

Amplitudes of Thermal Vibration at Fusion

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On the basis of theoretical results from the Debye-Waller theory of the thermal dependence of x-ray reflection intensity, relatively accurate values of the Lindemann constant are determined for ten metals by use of rigidity moduli at fusion with previously determined bulk moduli. Agreement of the derived value ρ of the critical ratio of root-mean-square amplitude of thermal vibration to nearest-neighbor distance at fusion, with the corresponding value from x-ray intensity data, is improved for the one case (Al) favorable for comparison. The average ρ over the body-centered cubic, face-centered cubic, and hexagonal lattice types is 0.111, in excellent agreement with the value 0.10₈ given by Grüneisen. Relatively accurate values of the Lindemann constant for Pb and Al imply that this quantity cannot be a strict constant over a lattice type; however, the assumption of an average over the lattice type yields an excellent approximation for the face-centered cubic elements.

I. INTRODUCTION

IN a previous paper¹ by the author, it was shown that the Lindemann law of melting can be derived under certain assumptions from the Debye-Waller theory² of the thermal dependence of the intensity of x-ray reflection by a solid. In a paper submitted for publication at about the same time, Cartz³ likewise pointed out this fact. He deduced values of Lindemann constants and of the amplitude of thermal vibration at fusion, consonant,³ in general, with those of I. The thermal amplitudes of I were determined from extrapolated bulk moduli under the assumption, which is unessential to the theory and was made in default of easily available data, that the Poisson ratio of a solid is approximately constant from the normal to the melting temperature. The purpose of this paper is to obtain improved values of the amplitudes by use of rigidity moduli at fusion with bulk moduli from I, and to examine the implications on the validity of Lindemann's law.

In view of this refinement, corresponding ones can be made in the theoretical results of I. Zener and Bilinsky⁴ have shown that the Debye method of obtaining an average wave velocity from the reciprocal cubes thereof should be modified for the Debye frequency appearing in the Debye-Waller formula to correspond to reciprocal squares. In conformity with this result, the coefficient s_m of the Debye frequency in I will be replaced by S_m , defined by

$$S_m = 3(3/4\pi)^{1/3} [(1 + \sigma_m)/(1 - \sigma_m) + 4(1 + \sigma_m)/(1 - 2\sigma_m)]^{-1/2}, \quad (1)$$

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

² P. Debye, Ann. Physik **42**, 49 (1914); I. Waller, Z. Physik **51**, 213 (1923).

³ L. Cartz, Proc. Phys. Soc. (London) **B68**, 951, 957 (1955). Direct comparison of Cartz's amplitudes with those of I is not easily possible, since he uses a mean-square amplitude three times that of I (i.e., the square of the body diagonal of three mutually perpendicular amplitudes) and does not insist rigorously that all thermodynamic variables be evaluated at the fusion point.

⁴ C. Zener and S. Bilinsky, Phys. Rev. **50**, 101 (1936).

in terms of the fusion value σ_m of Poisson's ratio. The value of S_m differs from s_m at most by the factor 1.07 (in the limit $\sigma_m \rightarrow \frac{1}{2}$). The volume v_m per atom in terms of the nearest-neighbor distance r_m in the lattice at fusion will be taken as

$$v_m = \lambda r_m^3, \quad (2)$$

where λ has the value $4/3\sqrt{3}$ and $1/\sqrt{2}$ for body-centered cubic and ideally close-packed lattices, respectively (it appeared only numerically as the latter value in I). The corresponding Lindemann constant c becomes

$$c = (\sqrt{3}/2\pi)\lambda^{1/3}/\rho, \quad (3)$$

where $\rho = [\langle u^2 \rangle_{av}]^{1/2}/r_m$ is the critical ratio of root-mean-square amplitude $[\langle u^2 \rangle]^{1/2}$ of thermal vibration to nearest-neighbor distance at fusion. The theory of I yields

$$c^2 = S_m^2 K_m V_m / RT_m, \quad (4)$$

where K_m and V_m are the bulk modulus and atomic volume at fusion, respectively, and R is the gas constant, to determine the Lindemann constant c for an element.

The value of the ratio ρ follows from Eq. (3), and thus the fusion value of the amplitude itself can be obtained by use of Eq. (2); for simplicity, results will be exhibited in terms of c and ρ only. Note that the theoretical results above yield values of the amplitude of thermal vibration at fusion unambiguously on the basis of the Debye-Waller theory, independently of any presumptions on the validity of the Lindemann law.

II. TREATMENT OF THE DATA

Since extrapolated values of the bulk modulus K_m at fusion are available from I, the corresponding Poisson ratio σ_m can be found if one additional elastic parameter is known for the polycrystalline material at fusion. For all the elements (except Na) discussed, Köster⁵ has determined Young's moduli by the method of transverse oscillations of a rod; he presents numerical values at normal temperature in tabular form, and shows the temperature variation graphically up to

⁵ W. Köster, Z. Metallkunde **39**, 1 (1948).

either the melting temperature or 1000°C. If Y_m is the fusion value of the modulus (determined by graphical extrapolation, if necessary), the corresponding value of σ_m follows as

$$\sigma_m = \frac{1}{2} \left[1 - \frac{1}{3} (Y_m / K_m) \right]. \quad (5)$$

Further, Bordoni⁶ has presented in graphical form, for a number of elements at temperatures up to about 600°K, the velocities of extensional waves in rods as measured by an ultrasonic pulse technique. Hence, linear extrapolation of Bordoni's data to the melting point permits an alternative determination of Y_m , and thus of σ_m from Eq. (5). In general, the results of Köster, supplemented by those of Bordoni, represent the main source of the data employed.

For the alkali metals, the only data available to determine the Poisson ratio correspond to measurements on single crystals; hence the question of determining a proper average σ_m to fix the Debye temperature at fusion arises. Analytic methods⁷ are available to determine the Debye temperature from an average over a sphere of the reciprocal cubes of the three propagation velocities for a cubic crystal, but these methods entail an amount of labor hardly commensurate with the accuracy of extrapolated data, in general. In this circumstance, use of a simpler averaging procedure is indicated. That used in I is reliable only when the anisotropy is small, which is not the case for the alkali metals (the Poisson ratios $\sigma_{\text{eff}, l}$ and $\sigma_{\text{eff}, t}$ used in I to obtain an average σ_m are actually the ratios σ_{111} and σ_{100}).⁸

The basis of the method used here is the fact that the melting temperature is not structure-sensitive for a pure element, since it is apparently the same for a single crystal and for a polycrystalline aggregate.⁹ To obtain the elastic constants of an aggregate from those of the single crystal, Voight¹⁰ has suggested the averaging over all lattice orientations of the relations expressing the stress in a single crystal in terms of the given strain; alternatively, Reuss¹¹ has proposed averaging the relations expressing the strain in terms of the given stress. The Voight and Reuss methods correspond to the assumption of uniform strain and stress, respectively, in an aggregate. Measured moduli for polycrystalline samples lie between the values computed on the two methods, of which the Voight value is higher; these facts have been explained theoretically by Hill.¹² Further, Hill noted that the polycrystalline value lies

closely midway between the Reuss and Voight values, empirically, which led him to suggest use of the corresponding mean in practical computation.

On the basis of Hill's work, the rigidity G of a polycrystalline aggregate of cubic crystals can be written as the arithmetical mean,

$$G = \frac{1}{2} \left\{ (c_{11} - c_{12} + 3c_{44}) / 5 + 5 / [4(c_{11} - c_{12})^{-1} + 3c_{44}^{-1}] \right\}, \quad (6)$$

of the Voight and Reuss values, in terms of the elastic stiffness constants c_{ij} . The arithmetical mean of the Voight and Reuss values of the bulk modulus K is simply the usual value,

$$K = \frac{1}{3} (c_{11} + 2c_{12}), \quad (7)$$

for a cubic crystal. The corresponding value σ_m of Poisson's ratio at fusion is given in terms of K_m and the fusion value G_m of G by

$$\sigma_m = \frac{1}{2} \left[1 - 3G_m / (3K_m + G_m) \right], \quad (8)$$

which will be used as an appropriate average. As a check on the method, the Debye temperature Θ at 80°K was computed for Na from the elastic constants of Quimby and Siegel.¹³ The result is $\Theta = 158^\circ\text{K}$; this value can be compared with $\Theta = 159^\circ\text{K}$ obtained from heat capacity data, and $\Theta = 164^\circ\text{K}$ obtained by Quimby and Siegel from an average of wave velocities (not reciprocal cubes thereof) over 360 points on a sphere.

A salient peculiarity in the evaluation of c from Eq. (4) can be noted. Since V_m and T_m are generally known with reasonable accuracy, the major uncertainty in c arises from error in the value of K_m and the value of Y_m or G_m used to determine σ_m . If Y_m is used, the error δc in c is given by

$$\begin{aligned} \frac{\delta c}{c} = & - \left(\frac{1 - 2\sigma_m}{2S_m} \right) \left(\frac{dS_m}{d\sigma_m} \right) \frac{\delta Y_m}{Y_m} \\ & + \left[\frac{1}{2} + \left(\frac{1 - 2\sigma_m}{2S_m} \right) \frac{dS_m}{d\sigma_m} \right] \frac{\delta K_m}{K_m}, \quad (9) \end{aligned}$$

in terms of errors in the data. The coefficient of $\delta K_m / K_m$ is a function only of σ_m showing a zero at $\sigma_m = 0.42$ and a minimum value -0.16 at $\sigma_m = 0$; since the coefficient of $\delta Y_m / Y_m$ is $\frac{1}{2}$ less that of $\delta K_m / K_m$, the latter coefficient is always small relative to that of $\delta Y_m / Y_m$. If G_m is used as a datum, the corresponding coefficients in the analog of Eq. (9) show a similar behavior, but the zero of the coefficient of $\delta K_m / K_m$ occurs at $\sigma_m = 0.5$. Thus, although Eq. (4) expresses c as a function of all the independent elastic parameters, the value is most sensitive to those determining the rigidity at fusion. As a general statement, the extrapolation necessary to obtain Y_m or G_m is considerably less than, and the accuracy correspondingly greater, than

⁶ P. G. Bordoni, *Ricerca sci.* **25**, 847 (1955).

⁷ P. M. Sutton, *Phys. Rev.* **99**, 1826 (1955). This author cites prior references.

⁸ C. Zener, *Elasticity and Anelasticity of Metals* (University of Chicago Press, Chicago, 1948), pp. 18, 156.

⁹ P. G. Bordoni and M. Nuovo, *Nuovo cimento* (supplement) **1**, 155 (1955).

¹⁰ W. Voight, *Lehrbuch der Kristallphysik* (B. G. Teubner, Leipzig, 1928), p. 962.

¹¹ A. Reuss, *Z. angew. Math. Meck.* **9**, 55 (1929).

¹² R. Hill, *Proc. Phys. Soc. (London)* **65**, 349 (1952).

¹³ S. L. Quimby and S. Siegel, *Phys. Rev.* **54**, 293 (1938).

is the case for K_m (extrapolations from 75–100°C to the melting point were necessary in I when only Bridgman's data were available). On the other hand, the error $\delta\sigma_m$ in the Poisson ratio at fusion is

$$\delta\sigma_m = -\frac{1}{2}(1-2\sigma_m)(\delta Y_m/Y_m - \delta K_m/K_m), \quad (10)$$

if Y_m is used as a datum, with a corresponding equation if G_m is used. Thus, the value of σ_m does not show insensitivity to δK_m . Hence, the values of Lindemann constants and vibration amplitudes obtained are considerably more reliable, in general, than the corresponding Poisson ratios.

For a cubic metal, the foregoing results mean that the Lindemann constant depends most strongly on the shear moduli, c_{44} and the difference $c_{11} - c_{12}$. In this restricted sense, a point of contact is made between the present theory and those identifying fusion with the vanishing of c_{44} (Born¹⁴) or of $c_{11} - c_{12}$ (Durand¹⁵).

III. LINDEMANN CONSTANTS

The discussion will be confined to elements with cubic or hexagonal lattices, since only for these lattice types can the theory of I be applied with a degree of strictness. In Table I, computed values of the Poisson ratio σ_m at the fusion temperature t_m are shown with corresponding values σ_0 at normal temperature for comparison, where the latter quantity is obtained from

TABLE I. Values of Lindemann constants.

| | Lattice | t_m (°C) | σ_0 | σ_m | $S_m^2 K_m V_m / RT_m$ | c | c_{Av} |
|----|---------|------------|-------------------|-------------------|------------------------|-----|------------------|
| Na | b.c.c. | 97.6 | 0.37 | 0.37 ^a | 7.2 | 2.7 | 2.7 |
| | | | 0.30 | 0.31 ^a | 7.0 | 2.6 | |
| Fe | b.c.c. | 1532 | 0.29 | 0.40 ^b | 4.8 | 2.2 | 2.2 |
| | | | 0.44 | 0.46 ^b | 6.2 | 2.5 | 2.6 ₄ |
| Pb | f.c.c. | 327.4 | 0.42 | 0.44 ^c | 9.3 | 3.1 | |
| | | | 0.44 | 0.46 ^d | 6.3 | 2.5 | |
| | | | 0.43 ₅ | 0.46 ^e | 6.6 | 2.6 | |
| | | | 0.43 ₅ | 0.46 ^e | 6.6 | 2.6 | |
| | | | 0.43 ₅ | 0.45 ^e | 6.6 | 2.6 | |
| | | | 0.34 | 0.38 ^b | 9.9 | 3.2 | 3.2 ₂ |
| Al | f.c.c. | 660.1 | 0.35 | 0.37 ^e | 11.4 | 3.4 | |
| | | | 0.33 | 0.40 ^f | 8.6 | 2.9 | |
| | | | 0.35 | 0.37 ^g | 11.0 | 3.3 | |
| | | | 0.35 | 0.34 ^g | 10.9 | 3.3 | |
| Ag | f.c.c. | 960.8 | 0.37 | 0.38 ^b | 8.9 | 3.0 | 3.0 |
| Cu | f.c.c. | 1083 | 0.34 | 0.37 ^b | 6.7 | 2.6 | 2.9 |
| | | | 0.36 | 0.31 ^e | 1 ₀ | 3.2 | |
| Ni | f.c.c. | 1453 | 0.33 | 0.35 ^b | 9.3 | 3.1 | 3.1 |
| Pt | f.c.c. | 1769 | 0.40 | 0.45 ^b | 4.3 | 2.1 | 2.1 |
| Zn | h.c.p. | 419.5 | 0.24 | 0.30 ^b | 17 | 4.1 | 4.1 |
| Mg | h.c.p. | 651 | (0.28) | 0.35 ^b | 9.0 | 3.0 | 3.2 |
| | | | (0.28) | 0.35 ^e | 1 ₂ | 3.4 | |

^a Quimby and Siegel (reference 13); first line, K_m from I; second line, K_m from ultrasonic single-crystal data.

^b Köster (reference 5).

^c Bordoni (reference 6).

^d Siegel and Cummerow (reference 19).

^e Bordoni and Nuovo (reference 9); first and second lines, extensional and torsional velocities, respectively, used with K_m from I; last line, extensional and torsional velocities from ultrasonic data used for K_m .

^f Birch and Bancroft (reference 21).

^g Sutton (reference 22); first line, K_m from I; second line, K_m from ultrasonic single-crystal data.

¹⁴ M. Born, J. Chem. Phys. 7, 591 (1939).

¹⁵ M. A. Durand, Phys. Rev. 50, 449 (1936).

the same sources of data and by the same method as is σ_m . The third column from the right gives the ratio $S_m^2 K_m V_m / RT_m$ obtained by use of values of V_m and K_m from I, unless otherwise noted. The penultimate and last columns show values of the Lindemann constant c from Eq. (4) and of the average value c_{Av} for an element, respectively. All computed values shown were rounded after computation from unrounded quantities.

For sodium, the elastic constants c_{ij} at fusion and at normal temperature were determined by graphical extrapolation of those measured by Quimby and Siegel¹³ over the temperature range -193°C to -63°C by an ultrasonic pulse technique. The results obtained are shown in the first line of Table I when values of G from Eq. (6) are combined with bulk moduli from I, and in the second line when these values of G are taken with bulk moduli computed from the elastic constants themselves by Eq. (7). Both sets of data imply only a small change in Poisson ratio from the normal to the fusion temperature. In spite of inconsistencies in the Poisson ratios,¹⁶ the two sets of data yield approximately the same value of the Lindemann constant; this behavior is consistent with the discussion of Sec. II, since the value of G_m is common to the two sets. The value of c_{Av} differs significantly from the result (3.8) of I, because of difference in the Poisson ratios.

The temperature variation of Young's modulus for α iron is given by Köster up to the transition temperature (906°C) to the γ phase. In the neighborhood of the α - γ transition, the rate of decrease of the modulus for α iron increases sharply relative to the value at lower temperature; this qualitative behavior has been noted independently.¹⁷ As a consequence, extrapolation of the Young's modulus for this phase yields an essentially vanishing value at the melting point. Since the δ -phase stable near fusion is merely a reappearance of the normal α phase, this result is in disagreement with the general behavior that accurate experiments near the melting point have led one to expect.^{9,18} However, Köster's values of Young's modulus for the γ phase show a closely linear variation with temperature from the α - γ transition point to the limit 1000°C appearing. Hence, the modulus of the γ phase was extrapolated linearly to the melting temperature 1532°C , on the presumption that this value would not differ greatly from that for the δ phase, stable over the relatively narrow range 1400°C to fusion. The results of Table I for iron show a relatively large change in Poisson ratio from the normal to the fusion temperature, and the result for c differs correspondingly from the value (3.2) of I.

In the case of lead, the first two lines of Table I

¹⁶ The lower values shown are close to that (0.315) for -183°C obtained by O. Bender [Ann. Physik 34, 359 (1939)] by an averaging procedure from single-crystal constants.

¹⁷ J. R. Frederick, J. Acoust. Soc. Am. 20, 586 (1948).

¹⁸ L. Hunter and S. Siegel, Phys. Rev. 61, 85 (1942).

correspond to the data of Köster (no extrapolation) and Bordoni (small extrapolation); the results differ somewhat as regards Poisson ratios and values of c . The values of the third line correspond to a σ_m obtained from an ultrasonic determination by Siegel and Cummerow¹⁹ of the temperature variation of Young's modulus up to 2° below the melting point. The results are in close agreement with those derived by means of Köster's data. The last three lines show results obtained with only slight extrapolation (from about 30° below melting) from ultrasonic determinations by Bordoni and Nuovo⁹ of the relative variation with temperature of the velocities of extensional and torsional waves in rods. Of the three lines, the first and second correspond to K_m from I, and a Y_m from the extensional velocity and a G_m from the torsional velocity, respectively; the last line corresponds to an independent K_m and a σ_m derived by joint use of the extensional and torsional velocities.²⁰ Again, the results agree well with those from Köster's data.

For aluminum, results of three computations similar to the first three for Pb are presented, but a check is possible from single-crystal constants. The first two lines of Table I for this metal give consonant results obtained from the data of Köster (no extrapolation) and Bordoni (moderate extrapolation). The values in the third line were computed from data on the variation of rigidity with temperature up to 13° below fusion, determined dynamically from the resonant frequency of a cylinder by Birch and Bancroft.²¹ The three values of c agree very well. The fourth line shows results from bulk moduli of I and rigidities obtained by Eq. (6) from elastic constants measured ultrasonically by Sutton²²; the fifth line shows corresponding results when Eq. (7) is used to obtain bulk moduli from the elastic constants themselves. Determination of fusion values of the constants required extrapolation from 500°C. The two values of c agree well with the preceding three, in spite of some discrepancies in Poisson ratios (and an abnormal¹⁷ slight decrease with temperature when only single-crystal data are used).

For the remaining face-centered elements of Table I, relatively large extrapolations were necessary in I to obtain K_m , but considerably smaller extrapolations (from about 1000°C to melting) are needed to obtain Y_m from Köster's results. Moderate increases in Poisson ratio up to fusion are shown (the decrease for Cu derived from Bordoni's data is anomalous¹⁷). For the hexagonal elements, increases of Poisson ratio to fusion

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

| | ρ (x-ray), from I | ρ (fusion), Table I | ρ (fusion), from I |
|----|---------------------------|-----------------------------|----------------------------|
| Al | 0.08 ₂ | 0.076 ₃ | 0.066 |
| Cu | 0.07 ₆ | 0.08 ₅ | 0.07 ₉ |

appear which are somewhat larger than average. In general, all values of σ_0 shown in Table I agree reasonably well²³ with values of I and with independent data.²⁴

For the two cases (Na and Al) where bulk moduli derived by extrapolation of statically determined values can be compared with extrapolated values from elastic constants of single crystals determined ultrasonically, the latter are significantly less (by some 25% or more). The difference appears also when only ultrasonic data for a polycrystalline sample (Pb) are used, and may represent an effect associated with grain boundaries when low-frequency or static measurements are made on polycrystalline specimens.⁸ The behavior appears as a greater curvature in the graph of K vs temperature, exhibited by the ultrasonic data,^{8,18} in general, and tends to justify the method of extrapolation of Bridgman's data employed in I. Further, the increase of Poisson ratio from normal to melting temperature seems generally smaller when derived with use (or partial use) of ultrasonic as against other measurements. Hunter and Siegel¹⁸ found sudden kinks in plotted elastic constants within a few degrees of the melting temperature, and Bordoni and Nuovo⁹ refer to similar behavior. The possibility of any such kinks has been neglected in extrapolation to the melting point, on the presumption that they are caused by secondary processes (possibly hole formation²⁵) not covered by the present theory.

IV. DISCUSSION

In Table II, x-ray values from I for Al and Cu, determined by the Debye-Waller formula, of the critical ratio ρ of vibration amplitude to nearest-neighbor distance at fusion are shown for comparison with values obtained by Eq. (3) from c_{Av} of Table I, and with the corresponding values from I. Agreement with ρ (x-ray) is improved by the present value for Al, but not for Cu. However, ρ (x-ray) for Al was determined by quadratic extrapolation of x-ray intensity data to the melting point, whereas sufficient data were available in the case of Cu (where the range of extrapolation is greater) for only a linear extrapolation.

Average values c_{Av} of the Lindemann constant c

¹⁹ S. Siegel and R. Cummerow, *J. Chem. Phys.* **8**, 847 (1940). The value of the modulus for normal temperature was taken from Köster.⁵

²⁰ In all three cases, normal values were fixed by the average value of σ_0 shown, and a bulk modulus from I.

²¹ F. Birch and R. Bancroft, *J. Chem. Phys.* **8**, 641 (1940). The last tabular entry on the rigidity variation was used, and the value at normal temperature was taken as an average from Forsythe.²⁴

²² P. M. Sutton, *Phys. Rev.* **91**, 816 (1953).

²³ That for Mg is in poor agreement with the value 0.35 given in I. No comparison value for Zn could be found, but the rather low value shown checks with independent data of Forsythe (reference 24) on rigidity and Young's modulus.

²⁴ W. E. Forsythe, *Smithsonian Physical Tables* (Smithsonian Institution, Washington, D. C., 1954).

²⁵ L. G. Carpenter, *J. Chem. Phys.* **21**, 2245 (1953); K. F. Stripp and J. G. Kirkwood, *J. Chem. Phys.* **22**, 1579 (1954).

TABLE III. Average values of Lindemann constants and critical ratios.

| Lattice | c_{Av} | $10^{-12}C_{Av}$ (erg/°K) ^{1/2} mole ^{-1/6} | ρ_{Av} |
|---------|------------------|---|-------------------|
| b.c.c. | 2.5 | 1.9 | 0.13 |
| f.c.c. | 2.8 ₆ | 2.2 ₀ | 0.11 ₁ |
| h.c.p. | 3.5 | 2.7 | 0.09 ₁ |

over the three lattice types²⁶ of Table I are shown in Table III. Corresponding average values of the molar Lindemann constant $C=N^{1/3}R^{1/2}c$ (N is Avogadro's number) and of ρ from Eq. (3) are shown likewise. The difference of ρ_{Av} for the body-centered elements from that for the face-centered elements is probably significant, in view of the consistency of the data in Table I, but the corresponding difference for the hexagonal elements probably is not significant on the basis of the data. The average value 0.11₁ of ρ over all three lattice types agrees excellently with the value of 0.10₅ (or somewhat less) estimated by Grüneisen,²⁷ in contrast to the considerably lower value 0.072 obtained in I from extrapolated bulk moduli on the assumption that the Poisson ratio of a solid is constant up to fission.

The most significant aspect of the data shown in Table I is the disparity in c_{Av} for Pb and Al, where the accuracy is high. Including probable errors, one obtains $c=2.6_4\pm 0.1_3$ and $c=3.2_2\pm 0.1_1$ for Pb and Al, respectively, and hence the difference of the two values seems definitely outside the range corresponding to probable error. On the basis of this counter-example, one can state that the Lindemann constant cannot be a strict constant over a lattice type. That the use of an average c over a lattice type represents a very good approximation, in general, can be shown from the corresponding correlation coefficient for the Lindemann relation over the face-centered cubic elements. For the line of regression²⁸ of $S_m K_m^{1/2}$ on $(RT_m/V_m)^{1/2}$,

²⁶ Each entry under an element in Table I was included separately; this procedure gives greater weight to the more reliable values.

²⁷ E. Grüneisen in *Handbuch der Physik* (Verlag Julius Springer, Berlin, 1926), Vol. 10, p. 51. In a previous publication [*Ann. Physik* 39, 258 (1912)], Grüneisen gave the value 0.085.

the correlation coefficient is $r=0.92$, and for that of $S_m^2 K_m$ on RT_m/V_m , the value is $r=0.89$. These results mean that for the first and the second case, a fraction $r^2=0.85$ and $r^2=0.79$, respectively, of the variance from a straight average of the dependent variable is removed by the presumed linear relation with an average c (unity implies perfect correlation).

It has been emphasized that the values of the Poisson ratio at fusion are far less reliable than the Lindemann constants. When K_m is obtained entirely from ultrasonic data (three cases, Na, Pb, Al), the average value of $\sigma_m - \sigma_0$ is 0.01 within the accuracy of the data. When K_m is obtained by extrapolation from static measurement, the average value of $\sigma_m - \sigma_0$ over the cubic metals is 0.02 when Fe is excluded (because of the presence of phase transitions). In both cases, consonant values of c are found, because of the lower K_m implied by the purely ultrasonic data, as already alluded to.

V. CONCLUSION

The fact implied by these results, that the Lindemann constant cannot be a true constant over a lattice type, is in agreement with the order of the approximations necessary to derive the Lindemann law from the order-disorder fusion theory of Lennard-Jones and Devonshire.²⁸ The evaluation of the Grüneisen constant in terms of fusion parameters, as given in I, shows excellent agreement with values obtained from Grüneisen's law, and the result yields the Simon fusion equation very directly.²⁹ The relation in question requires only that the critical ratio ρ be constant along a fusion curve (if σ_m is at most slowly varying), and it may well be that this approximate constancy along the melting curve for a particular element represents the true content of the Lindemann relation. An application of the relation to determine temperatures in the earth's interior (to be presented elsewhere) yields results concordant with this view.

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²⁸ J. E. Lennard-Jones and A. F. Devonshire, *Proc. Roy. Soc. (London)* A170, 464 (1939).

²⁹ J. J. Gilvarry, *Phys. Rev.* 102, 325 (1956).