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# The Thermal Expansion of Pure Metals. II: Molybdenum, Palladium, Silver, Tantalum, Tungsten, Platinum, and Lead

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Extremely accurate determinations of the linear thermal expansions have been made interferometrically from room temperature to the temperature of liquid nitrogen for Mo, Pd, Ag, Ta, W, Pt, and Pb. Comparisons are made with the Grueneisen theory.

THIS research is an extension of work on other metals reported in a paper of the same title.[1] It was undertaken in order to obtain much needed data on the true coefficients of thermal expansion and also to subject the well-known Grueneisen relationship to further experimental test.

The Grueneisen theory[2] expresses the true linear coefficient of thermal expansion as a function of the specific heat and two constants, $Q_0$ and $(M+N+3)/6$, as follows:

$$\beta=\frac{C_v}{3Q_0\left[1-\frac{M+N+3}{6}\frac{E}{Q_0}\right]^2}. \qquad (1)$$

Here $\beta$ is the true coefficient of thermal expansion, $C_v$ the specific heat at constant volume, and

$$E=\int_0^T C_v dt.$$

$M$ and $n$ are the exponents in the attractive and repulsive terms, respectively, in the Mie equation relating the potential energy to the distance between vibrating atoms in a monatomic solid. The constant $Q_0$ is expressible in terms of specific heat and coefficient of thermal expansion. For further details the reader is referred to the above-mentioned paper.

TABLE I.

| Metal | Source | Purity |
|---|---|---|
| Mo | Westinghouse Lamp Co. | >99.95 Wt. % Mo |
| Pd | International Nickel Co. | >99.99 Wt. % Pd |
| Ag | Handy and Harmon | 99.999 Wt. % Ag |
| Ta | Fansteel Metallurgical Corp. | 99.9 Wt. % Ta<br>0.01 Wt. % Fe<br>0.003 Wt. % C |
| W | Westinghouse Lamp Co. | >99.95 Wt. % W |
| Pt | Refined in B.T.L. | >99.99 Wt. % Pt |
| Pb | National Lead Co. | >99.99 Wt. % Pb |

In obtaining a fit of the Gueneisen curve to the data one was able in most cases to use the characteristic Debye temperature $\theta$, found from specific heat measurements, along with values of $Q_0$ and $(M+N+3)/6$ obtained by fitting the curve to the data at one point.

## METHOD OF MEASUREMENTS

The measurements were made with an interferometric dilatometer previously described by us,[3] in the manner used in our initial work on pure metals.

## EXPERIMENTAL RESULTS

The sources of the metals used in this investigation, and their degree of purity as reported by their sources are shown in Table I.

TABLE II. Molybdenum.

| Temp. °C | $\Delta l/l_0 \times 10^4$ | Temp. °C | $\Delta l/l_0 \times 10^4$ |
|---|---|---|---|
| −187.0 | −7.904 | −59.5 | −2.964 |
| −182.5 | −7.784 | −54.7 | −2.723 |
| −172.0 | −7.543 | −49.0 | −2.482 |
| −165.5 | −7.302 | −44.5 | −2.241 |
| −156.5 | −7.061 | −39.5 | −2.000 |
| −149.5 | −6.820 | −35.0 | −1.759 |
| −143.0 | −6.579 | −29.9 | −1.518 |
| −136.0 | −6.338 | −25.0 | −1.277 |
| −129.5 | −6.097 | −20.0 | −1.036 |
| −123.5 | −5.856 | −15.6 | −0.795 |
| −117.0 | −5.615 | −10.7 | −0.554 |
| −111.5 | −5.374 | −6.8 | −0.313 |
| −107.0 | −5.133 | −1.5 | −0.072 |
| −100.7 | −4.892 | 0 | 0 |
| −94.8 | −4.651 | 3.0 | 0.168 |
| −90.0 | −4.410 | 7.5 | 0.409 |
| −85.0 | −4.169 | 12.0 | 0.650 |
| −80.0 | −3.928 | 17.1 | 0.891 |
| −74.9 | −3.687 | 21.0 | 1.133 |
| −69.5 | −3.446 | 25.0 | 1.350 |
| −64.0 | −3.205 | | |

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[1] F. C. Nix and D. MacNair, Phys. Rev. **60**, 597 (1941).

[2] E. Grueneisen, *Handbuch der Physik*, Vol. 10, p. 1.

[3] F. C. Nix and D. MacNair, Rev. Sci. Inst. **12**, 66 (1941).

TABLE III. Palladium.

| Temp. °C | $\Delta l/l_0 \times 10^4$ | Temp. °C | $\Delta l/l_0 \times 10^4$ |
|---|---|---|---|
| -187.0 | -19.399 | -65.0 | -7.425 |
| -183.0 | -18.955 | -61.5 | -6.961 |
| -179.0 | -18.564 | -57.0 | -6.497 |
| -173.0 | -18.099 | -52.6 | -6.033 |
| -166.5 | -17.635 | -48.7 | -5.546 |
| -163.5 | -17.171 | -44.5 | -5.105 |
| -156.0 | -16.707 | -40.2 | -4.641 |
| -153.0 | -16.266 | -36.5 | -4.177 |
| -147.0 | -15.825 | -32.5 | -3.713 |
| -139.8 | -15.222 | -28.5 | -3.249 |
| -131.0 | -14.387 | -24.1 | -2.785 |
| -128.0 | -14.039 | -20.3 | -2.320 |
| -121.2 | -13.551 | -16.6 | -1.856 |
| -117.0 | -13.111 | -12.6 | -1.392 |
| -112.0 | -12.530 | -8.6 | -0.928 |
| -105.5 | -11.881 | -4.5 | -0.464 |
| -100.0 | -11.185 | 0 | 0 |
| -95.2 | -10.744 | 3.1 | 0.371 |
| -91.0 | -10.280 | 8.1 | 0.928 |
| -86.0 | -9.746 | 12.1 | 1.392 |
| -82.3 | -9.259 | 16.0 | 1.856 |
| -78.0 | -8.818 | 21.0 | 2.320 |
| -73.0 | -8.354 | 26.0 | 2.901 |
| -70.0 | -7.890 | | |

TABLE IV. Silver.

| Temp. °C | $\Delta l/l_0 \times 10^4$ | Temp. °C | $\Delta l/l_0 \times 10^4$ |
|---|---|---|---|
| -186.0 | -31.853 | -67.7 | -12.519 |
| -181.0 | -31.057 | -63.0 | -11.680 |
| -176.0 | -30.133 | -58.6 | -10.841 |
| -170.0 | -29.421 | -54.0 | -10.003 |
| -163.0 | -28.540 | -49.6 | -9.164 |
| -158.5 | -27.617 | -44.6 | -8.325 |
| -152.0 | -26.779 | -40.2 | -7.528 |
| -147.0 | -25.940 | -36.0 | -6.647 |
| -141.0 | -25.101 | -30.5 | -5.809 |
| -136.0 | -24.262 | -26.8 | -4.970 |
| -132.0 | -23.465 | -22.0 | -4.131 |
| -127.5 | -22.669 | -17.5 | -3.292 |
| -121.5 | -21.830 | -13.2 | -2.453 |
| -116.2 | -20.928 | -9.0 | -1.615 |
| -111.5 | -20.068 | -4.0 | -0.775 |
| -106.9 | -19.292 | 0 | 0 |
| -102.0 | -18.475 | 4.8 | 0.901 |
| -97.0 | -17.552 | 8.9 | 1.741 |
| -92.0 | -16.713 | 13.5 | 2.579 |
| -87.0 | -15.874 | 18.0 | 3.418 |
| -83.2 | -15.098 | 19.8 | 3.838 |
| -78.5 | -14.302 | 21.8 | 4.257 |
| -73.0 | -13.358 | 24.5 | 4.697 |

TABLE V. Tantalum.

| Temp. °C | $\Delta l/l_0 \times 10^4$ | Temp. °C | $\Delta l/l_0 \times 10^4$ |
|---|---|---|---|
| -181.5 | -10.940 | -63.0 | -4.072 |
| -172.0 | -10.449 | -55.7 | -3.581 |
| -162.5 | -9.959 | -47.3 | -3.091 |
| -154.0 | -9.468 | -40.0 | -2.600 |
| -144.1 | -8.978 | -32.0 | -2.109 |
| -136.0 | -8.487 | -24.5 | -1.619 |
| -127.5 | -7.996 | -17.0 | -1.128 |
| -119.5 | -7.506 | -9.1 | -0.637 |
| -111.0 | -7.015 | -1.0 | -0.147 |
| -102.8 | -6.525 | 0 | 0 |
| -95.0 | -6.034 | 6.0 | 0.343 |
| -87.2 | -5.543 | 13.5 | 0.834 |
| -79.4 | -5.053 | 21.0 | 1.325 |
| -71.2 | -4.562 | 28.0 | 1.864 |

TABLE VI. Tungsten.

| Temp. °C | $\Delta l/l_0 \times 10^4$ | Temp. °C | $\Delta l/l_0 \times 10^4$ |
|---|---|---|---|
| -171.0 | -6.597 | -52.5 | -2.272 |
| -162.5 | -6.353 | -50.0 | -2.199 |
| -154.8 | -6.109 | -47.0 | -2.028 |
| -146.0 | -5.864 | -45.0 | -1.955 |
| -139.0 | -5.620 | -40.8 | -1.784 |
| -132.0 | -5.376 | -36.0 | -1.539 |
| -125.8 | -5.131 | -30.0 | -1.295 |
| -118.5 | -4.887 | -24.1 | -1.051 |
| -112.3 | -4.643 | -18.7 | -0.806 |
| -106.8 | -4.472 | -13.2 | -0.562 |
| -105.0 | -4.398 | -8.0 | -0.317 |
| -99.0 | -4.154 | -2.1 | -0.073 |
| -94.7 | -3.983 | 0 | 0 |
| -88.0 | -3.739 | 3.1 | 0.171 |
| -82.2 | -3.494 | 8.5 | 0.415 |
| -75.7 | -3.250 | 14.0 | 0.659 |
| -70.5 | -3.006 | 18.8 | 0.904 |
| -63.5 | -2.761 | 27.5 | 1.295 |
| -58.0 | -2.517 | | |

On Tables II to VIII we give our data; the left-hand column of each table containing the temperature in degrees centigrade, the right-hand column containing the thermal expansion as $\Delta l/l_0 \times 10^{-4}$, where $\Delta l$ is the change in length from °C, and $l_0$ is the length of specimens at 0°C. From large scale plots of the data given in Tables II to VIII one obtains graphically the slope of a curve at a temperature $T$ giving the "true" coefficient of thermal expansion, $(1/l_0)(dl/dT)$. The dots in Figs. 1 to 7 give the true coefficients of thermal expansion $\beta$ thus obtained, as a function of temperature in degrees Kelvin. The full drawn lines are Grueneisen curves obtained with the respective values for $\theta$, $Q_0$ and $(M+N+3)/6$.

## DISCUSSION OF RESULTS

### Molybdenum

The Grueneisen curve for Mo was obtained with values of 388 degrees for $\theta$, $365\times 10^3$ cal. for $Q_0$ and 6.83 for $(M+N+3)/6$. In older work, Disch[4] reports $\Delta l/l_0$ values at only two temperatures, $3.70\times 10^{-4}$ and $7.9\times 10^{-4}$ at $-78°$ and $-190$°C, respectively. For these two points, with

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[4] J. Disch, Zeits. f. Physik 5, 173 (1921).

TABLE VII. Platinum.

| Temp. °C | $\Delta l/l_0 \times 10^4$ | Temp. °C | $\Delta l/l_0 \times 10^4$ |
|---|---|---|---|
| −188.0 | −15.301 | −30.3 | −2.763 |
| −186.0 | −15.208 | −25.3 | −2.299 |
| −181.0 | −14.860 | −20.2 | −1.834 |
| −174.0 | −14.373 | −15.1 | −1.370 |
| −168.5 | −13.908 | −10.0 | −0.905 |
| −161.0 | −13.467 | −5.0 | −0.441 |
| −154.9 | −13.003 | 0 | 0 |
| −148.5 | −12.561 | 2.0 | 0.139 |
| −142.0 | −12.051 | 5.9 | 0.487 |
| −136.0 | −11.586 | 10.5 | 0.952 |
| −130.0 | −11.122 | 16.0 | 1.416 |
| −124.5 | −10.657 | 21.0 | 1.881 |
| −117.6 | −10.193 | 26.2 | 2.345 |
| −112.0 | −9.729 | 28.0 | 2.601 |
| −106.1 | −9.264 | 33.0 | 2.993 |
| −101.1 | −8.800 | 38.0 | 3.466 |
| −94.9 | −8.336 | 42.9 | 3.930 |
| −90.0 | −7.871 | 48.0 | 4.394 |
| −83.9 | −7.409 | 53.0 | 4.858 |
| −79.5 | −6.942 | 58.3 | 5.312 |
| −73.9 | −6.478 | 63.0 | 5.776 |
| −68.0 | −6.014 | 68.5 | 6.240 |
| −63.0 | −5.549 | 73.5 | 6.704 |
| −57.0 | −5.085 | 78.7 | 7.168 |
| −52.0 | −4.621 | 84.0 | 7.632 |
| −46.5 | −4.156 | 89.5 | 8.096 |
| −41.1 | −3.692 | 95.0 | 8.560 |
| −36.0 | −3.227 | | |

TABLE VIII. Lead.

| Temp. °C | $\Delta l/l_0 \times 10^4$ | Temp. °C | $\Delta l/l_0 \times 10^4$ |
|---|---|---|---|
| −188.0 | −50.398 | −75.2 | −20.833 |
| −181.0 | −49.056 | −69.7 | −19.666 |
| −177.5 | −48.058 | −66.0 | −18.437 |
| −173.0 | −46.706 | −62.0 | −17.300 |
| −168.5 | −45.463 | −57.0 | −15.978 |
| −163.5 | −44.401 | −52.5 | −14.749 |
| −157.5 | −43.119 | −48.1 | −13.520 |
| −153.0 | −41.820 | −43.6 | −12.291 |
| −149.5 | −40.568 | −39.0 | −11.062 |
| −143.5 | −39.423 | −34.6 | −9.833 |
| −139.0 | −38.402 | −30.0 | −8.604 |
| −135.0 | −36.873 | −25.8 | −7.375 |
| −129.5 | −35.644 | −21.0 | −6.146 |
| −125.0 | −34.415 | −17.4 | −4.916 |
| −120.6 | −33.186 | −12.5 | −3.687 |
| −115.0 | −31.957 | −9.0 | −2.458 |
| −110.2 | −30.781 | −4.5 | −1.229 |
| −103.0 | −28.775 | 0 | 0 |
| −99.0 | −27.669 | 4.2 | 1.229 |
| −98.0 | −27.032 | 8.9 | 2.458 |
| −92.5 | −25.842 | 12.2 | 3.687 |
| −88.0 | −24.621 | 17.0 | 4.916 |
| −83.2 | −23.353 | 21.2 | 6.146 |
| −79.5 | −22.155 | 25.0 | 7.375 |

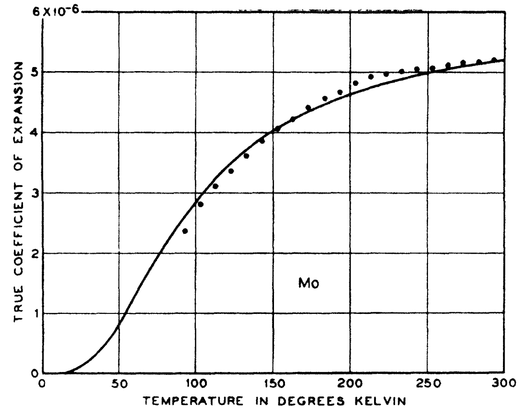

FIG. 1. True coefficient of thermal expansion *vs.* temperature for Mo. The dots are experimentally derived coefficients. The solid curve is the Grueneisen plot with $\theta = 388°K$, $1/6(M+N+3) = 6.83$, $Q_0 = 365 \times 10^3$ cal.

an extrapolation from −187° to −190°C for the latter temperature, we obtain $\Delta 1/l_0$ values of $3.90 \times 10^{-4}$ and $8.0 \times 10^{-4}$, respectively. In more recent work, Erfling[5] reports only two values for the mean temperature coefficient of expansion, $\bar{\beta}$, of $5.00 \times 10^{-6}$ for the interval of 0° and +20°C and $4.20 \times 10^{-6}$ for 0° to −183°C compared with our values for these same intervals of $5.35 \times 10^{-6}$ and $4.25 \times 10^{-6}$, respectively. From these scant data Erfling infers a $\theta$ value of 380 compared with our value of 388.

## Palladium

The full drawn line of Fig. 2 is the Grueneisen curve, with a characteristic Debye temperature of 300 degrees, a $(M+N+3)/6$ value of 0.4911 and a $Q_0$ value of $163.7 \times 10^3$ cal. The only other study of thermal expansion of Pd at low temperatures contains data at one temperature interval only. Henning[6] reports the thermal expansion from +16° to −191°C to be 21.17 $\times 10^{-4}$, in good agreement with our value, obtained by extrapolating from −187° to −191°C, of $21.31 \times 10^{-4}$.

## Silver

The constants used in obtaining the Grueneisen curve for Ag given in Fig. 3 are, $\theta = 215$, $Q_0 = 108.8 \times 10^3$ cal. and 2.42 for $(M+N+3)/6$.

Previous work from room temperature to the temperature of liquid nitrogen include fairly detailed studies by Buffington and Latimer[7] on silver of unknown purity, and Dorsey[8] on silver

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[5] H. D. Erfling Ann. d. Physik **34**, 136 (1939).

[6] F. Henning, Ann. d. Physik **22**, 631 (1907).

[7] R. M. Buffington and W. M. Latimer, J. Am. Chem. Soc. **48**, 2305 (1926).

[8] H. G. Dorsey, Phys. Rev. **25**, 88 (1907).

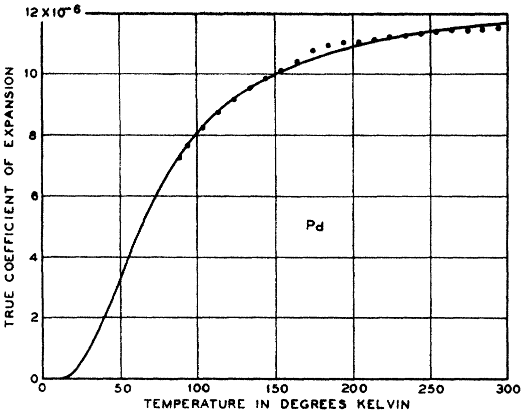

FIG. 2. True coefficient of thermal expansion *vs.* temperature for Pd. The dots are experimentally derived coefficients. The solid curve is the Grueneisen plot with $\theta = 300°\text{K}$, $1/6(M+N+3) = 0.4911$, $Q_0 = 163.7 \times 10^3$ cal.

stated to be very pure. We are only in fair agreement with these researches. Ebert[9] gives the thermal expansion from 0°C to $-190°\text{C}$ to be $32.30 \times 10^{-4}$ compared with our value, obtained by extrapolating to $-190°$ from $-186°\text{C}$, of $32.35 \times 10^{-4}$. Henning[6] reports the thermal expansion from $+16°\text{C}$ to $-191°\text{C}$ to be $35.27 \times 10^{-4}$ which compares with our value of $35.50 \times 10^{-4}$.

## Tantalum

The Grueneisen curve for Ta in Fig. 4 was obtained with values of 252 for $\theta$, $292.4 \times 10^3$ cal. for $Q_0$ and 0.2924 for $(M+N+3)/6$.

The only reference to similar studies in the temperature region covered in this investigation is by Disch.[4] He gives the thermal expansion, $\Delta l/l_0$, for $-78°\text{C}$ to be $4.6 \times 10^{-4}$ which is not in good agreement with our value of $5.00 \times 10^{-4}$ for the same temperature.

## Tungsten

The constants in the Grueneisen curve for W of Fig. 5 are 310° for $\theta$, $471.2 \times 10^3$ cal. for $Q_0$ and the surprisingly large value of 30.63 for $(M+N+3)/6$.

The work of Disch[4] with tungsten of unknown purity permits a comparison to be made at $-78°\text{C}$. He reports a value of $\Delta l/l_0$ to be $3.3 \times 10^{-4}$ which is identical with our value as taken from the plot of data given in Table V. Hidnert and Sweeney,[10] working with tungsten containing 99.98 percent W, report a value of $4.3 \times 10^{-6}$ for

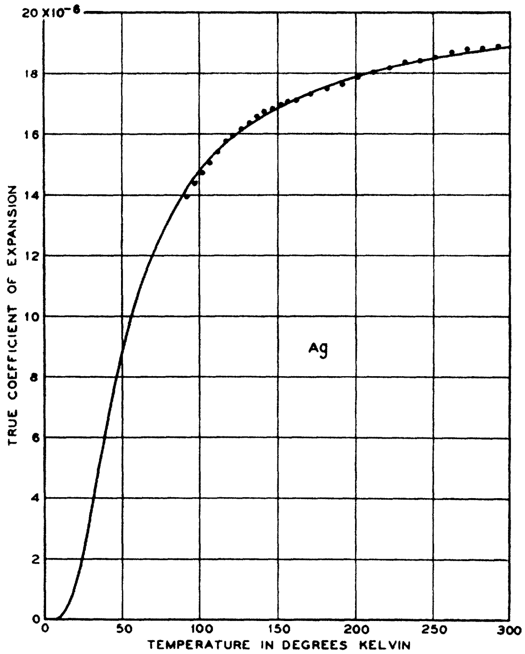

FIG. 3. True coefficient of thermal expansion *vs.* temperature for Ag. The dots are experimentally derived coefficients. The solid curve is the Grueneisen plot with $\theta = 215°\text{K}$, $1/6(M+N+3) = 2.42$, $Q_0 = 108.8 \times 10^3$ cal.

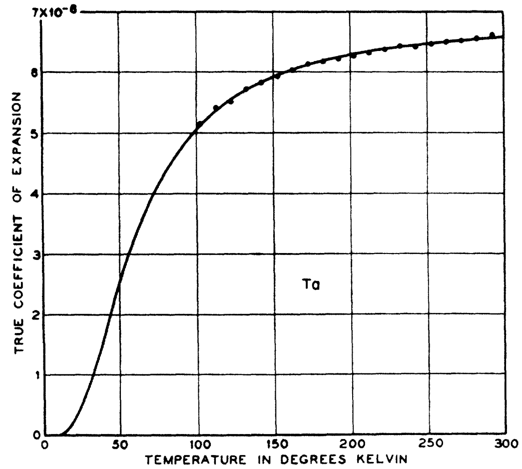

FIG. 4. True coefficient of thermal expansion *vs.* temperature for Ta. The dots are experimentally derived coefficients. The solid curve is the Grueneisen plot with $\theta = 252°\text{K}$, $1/6(M+N+3) = 0.2924$, $Q_0 = 292.4 \times 10^3$ cal.

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[9] H. Ebert, Zeits. f. Physik **47**, 712 (1928).

[10] P. Hidnert and W. T. Sweeney, Sci. Pap. Bur. Stand. **20**, 483 (1925).

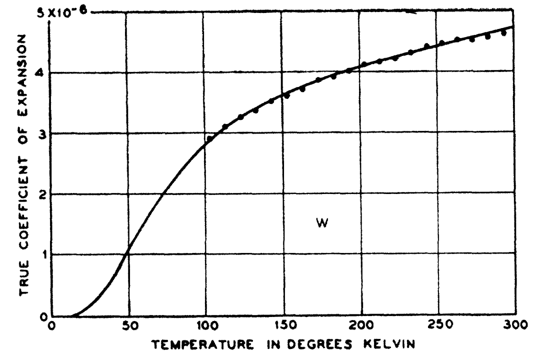

FIG. 5. True coefficient of thermal expansion *vs.* temperature for W. The dots are experimentally derived coefficients. The solid curve is the Grueneisen plot with $\theta=310°\text{K}$, $1/6(M+N+3)=30.63$, $Q_0=471.2\times10^3$ cal.

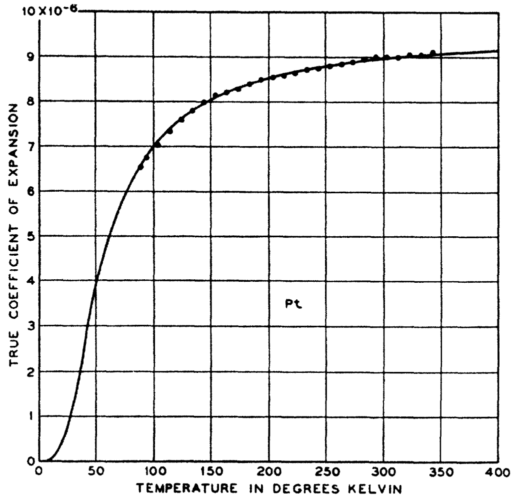

FIG. 6. True coefficient of thermal expansion *vs.* temperature for Pt. The dots are experimentally derived coefficients. The solid curve is the Grueneisen plot with $\theta=230°\text{K}$, $1/6(M+N+3)=2.21$, $Q_0=221\times10^3$ cal.

the mean temperature coefficient of expansion, $\bar{\beta}$, for the temperature interval 0° to $-50°$C and $4.2\times10^{-6}$ for the temperature interval $-50°$ to $-100°$C. These values compare favorably with our results of $4.39\times10^{-6}$ and $3.96\times10^{-6}$ for the same respective temperature intervals.

## Platinum

The full drawn line of Fig. 6, the Grueneisen curve, was obtained with values of 230 for $\theta$, $221\times10^3$ cal. for $Q_0$ and 2.21 for $(M+N+3)/6$.

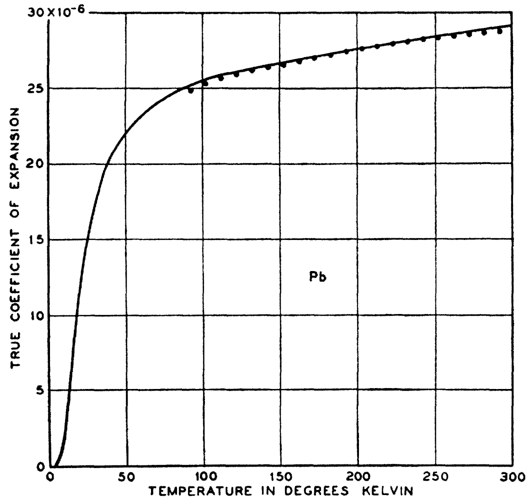

FIG. 7. True coefficient of thermal expansion *vs.* temperature for Pb. The dots are experimentally derived coefficients. The solid curve is the Grueneisen plot with $\theta=88°\text{K}$, $1/6(M+N+3)=3.19$, $Q_0=77.84\times10^3$ cal.

Our experimental values are in fair agreement with Dorsey; however, the agreement is rather poor with the results of Henning[6] and of Valentiner and Wallot.[11]

## Lead

The fit between our experimental results and the Grueneisen curve was obtained with following values for the constants of the latter curve $\theta=88°$, $Q_0=77.84\times10^3$ cal., $(M+N+3)/6=3.190$. These values are in fair agreement with Ebert's[9] values of 92° for $\theta$, $79.6\times10^3$ cal. for $Q_0$ and 3.2 for $(M+N+3)/6$ obtained from rather meager data. We are only in fair agreement with the experimental results of Ebert,[9] Grueneisen,[12] and Dorsey.[13]

The agreement between the Grueneisen theory and experiment is very good for the metals Pt, Pb and Ag with values obtained for $\frac{1}{6}(M+N+3)$ near those theoretically expected. The values of $\frac{1}{6}(M+N+3)$ for W and Mo are higher than the theory demands and much too low for the metals Ta and Pd.

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[11] S. Valentiner and J. Wallot, Ann. d. Physik **46**, 837 (1915).

[12] E. Grueneisen, Ann. d. Physik **33**, 33 (1910).

[13] H. G. Dorsey, Phys. Rev. **27**, 1 (1908).