is applicable. Similarly, one obtains

$$k\frac{d^2 T_m}{dP_m^2} = -\left[\epsilon_0 - 1 - \frac{d \ln\epsilon_0}{d \ln v} + \frac{d\epsilon_0}{d \ln v} - \frac{d^2 \ln\epsilon_0}{d(\ln v)^2}\right]\frac{\Omega v}{\epsilon_0 p}$$
$$+ O(T_m^2), \quad (36)$$

where the coefficient of $\Omega v/\epsilon_0 p$ in square brackets is always positive. Hence, the fusion curve on the assumptions made is completely normal in the sense of Bridgman; the hypothesis of Tammann,[29] that the fusion temperature rises to a maximum and then falls, and that of Schames,[30] that an asymptotic fusion temperature exists, are both denied. The proof given applies only to the range of atomic number, pressure, and Poisson ratio where the general perturbation method of II and III is applicable, so that the signs of the pertinent derivatives can be inferred from the leading term of zero order. From results of I, or by means of Clapeyron's equation applied to Eq. (35), one obtains

$$L/\Delta v = \epsilon_0(\epsilon_0 - 1 - d \ln\epsilon_0/d \ln v)^{-1}p + O(T_m^2) \quad (37)$$

for the ratio of the latent heat of fusion L per atom to the corresponding change Δv, from solid to liquid, in volume per atom. Since this equation specifies only the ratio $L/\Delta v$, it yields no direct information on the existence or nonexistence of a critical point (where L and Δv must vanish simultaneously so that their ratio remains finite), but it is consistent with the latter possibility, since the coefficient of $\epsilon_0 p$ is positive.

Equation (37) corresponds to the evaluation of the Grüneisen constant from fusion parameters, as given by Eq. (33) of I. Hence, this relation persists for high pressure. However, the evaluation of the Grüneisen constant at fusion from Grüneisen's law, as given by Eq. (25) of I for low pressure, must be modified to correspond to the generalized Grüneisen law (19) at high pressure. As noted, the generalized law is subject to the condition $T \leqslant T_m$, but the limiting form (22) is independent of this restriction. One can show from Eqs. (21) and (29) that the generalized form reduces approxi-

[29] G. Tammann, *Kristallisieren und Schmelzen* (Verlag von J. A. Barth, Leipzig, 1903), p. 90; *Aggregatzustände* (Verlag von L. Voss, Leipzig, 1923), p. 94.

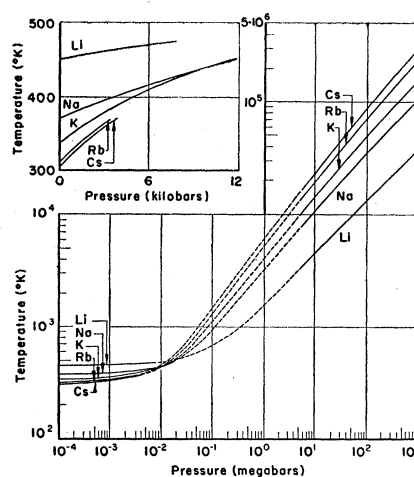[30] L. Schames, Ann. Physik 38, 830 (1912); 29, 887 (1912).

FIG. 5. Comparison of the fusion curves for the alkali metals predicted by the extrapolated Lindemann law (for $\sigma_m = 0.37$) at high pressure with Bridgman's experimental fusion curves at low pressure; the dashed portions correspond to a reasonable fairing at intermediate pressures of the two curves into one another for each element. In the inset, the fusion curves of Bridgman are shown on a linear scale.

mately to the latter form, below fusion, for the larger values of Z and for the larger scaled pressures.

For the Thomas-Fermi atom model at zero temperature, one notes from Eq. (4) that $p \propto v^{-\epsilon_0}$ for small changes in v, where ϵ_0 has the value $10/3$ corresponding to an infinite atom and the value $5/3$ in the Fermi-Dirac limit. Equation (27) implies, therefore, that the temperature variation of the melting pressure goes from $P_m \propto T_m^{10/7}$ to $P_m \propto T_m^{5/2}$ as the pressure varies from zero to infinity. Simon's empirical equation[12] for low pressure predicts $P_m + A \propto T_m^B$, where A and B are constants; the value of B is about 4 for metals and about 2 for other substances. However, Domb's derivation[11] of the equation from the model of Lennard-Jones and Devonshire[10] yields $B = 1 + 3/n$ for moderately high pressure, where n (about 9 to 12) is the (negative) exponent of the repulsive term in a Lennard-Jones potential; in this case, the constant A can be ignored. Hence, Eq. (27) is substantially consistent with Domb's result for the moderate-pressure range.

A significant feature of the melting formula (29) is the scaling of the melting temperature with atomic number as $Z^{7/3}$ for x_b fixed.[31] Computed melting temperatures from this equation are shown in Fig. 5 for the alkali metals as a function of pressure above 5 megabars, for a value of Poisson's ratio equal to the average 0.37 over the close-packed elements[26]; the order of increasing melting temperature is Li to Cs. The experimental results of Bridgman[32] for the melting

[31] The leading term of Eq. (34) states that the melting temperature scales as $Z^{5/3}$ for fixed volume, or as Z for fixed pressure, in the Fermi-Dirac limit; in this case, more explicit scaling is possible, because ϕ_b from results of II can be obtained directly in terms of x_b and thus of v.

[32] P. W. Bridgman, Phys. Rev. 3, 153 (1914); 27, 68 (1926); Proc. Am. Acad. Arts Sci. 56, 59 (1921).

temperatures as a function of pressure are shown on the same diagram; the order of increasing melting temperature is Cs to Li at the lowest pressures, or the reverse of that predicted by Eq. (29). The fusion curves of Bridgman are shown on a linear scale in the inset on Fig. 5; one notes that the curves for Na and K cross near the upper limit of pressure. As interpreted by Bridgman on the basis of a graphical extrapolation, the data indicate almost with certainty that the curve for K will cross that of Li; they imply with high probability that the curve for Na likewise will cross that of Li; and they suggest strongly that the curves for Rb and Cs eventually will cross those of the other alkali metals with increasing pressure. Hence, Bridgman[32,33] has hypothesized that at pressures above the order of 25 kilobars, the normal melting order with respect to atomic number in the alkali metal family will be reversed completely. The dashed lines in Fig. 5 have been drawn to correspond to a reasonable fairing of the curves for low and high pressure into one another; complete reversal of the normal fusion order occurs in the neighborhood of 25 kilobars, in agreement with Bridgman's hypothesis.

IV. THERMODYNAMIC FUNCTIONS OF THE LATTICE

The salient thermodynamic functions of the lattice have been listed in Sec. I. The lattice contribution S_l per atom to the entropy is given by[21]

$$S_l = 3k[(4/3)D(x) - \ln(1 - e^{-x})], \quad (38)$$

which, for $x \ll 1$ or $x \sim 1$, reduces to

$$S_l = 3k[4/3 + \ln(T/\Theta)]. \quad (39)$$

By comparison of the latter equation with S_e as given by Eq. (7), a limiting temperature can be set such that S_l is dominated by S_e. Since $S_l \sim 4k$ for $T \sim \Theta$, and the logarithmic function in Eq. (39) is slowly varying, the condition $T \gtrsim T_1$ can be used as a rough criterion that S_e dominate S_l, where T_1 of Eq. (21) is the limiting temperature for dominance of $C_{v,e}$ over $C_{v,l}$. Other thermodynamic functions of the lattice on the Debye model, such as the Gibbs function and enthalpy, are easily obtained from the functions given.

To determine the thermodynamic functions of the lattice at any temperature and pressure, it is sufficient to know the lattice Grüneisen parameter γ_l and the Debye temperature Θ, which enter parametrically into the functions. The latter parameters have been evaluated to zero order on the Thomas-Fermi model by Eqs. (18) and (23), respectively, on the assumption $P_l \ll P_e$ (which remains to be justified). Terms of higher order in γ_l and Θ can be included by means of the general perturbation procedure of II and III, or alternatively, results of the Thomas-Fermi model as generalized to arbitrary temperature[16] can be used to

³³ P. W. Bridgman, The Physics of High Pressure (G. Bell and Sons, Ltd., London, 1949), p. 211.

evaluate the parameters directly. These considerations yield a general prescription for obtaining the thermodynamic functions of the lattice at low temperature, which is the analog of the method given by Feynman, Metropolis and Teller[16] for obtaining the corrections in thermodynamic functions due to the atomic nucleus at high temperature.

The upper limit of temperature for validity of these expressions for the thermodynamic functions of the lattice is the melting temperature T_m. For $T \gg \Theta$ or $T \sim \Theta$, the thermodynamic functions assume their equipartition values, so that the lattice pressure becomes

$$P_l = 3\gamma_l kT/v, \quad (40)$$

which is a result obtained previously by others[17] (by a method equivalent in its assumptions to the Grüneisen theory). The thermal energy E_l of the lattice becomes[17]

$$E_l = 3kT, \quad (41)$$

which corresponds to $C_{v,l} = 3k$. For equipartition, the dependence of the thermodynamic functions of the lattice [except those involving the entropy of Eq. (39)] on Poisson's ratio disappears, since this ratio enters the functions only through the parameter $x = \Theta/T$. From the considerations of Sec. III, equipartition is always reached below the fusion temperature, except for the lowest values of Z at the lowest scaled pressures.

An upper limit $P_{l,m}$ on the lattice pressure can be obtained by evaluating P_l at fusion, which yields

$$P_{l,m} = 3\Omega\gamma_l\epsilon_0 p + O(T_m{}^2), \quad (42)$$

by means of Eqs. (27) and (40). One notes that, to zero order, the ratio $P_{l,m}/p$ of maximum lattice pressure to electronic pressure is independent of the atomic number Z. The limits of variation of the ratio are not large, since the limit of $\gamma_l\epsilon_0$ in the Fermi-Dirac limit is 10/9 and the limit for an infinite atom is 5. Corresponding to these two limits, the ratios of the maximum lattice pressure to the electronic pressure are $10\Omega/3$ and 15Ω, or, numerically, about 4% in the Fermi-Dirac limit and about 18% in the limit of an infinite atom for an average Poisson ratio of 0.37. These considerations justify the basic assumption $P_l \ll P_e$, on which the entire treatment of this paper is based. A maximum thermal energy $E_{l,m}$ of the lattice can be obtained from Eqs. (28) and (41) as the fusion value

$$E_{l,m} = 3\Omega\epsilon_0(\gamma_0 - 1)u + O(T_m{}^2), \quad (43)$$

where u is the zero-temperature Thomas-Fermi energy and γ_0 is defined by $u = pv/(\gamma_0 - 1)$.

This method of obtaining the thermodynamic functions of the lattice is valid only for pressures below the Fermi-Dirac limit, because of neglect of the Reitz frequency.[18] The question of the transition from the thermodynamic functions given here to the corresponding ones in the Fermi-Dirac limit has been discussed by McMillan.[19]

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.

[34] N. F. Mott, Proc. Roy. Soc. (London) **A146**, 465 (1934).

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]

$$\log(P_m + A) = B \log T_m + C, \qquad (1)$$

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

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

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,

$$P_m' = T_m'^B - 1, \qquad (3)$$

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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[3] M. Ruhemann and B. Ruhemann, *Low Temperature Physics* (Cambridge University Press, London, 1937), p. 97.

[4] Holland, Huggill, Jones, and Simon, Nature **165**, 147 (1950); Holland, Huggill, and Jones, Proc. Roy. Soc. (London) **A207**, 268 (1951); J. S. Dugdale and F. E. Simon, Proc. Roy. Soc. (London) **A218**, 291 (1953).

[5] F. Simon and G. Glatzel, Z. anorg. u. allgem. Chem. **178**, 309 (1929).