the effects of volume expansion.[6] Remember that the absolute value of the resistivity is not well predicted by pseudopotential models.[5]

As another test of the approximations leading to (1) we would mention the temperature coefficient of the Knight shift in liquid Na. One of us (M.T.)[7] showed that the appropriate formula, similar to (1), could give reasonable agreement with experiment provided again one was careful to distinguish constant-pressure and constant-volume results.

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LINDEMANN AND GRÜNEISEN LAWS AND A MELTING LAW AT HIGH PRESSURE

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Recently, a new melting law for high pressures has been proposed by Kennedy.[1] In terms of the relative compression $\Delta_0 V/V_0$ of the solid at normal temperature at a pressure P, the purely empirical result can be expressed as

$$T_M = T_0(1 + C\Delta_0 V/V_0), \tag{1}$$

where T_M is the absolute temperature at fusion under the melting pressure $P_M = P$ and T_0 is the corresponding normal value. The purpose of this communication is to use the Lindemann law as reformulated by Gilvarry,[2,3] which was applied by Gilvarry[4] to fusion at extremely high pressures, to derive Eq. (1) and to point out the connection of the result with the Grüneisen[5] theory of the normal properties of solids. Further, it will be shown that Eq. (1) is equivalent in the special case of a restricted range of melting temperatures to a relation given previously by Gilvarry,[6] in which the constant C appears in terms of the Grüneisen parameter of the solid at the normal fusion point.

For a polyatomic solid having n atoms in the stoichiometric compound, the Lindemann law for the melting temperature T_M in the case of classical excitation of the lattice vibrations can be written from I and II as

$$nRT_M = \Omega K_M V_M, \tag{2}$$

where K_M and V_M are the bulk modulus and molecular volume, respectively, of the solid at fusion, R is the gas constant, and Ω is an approximate constant defined in I. Selecting the volume V and absolute temperature T as independent variables, one can express the variable value K_M of the bulk modulus K in terms of its value K_0 at the initial point (V_0, T_0) chosen on the fusion curve by

$$K_M = K_0 + \int_{V_0}^{V_M} \left(\frac{\partial K}{\partial V}\right)_{T_0} dV + \int_{T_0}^{T_M} \left(\frac{\partial K}{\partial T}\right)_{V_M} dT. \tag{3}$$

The path of integration in the V, T plane consists of the horizontal line segment from $V = V_0$ to $V = V_M$ at the constant temperature T_0, followed by the vertical line segment from $T = T_0$ to $T = T_M$ at the constant volume V_M, as implied by subscripts on partial derivatives and by limits of integration. Using the mean-value theorem to replace integrands by averages, one obtains

$$T_M = T_0 \left[1 - \frac{V_0 - V_M}{V_0}\right] \left[1 - \left\langle \left(\frac{\partial K}{\partial V}\right)_{T_0} \right\rangle_{\text{av}} \frac{V_0 - V_M}{K_0} + \left\langle \left(\frac{\partial K}{\partial T}\right)_{V_M} \right\rangle_{\text{av}} \frac{T_M - T_0}{K_0}\right], \tag{4}$$

from Eq. (2) as an exact consequence of Lindemann's law. Equation (4) yields Eq. (1) directly, with the constant C given by

$$C=-\left[\frac{V_0}{K_0}\left\langle\left(\frac{\partial K}{\partial V}\right)_{T_0}\right\rangle_{\text{av}}+1\right]\times\left[1-\frac{T_0}{K_0}\left\langle\left(\frac{\partial K}{\partial T}\right)_{V_M}\right\rangle_{\text{av}}\right]^{-1}, \tag{5}$$

when terms of order $(V_0-V_M)^2$ and $(V_0-V_M)\times(T_M-T_0)$ are ignored. Neglect of these remainder terms implies that C can be only an approximate constant when fitted by Eq. (1) to experimental data, in general, as follows also from the weak dependence necessarily exhibited by the mean values of partial derivatives in Eq. (5) on the ranges of the variables over which they are averaged.

To reduce Eq. (5) to more tractable form, consider the Grüneisen parameter γ of the solid as written in I, $\gamma=-\frac{1}{2}(\partial\ln K/\partial\ln V)_T-\frac{1}{6}$. Equation (5) yields

$$C=(1+g)^{-1}[2\epsilon_{\text{av}}\kappa_{\text{av},0}(\gamma_{\text{av},0}+\tfrac{1}{6})-1], \tag{6}$$

where $\epsilon_{\text{av}}=V_{\text{av}}/V_0$, $\kappa_{\text{av},0}=K_{\text{av},0}/K_0$, and

$$\gamma_{\text{av},0}=-\tfrac{1}{2}(\partial\ln K/\partial\ln V)_{\text{av},0}-\tfrac{1}{6}, \tag{7}$$

in which V_{av} is an average value of the volume over the range V_0 to V_M, $K_{\text{av},0}$ is a corresponding average of K over volume at the fixed temperature T_0, and $(\partial\ln K/\partial\ln V)_{\text{av},0}$ represents a similar average at fixed temperature T_0. The parameter g is determined by

$$g=\kappa_{M,\text{av}}(\eta_{M,\text{av}}-2\gamma_{M,\text{av}}-\tfrac{1}{3})\alpha_{M,\text{av}}T_0, \tag{8}$$

in which $\kappa_{M,\text{av}}$, $\eta_{M,\text{av}}$, $\gamma_{M,\text{av}}$, and $\alpha_{M,\text{av}}$ represent mean values of K/K_0, $-(K\alpha)^{-1}(\partial K/\partial T)_P$, γ, and α, respectively,[7] over the temperature range T_0 to T_M at the fixed volume V_M, where α is the volumetric coefficient of thermal expansion. For experimentally determined fusion curves in the extreme cases of the highly compressible alkali metals[8] and the relatively incompressible metal iron,[9] one can show that g can be neglected relative to unity; the conclusion is probably general.

Note that the mean values of dependent variables entering Eqs. (5) and (6) do not represent averages along the fusion curve itself, as taken in III to derive the Simon equation $P_M=A[(T_M/T_0)^B-1]$ from the Lindemann law and Grüneisen theory. For T_M sufficiently close to T_0, however, averages as taken here and corresponding averages along the fusion curve can both be replaced by values at the initial point (V_0, T_0), approximately, and the value γ_0 of the Grüneisen parameter at this point can be used as an approximation to $\gamma_{\text{av},0}$ of Eq. (7) and to γ_{av} of III. In this limit, C of Eq. (6) reduces to the value

$$C=2(\gamma_0-\tfrac{1}{3}), \tag{9}$$

and the law of corresponding states given in III states that

$$T_M/T_0=(V_0/V_M)^{2(\gamma_0-\frac{1}{3})}, \tag{10}$$

which a binomial expansion shows to agree with Eq. (1) when C has the value of Eq. (9). Under the same condition, B becomes $\frac{1}{2}(6\gamma_0+1)/(3\gamma_0-1)$ and Eq. (1) is equivalent to Simon's result with

$$C=(B-1)^{-1},\quad B=(C+1)/C, \tag{11a, b}$$

for the constant C in terms of the Simon exponent B and the converse, respectively. The relation $\gamma_0=\frac{1}{2}q\Delta V/L+\frac{1}{3}$ derived in I for γ_0 and the corresponding value from Grüneisen's law yield

$$C=qK_0\Delta V/L,\quad C=2(\alpha_0K_0V_0/C_{V,0}-\tfrac{1}{3}), \tag{12a, b}$$

respectively, where q is a parameter closely equal to unity, ΔV and L are the change in volume and the latent heat at fusion, respectively, and α_0 and $C_{V,0}$ are values at the initial point of α and the heat capacity C_V for constant volume, respectively.

Values of $\gamma_{\text{av},0}$ for the alkali metals deduced by means of Eq. (6) from the constants C given by Kraut and Kennedy[1] are compared in Table I with corresponding values of γ_{av} from III and of γ_0 from I; the final entry in each case is the value of γ under standard conditions from Grüneisen's law. The parameter ϵ_{av} was determined from the arithmetical mean compression $\langle\Delta_0V/V_0\rangle_{\text{av}}=1-\epsilon_{\text{av}}$ from data of Bridgman[10] for the alkali metals corresponding to the pressure ranges (extending up to 50 kbar) indicated by experimental points in the plot

Table I. Comparison of the mean Grüneisen parameter $\gamma_{\mathrm{av},0}$ as deduced from the constant C with other values of γ.

	$\langle\Delta_0 V/V_0\rangle_{\mathrm{av}}$	C	$\gamma_{\mathrm{av},0}$	γ_{av}	γ_0	γ
Li	0.149[a]	0.537[b]	0.327	...[c]	0.81[d]	1.17[e]
Na	0.202	1.65	0.560	$(1._2)$	1.1_5	1.37
K	0.340_5	1.61	0.300	0.9_5	1.2	1.41
Rb	0.293	1.62	0.378	1.4	1.6_5	1.86

[a] From data of Bridgman (Ref. 10).

[b] From Kraut and Kennedy (Ref. 1) as converted to values corresponding to use of absolute rather than centigrade temperatures in Eq. (1).

[c] Gilvarry (Ref. 6).

[d] Gilvarry (Ref. 2).

[e] From Grüneisen (Ref. 5) as corrected by Gilvarry (Ref. 2).

of T_M vs $\Delta_0 V/V_0$ by Kraut and Kennedy. Birch's isothermal equation of state[11] in the form $P = (\frac{3}{2})K_0(\epsilon_{\mathrm{av}}^{-7/3} - \epsilon_{\mathrm{av}}^{-5/3})$ was used to compute $\kappa_{\mathrm{av},0} = \frac{1}{2}(7\epsilon_{\mathrm{av}}^{-7/3} - 5\epsilon_{\mathrm{av}}^{-5/3})$. One sees that the values of $\gamma_{\mathrm{av},0}$ fall in the normal range (up to about 3)[12] for Grüneisen constants of solids. No theoretical reason exists for $\gamma_{\mathrm{av},0}$ to be identical with γ_{av}, since the latter parameter represents an average along the fusion curve and corresponds to a range of pressure up to only 12 kbar. Clearly, the values of $\gamma_{\mathrm{av},0}$ and γ_0 are consistent with the known positive sign[7] of the derivative $(\partial\gamma/\partial \ln V)_T$ at the initial fusion temperature T_0 for each element.

Contrary to possible implications of the discussions by Kraut and Kennedy[1] and by Kennedy,[13] it would seem from the present results that Eq. (1) represents an interpolation (or extrapolation) formula in the same sense established for the Simon equation in III on the basis of the Lindemann law (and hence the relation does not yield a fundamental criterion of melting). In consonance with this interpretation, the result of II from the Simon equation for the melting point of iron at the boundary of the inner core of the earth, given as $5._9 \times 10^3$ °C with a stated limit of error of ±25%, agrees within the corresponding bounds with Kennedy's estimate[13] of 3725°C from Eq. (1), for a reasonably presumed error limit of ±25%. Note that Kennedy's estimation neglects the effect of the terms of order $(V_0 - V_M)^2$ and $(V_0 - V_M)(T_M - T_0)$ implicit in Eq. (4), which can be evaluated from this work.

These results obviously permit one to find the form of Eq. (1) corresponding to low melting temperatures (as in molecular crystals), when the quantization parameter Q_M of I does not reduce to unity.

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