

MELTING LAW AT HIGH PRESSURES

S. N. Vaidya and E. S. Raja Gopal

Department of Physics, Indian Institute of Science, Bangalore, India

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It has been customary in the past to use Simon's formula

$$P/a = (T_m/T_m^0)^c - 1$$

to correlate the melting point T_m of solids at a high pressure P , using two empirical constants a and c . (T_m^0 is the melting point at zero pressure.) The validity and deficiencies of the equation have been discussed by several workers.¹ Recently, Kraut and Kennedy² have suggested a new melting equation

$$t_m = t_m^0(1 + C_1|\Delta v/v|) \quad (1)$$

in which t_m is measured in °C. This equation agrees very well with the melting point and compressibility data for Li, Na, K, and Rb.

We wish to point out that a modified equation

$$T_m = T_m^0[1 + 2(\gamma - \frac{1}{3})|\Delta v/v|] \quad (2)$$

(T_m measured in °K) can be derived on the basis of rather simple considerations. It involves the Grüneisen constant γ which can be obtained from completely independent measurements. Data are also presented to show that the equation correlates the melting points and compressibilities of a number of other metals and that the values of γ obtained from Eq. (2) agree reasonably well with the values obtained from other sources.

We start from the Lindemann melting equation

$$T_m = c_2 M \Theta^2 v^{2/3}, \quad (3)$$

where M is the molecular weight, Θ the Debye temperature, and v the molar volume. It can be established on the basis of simple models of melting.³ The volume derivate of Θ is related to the Grüneisen constant, γ , by the relation

$$(d\Theta/dv) = -\gamma\Theta/v. \quad (4)$$

Using this value of $d\Theta/dv$ in dT_m/dv as obtained from Eq. (3), one gets

$$T_m = T_m^0[1 + (\frac{2}{3} - 2\gamma)\Delta v/v]. \quad (5)$$

$\Delta v/v$, the compression of the solid, is negative and so Eq. (2) follows immediately.

In Fig. 1, the melting-point data for tin⁴ (below the polymorphic transition point at 38 kbar and 200°C), In,⁴ Se,⁵ Al,⁶ and Tl⁶ are plotted against the values of compressions obtained from Bridgman's work.⁷ The plots are consistent with Eqs. (1) and (2). Similar consistency was also obtained by Kraut and Kennedy² for Li, Na, K, and Rb. For all these metals, the values of Grüneisen constant, as obtained from our Eq. (2), are given in Table I as $\gamma(\text{calc})$. For comparison, the values of γ as deduced from thermal measurements⁸ and the pressure dependence of compressibility⁹ are also given.

In view of the wide scatter in the values of γ as given in the literature, one may conclude that Eq. (2) gives a reasonable account of the experimental data. It may be pointed out that in practice, γ is found to be slightly pressure dependent, and Eq. (2) gives a value averaged over a wide pressure range. Moreover, v in Eq. (3), and hence in Eq. (2), is the volume near the melting point, whereas the room-temperature values of compression are used in Fig. 1 and Table I. If accurate data on compressions of various metals become available over wide ranges of pressures, a more crit-

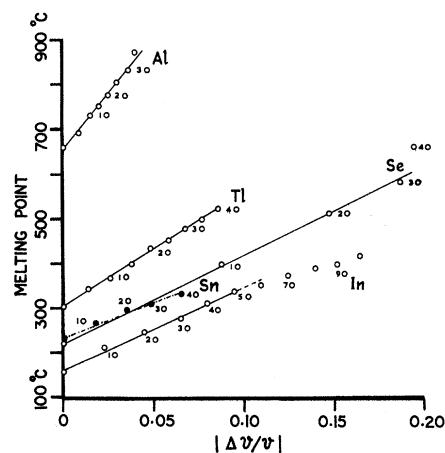


FIG. 1. Plot of melting points of various elements as a function of the numerical compression at the same pressure. The numbers near the experimental points denote the value of pressure in kbar.

Table I. Values of the Grüneisen constant, γ , as obtained from our Eq. (2).

	γ (calculated)	γ (thermal)	γ (compressibility data)
Li	0.60 ^a	1.17 ^d	1.53, ^g 0.63 ^h
Na	1.15 ^a	1.25 ^d	1.18 ^g
K	1.14 ^a	1.34 ^d	1.29 ^g
Rb	1.14 ^a	1.48 ^d	0.90 ^g
Sn	1.81 ^b	2.14, ^d 2.03 ^e	2.01, ⁱ 1.85 ^j
In	2.61	2.21 ^e	2.24 ^j
Se	2.26	2.63 ^f	
Al	2.83	2.17 ^d	1.96 ^g
Tl	2.56	2.73, ^d 2.96 ^e	2.13 ^j
Ni	2.63 ^c	1.88, ^d 1.91 ^e	2.18, ⁱ 1.81 ^j

^aFrom the values of constant C_1 in Eq. (1) as given by Kraut and Kennedy.²

^bBelow polymorphic transition.

^cMelting-point data from H. M. Strong and F. P. Bundy, Phys. Rev. **115**, 278 (1959). Compression data from Ref. 7. Plot lies above the range of Fig. 1.

^dFrom thermal measurements (Ref. 8).

^eFrom thermal measurements (Ref. 10).

^fCalculated from available thermal data.

^gFrom pressure dependence of compressibility data (Ref. 9).

^hJ. C. Slater, Phys. Rev. **57**, 744 (1940).

ⁱFrom L. V. Al'tshuler, A. A. Bakanova, and R. F. Trunin, Zh. Eksperim. i Teor. Fiz. **42**, 91 (1962) [translation: Soviet Phys.-JETP **15**, 65 (1962)].

^jFrom shock-wave experiments (Ref. 10).

ical test of our Eq. (2) will become possible.

It should be emphasized that the melting equation in the present form does not involve any

adjustable parameter. Equation (2) can be employed with reasonable confidence, using the values of γ , which can be easily obtained from thermal and other measurements. This point is of importance in geophysical and other applications.

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Note added in proof.—We have been informed that related work has been published by J. Gilvarry, Phys. Rev. Letters **16**, 1089 (1966); this work is unfortunately not yet available to us.

¹S. E. Babb, Rev. Mod. Phys. **35**, 400 (1963); G. C. Kennedy, J. Geophys. Res. **70**, 1979 (1965); Phys. Rev. **102**, 325 (1956).

²E. A. Kraut and G. C. Kennedy, Phys. Rev. Letters **16**, 608 (1966).

³D. Pines, *Elementary Excitations in Solids* (W. A. Benjamin, Inc., New York, 1963), pp. 34-37.

⁴J. D. Dudley and H. T. Hall, Phys. Rev. **118**, 1211 (1960).

⁵B. C. Deaton and F. A. Blum, Phys. Rev. **137**, A1131 (1965).

⁶A. Jayaraman, W. Klement, R. C. Newton, and G. C. Kennedy, J. Phys. Chem. Solids **24**, 7 (1963).

⁷P. W. Bridgman, Proc. Am. Acad. Arts Sci. **72**, 207 (1938); **74**, 425 (1942); **76**, 55 (1948); **77**, 187 (1949).

⁸E. Grüneisen, *Handbuch der Physik* (Verlag von Julius Springer, 1926), Vol. X, p. 29.

⁹J. J. Gilvarry, J. Chem. Phys. **23**, 1925 (1955).

¹⁰M. H. Rice, R. G. McQueen, and J. M. Walsh, in *Solid State Physics* (Academic Press, Inc., New York, 1958), Vol. 6, p. 1.

ULTRASONIC EVIDENCE FOR STRONG COUPLING OF ELECTRONS TO TRANSVERSE PHONONS IN SINGLE-CRYSTAL INDIUM*

J. R. Leibowitz and K. Fossheim†

Department of Physics and Astronomy, University of Maryland, College Park, Maryland

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When the phonon angular frequency ω and wave number q satisfy the conditions $\omega > 10^{10}$ sec⁻¹ and $ql \gg 1$, where l is the electron mean free path, then the "electromagnetic" and collision-drag interactions may be neglected, and free-electron theory predicts that transverse phonons and the conduction electrons in a metal are not coupled.¹ Electron-phonon coupling associated with shear deformation of the Fermi surface can become effective only for arbitrary Fermi surfaces.² Since the latter mech-

anism is ordinarily assumed to be very small relative to electromagnetic interaction, the free-electron prediction of essential decoupling of transverse phonons from conduction electrons in the simpler metals has been regarded generally as a very reasonable one in the regime of total breakdown of electromagnetic screening. We should like to report experimental evidence for strong "residual" coupling of low-temperature transverse phonons to the conduction electrons in indium.³ To our knowledge,