

The Thermal Expansion of Pure Metals: Copper, Gold, Aluminum, Nickel, and Iron

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Extremely accurate determinations of the linear thermal expansions have been made interferometrically from -196°C to temperatures about $+400^{\circ}\text{C}$ for Al and $+700^{\circ}\text{C}$ for Fe, Ni, Cu and Au. The relationship between true thermal coefficient of expansion and temperature conforms very well to the Grueneisen-Debye theory when values are chosen for the Debye characteristic temperatures which turn out to agree well with those chosen to achieve agreement with the Debye theory of specific heats. Our values for these characteristic temperatures are: 410°K for Ni, 420°K for Fe, 400°K for Al, 325°K for Cu, and 190°K for Au. The magnetic Curie temperature for Ni is found to be 352°C . In plotting true coefficient of thermal expansion *versus* temperature Simon and Bergmann found a horizontal plateau at about 175° to 235°K for Ni and Fe; but we do not confirm this.

IN view of the discrepancies in the recorded values of true coefficients of thermal expansion for pure metals over a rather wide range of temperatures, we thought it worth while to reinvestigate a series of very pure metals from the temperature of liquid nitrogen up to about 700°C , by means of an interferometer dilatometer with photographic recording recently developed in these Laboratories. Another important purpose was to test the validity of the Grueneisen theory¹ of thermal expansion over a similarly wide temperature range.

The Grueneisen theory presents the following expression for the true linear coefficient of thermal expansion as a function of the specific heat and two constants, Q_0 and $\frac{1}{6}(m+n+3)$:

$$\beta = C_v / 3Q_0 \left[1 - \frac{m+n+3}{6} \frac{E}{Q_0} \right]^2, \quad (1)$$

where β is the true linear coefficient of thermal expansion, C_v the specific heat at constant volume; $E = \int_0^T C_v dT$; 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 defined in terms of specific heat and coefficient of thermal expansion, or in terms of atomic volume, Grueneisen's constant γ , and compressibility K_0 ,

as follows:

$$Q_0 = \frac{(C_p)}{[(1/V)(\partial V/\partial T)]} = \frac{V_0}{\gamma K_0}. \quad (2)$$

The constants necessary to evaluate β as a function of temperature are Q_0 , m , n , and the Debye constant θ which determines C_v and E ; one can, in principle, get their values from measurements of specific heats and compressibility. The constant γ , commonly known as "Grueneisen's constant," can be obtained either from the Grueneisen relation

$$\gamma = \frac{(\text{thermal expansion}) (\text{volume})}{(\text{specific heat at const. vol.}) (\text{compressibility})} \quad (3)$$

or, as Slater² has recently shown, from the constants used in Bridgman's expression relating change in volume to pressure. Slater has shown that values of γ thus obtained are in good agreement with those obtained from the Grueneisen relationship. Grueneisen further showed that γ is related to the exponent n in the repulsion term in the following manner

$$\gamma = \frac{1}{6}(n+2). \quad (4)$$

In the applications of Eq. (1) it has been customary to assume the exponent m of the attractive term to be equal to 3.

The characteristic Debye temperatures θ used to obtain C_v and E in Eq. (1) are taken from experimental specific heat values.

In actual practice one must fit the constants

¹E. Grueneisen, *Handbuch der Physik* (1926), Vol. 10, p. 1.

²J. C. Slater, *Phys. Rev.* **57**, 744 (1940).

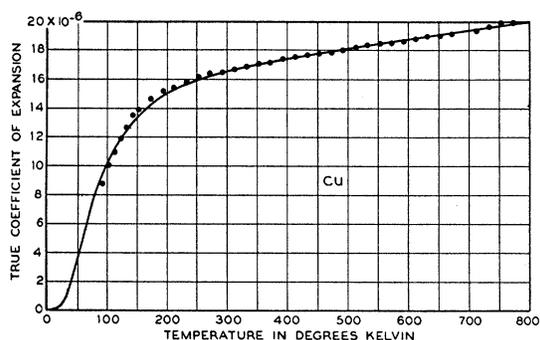


FIG. 1. True coefficient of thermal expansion *vs.* temperature for Cu. The dots are experimentally derived coefficients. The solid curve is the Grueneisen plot with $\theta = 325$, $\frac{1}{6}(m+n+3) = 2.8$, $Q_0 = 120 \times 10^3$ cal.

$\frac{1}{6}(m+n+3)$ and Q_0 to at least one point of the experimental data, and in some cases two points, in order to obtain a good fit between the Grueneisen curve and the experimental points. In some cases it was necessary to make slight adjustments in the value of θ in order to obtain a satisfactory fit. In the captions of the figures given below we give the values of θ , Q_0 , and $\frac{1}{6}(m+n+3)$ used in order to obtain the agreement between the experimental data and the Grueneisen curve of the respective figures.

METHOD OF MEASUREMENTS

The measurements were made with an interferometric dilatometer previously described by us,³ involving photographic recording; it permits slow rates of heating and cooling, so that sufficient time can be allowed for the specimens to come to thermal equilibrium with the refraction thermometer. The specimens were about 6 mm in length. All specimens were sealed in evacuated Pyrex glass tubing and subjected to a prolonged annealing to remove the effects of cold working. The low temperature portion of each test was made at a cooling rate of 20°C per hour from room temperature, with system containing the gas at a pressure of 3 mm of Hg. The fringe systems were photographed at intervals of about 30 seconds, thereby yielding a quasi-continuous record of both expansion and thermometer fringes. The complete unison of motion of the

two sets of fringes assured thermal equilibrium of the specimens and refraction thermometer. The temperature was held constant at the lowest temperature obtainable for a period of two hours, in order to obtain a further check on assuring thermal equilibrium. In the temperature region above room temperature, the gas at a pressure of 3 mm of Hg was used in order to facilitate the establishment of thermal equilibrium up to +150°C at a heating rate of 15°C per hour at which point the system was held at a constant temperature while it was evacuated to a pressure of 10^{-5} mm of Hg. At higher temperatures the heating rate was increased to 20°C per hour.

TABLE I. Thermal expansion of copper.

$T^\circ\text{C}$	$\Delta l/l_0 \times 10^4$	$T^\circ\text{C}$	$\Delta l/l_0 \times 10^4$	$T^\circ\text{C}$	$\Delta l/l_0 \times 10^4$
-185.5	-25.956	-8.0	-1.285	173.4	29.653
-179.0	-25.443	-4.5	-.7710	178.0	30.607
-173.0	-24.903	-1.5	-.2570	183.1	31.560
-168.5	-24.415	0	0	189.0	32.514
-164.5	-23.926	1.5	.2570	193.8	33.468
-159.5	-23.387	4.2	.7710	199.8	34.422
-154.0	-22.924	7.5	1.285	204.0	35.376
-152.0	-22.410	11.0	1.799	209.8	36.330
-147.0	-21.840	13.4	2.313	215.4	37.280
-142.5	-21.382	16.0	2.827	220.8	38.238
-137.5	-20.817	19.2	3.341	226.2	39.192
-134.0	-20.303	22.1	3.855	232.6	40.146
-131.2	-19.789	25.0	4.326	243.5	42.054
-123.0	-18.761	28.5	4.807	249.0	43.007
-119.2	-18.247	31.7	5.288	259.0	44.915
-116.0	-17.810	37.0	6.249	263.2	45.869
-112.0	-17.219	42.3	7.211	268.1	46.823
-108.0	-16.705	47.1	8.172	273.5	47.777
-104.5	-16.216	54.0	9.133	279.0	48.732
-100.5	-15.677	59.6	10.095	283.8	49.685
-97.2	-15.163	65.5	11.056	288.8	50.639
-93.5	-14.649	71.0	12.018	293.0	51.593
-90.5	-14.160	77.0	12.979	298.8	52.547
-86.1	-13.621	83.0	13.941	303.7	53.501
-83.2	-13.107	89.0	14.902	311.9	54.931
-80.2	-12.644	92.0	15.383	314.0	55.408
-77.0	-12.130	94.5	15.863	318.8	56.362
-73.2	-11.565	100.7	17.252	323.7	57.316
-70.0	-11.051	104.0	17.729	328.8	58.270
-66.2	-10.537	107.0	18.206	338.2	60.178
-62.0	-10.023	108.9	18.583	343.9	61.132
-60.2	-9.535	112.0	19.159	353.2	63.040
-56.6	-8.995	114.6	19.636	362.6	64.948
-53.0	-8.481	117.0	20.113	372.1	66.855
-49.0	-7.967	120.5	20.590	384.0	68.763
-46.5	-7.543	122.6	21.067	394.1	70.671
-44.1	-6.965	126.0	21.544	403.8	72.579
-39.5	-6.425	128.8	22.021	412.8	74.487
-36.1	-5.911	132.0	22.498	422.0	76.395
-33.1	-5.397	134.7	22.975	432.5	78.303
-29.6	-4.883	138.0	23.452	442.0	80.210
-27.0	-4.369	140.1	23.929	452.1	82.142
-23.2	-3.855	146.0	24.883	462.0	84.026
-20.3	-3.341	151.4	25.837	471.2	85.934
-17.3	-2.827	157.8	26.791	481.0	87.842
-14.5	-2.313	162.5	27.745	489.7	89.750
-11.0	-1.799	168.0	28.699	500.1	91.657

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

TABLE II. *Thermal expansion of gold.*

<i>T</i> °C	$\Delta l/l_0 \times 10^4$										
-187.0	-24.481	-15.0	-2.134	124.8	17.549	276.1	40.028	417.0	62.477	603.0	93.525
-185.0	-24.049	-11.0	-1.586	129.5	18.213	279.6	40.633	420.5	63.054	606.0	94.101
-179.0	-23.473	-6.1	- .9805	133.0	18.675	283.8	41.210	424.0	63.630	609.8	94.677
-175.0	-22.897	-2.7	- .4037	137.6	19.336	287.0	41.786	428.0	64.207	613.8	95.311
-170.0	-22.318	0	0	141.0	19.883	290.8	42.334	431.6	64.783	616.5	95.888
-164.5	-21.741	2.0	.1730	145.0	20.459	294.0	42.939	435.3	65.359	619.8	96.406
-160.0	-21.165	4.10	.5189	149.5	21.036	297.7	43.515	439.7	65.936	623.7	97.040
-154.7	-20.589	10.0	1.327	152.9	21.556	301.4	44.092	443.0	66.570	628.0	97.559
-150.0	-20.013	14.0	1.903	156.5	22.132	305.1	44.668	446.0	67.088	630.0	98.135
-145.0	-19.436	18.0	2.480	161.0	22.767	308.0	45.215	449.8	67.665	633.0	98.712
-140.5	-18.857	22.0	3.088	164.0	23.285	311.6	45.763	453.7	68.241	636.8	99.288
-137.0	-18.310	25.0	3.490	168.1	23.890	315.6	46.368	457.0	68.817	640.5	99.951
-131.1	-17.734	25.0	3.489	172.5	24.467	318.8	46.916	460.8	69.394	644.0	100.49
-126.5	-17.128	29.7	4.181	175.2	25.014	322.2	47.521	463.8	69.970	647.0	101.02
-122.5	-16.552	34.0	4.758	180.0	25.590	326.0	48.068	467.6	70.546	650.5	101.59
-117.3	-15.973	38.0	5.334	183.2	26.166	330.0	48.674	471.6	71.123	654.0	102.17
-112.7	-15.397	42.6	5.911	188.2	26.772	333.9	49.221	475.1	71.699	657.5	102.75
-108.0	-14.821	45.8	6.488	191.0	27.318	337.4	49.798	478.9	72.276	661.0	103.32
-104.0	-14.244	50.1	7.093	195.6	27.924	341.0	50.403	489.0	74.005	663.0	103.90
-99.5	-13.668	54.0	7.641	199.0	28.471	344.8	50.950	492.0	74.581	668.0	104.48
-95.0	-13.092	58.5	8.247	203.0	29.047	347.8	51.527	506.2	76.829	672.0	105.11
-90.5	-12.516	62.0	8.795	206.8	29.653	351.3	52.103	510.5	77.578	675.0	105.63
-86.2	-11.939	66.0	9.371	211.0	30.229	354.8	52.679	514.8	78.183	677.0	106.20
-82.0	-11.360	70.0	9.948	215.0	30.864	358.2	53.256	517.3	78.673	681.0	106.78
-78.5	-10.784	74.2	10.525	218.2	31.355	362.5	53.832	529.8	80.748	684.8	107.36
-73.8	-10.208	78.8	11.101	222.4	31.931	366.0	54.408	557.0	85.744	688.0	107.93
-69.0	-9.629	83.0	11.707	226.3	32.508	368.8	54.985	559.0	86.032	691.0	108.51
-65.0	-9.055	87.0	12.255	230.8	33.140	373.0	55.561	568.0	87.588	694.5	109.14
-60.2	-8.479	91.0	12.832	234.6	33.716	377.0	56.137	569.1	87.819	697.6	109.66
-56.5	-7.900	94.0	13.293	238.5	34.236	380.3	56.714	572.7	88.337	701.0	110.30
-52.0	-7.324		12.832	243.2	34.868	384.4	57.290	575.0	88.798	705.0	110.90
-48.2	-6.747		12.255	246.2	35.389	387.1	57.867	576.0	88.914	708.2	111.39
-44.6	-6.171		11.678	249.8	35.965	391.2	58.443	579.0	89.490	711.0	111.97
-40.0	-5.595	100.0	14.12	254.0	36.541	395.1	59.019	583.1	90.153	714.0	112.54
-36.0	-5.045	104.2	14.638	257.6	37.118	398.8	59.596	586.0	90.700	717.0	113.18
-31.2	-4.439	108.5	15.215	261.3	37.694	403.1	60.172	589.0	91.219	720.5	113.70
-27.0	-3.863	112.3	15.791	264.9	38.270	405.9	60.748	592.3	91.795	723.8	114.27
-23.0	-3.287	117.0	16.370	268.8	38.847	409.9	61.325	596.0	92.429	726.0	114.85
-19.0	-2.711	121.0	16.946	272.7	39.423	413.0	61.901	599.0	92.948	729.8	115.43

EXPERIMENTAL RESULTS

Copper

The copper used in these experiments was taken from rods produced by Adam Hilger for use as spectroscopic standards which, according to their analysis, possess a copper content of 99.979 percent and oxygen of 0.02 percent. We give in Table I the data obtained, the first column containing the temperature in degrees centigrade and the second column the thermal expansivity, $(\Delta l/l_0) \times 10^4$, where l_0 is the length of specimens at 0°C and Δl is the change in length. In Fig. 1 is plotted the true coefficient of thermal expansion, $(1/l_0)(dl/dT)$, as a function of temperature in degrees Kelvin; the curve is graphically obtained from the plot of data of Table I. The dots represent the experimental points; the solid curve is the Grueneisen curve

obtained with a characteristic Debye temperature of 325, 2.8 for $\frac{1}{6}(m+n+3)$ and 120×10^3 cal. for Q_0 .

The temperature region from room temperature to 800°K has been previously studied by Eucken and Dannoehl;⁴ Rosenbohm;⁵ Henning;⁶ and Uffelman.⁷ The low temperature region has been previously investigated by Adenstedt;⁸ Buffington and Latimer;⁹ Henning;⁶ Dorsey;¹⁰ Keesom, van Agt and Jansen;¹¹ Borelius and

⁴ A. Eucken and W. Dannoehl, *Zeits. f. Elektrochemie* **40**, 814 (1934).

⁵ E. Rosenbohm, *Physica* **5**, 385 (1938).

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

⁷ F. L. Uffelman, *Phil. Mag.* **10**, 633 (1930).

⁸ H. Adenstedt, *Ann. d. Physik* **26**, 69 (1936).

⁹ R. M. Buffington and W. M. Latimer, *J. Am. Chem. Soc.* **48**, 2305 (1926).

¹⁰ H. G. Dorsey, *Phys. Rev.* **25**, 88 (1907).

¹¹ W. H. Keesom, F. P.G.A.J. van Agt, and A. F. J. Jansen *Proc. k. Acad. Amst.* **29**, 786 (1926).

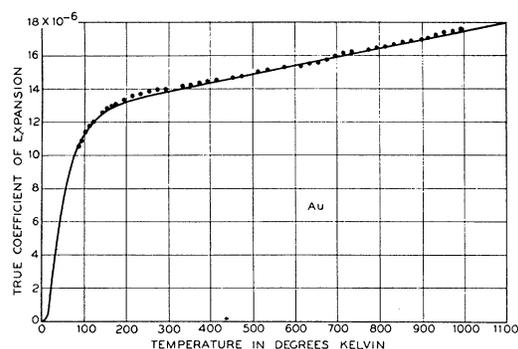


FIG. 2. True coefficient of thermal expansion vs. temperature for Au. The dots are experimentally derived coefficients. The solid curve is the Grueneisen plot with $\theta = 190$, $\frac{1}{6}(m+n+3) = 3.4$, $Q_0 = 148.8 \times 10^3$ cal.

Johansson;¹² Simon and Bergmann;¹³ and Aoyama and Ito.¹⁴ We are in quite good agreement with the work of Adenstedt; Buffington and Latimer; and Dorsey. The values reported by Simon and Bergmann are much too high near room temperature and too low near 95°K. We are in excellent agreement with the values of Q_0 and $\frac{1}{6}(m+n+3)$ obtained by Adenstedt, but we obtain a value of 325 for θ somewhat higher than Adenstedt's value of 315.

Gold

The gold used in these expansion experiments was obtained from Handy and Harmon as a spectroscopic standard, containing 99.99+ percent Au, the impurities being traces of Ag, Cu, and Pd. The data are presented in Table II with the temperatures given in degrees centigrade and expansivity as $(\Delta l/l_0) \times 10^4$. The true coefficient of thermal expansions, obtained graphically from a plot of the data given in Table II, is given by the dots as a function of temperature in degrees Kelvin in Fig. 2. The solid line is the Grueneisen curve obtained by using a characteristic Debye temperature of 190, a value of 3.4 for $\frac{1}{6}(m+n+3)$, and 148.8×10^3 cal for Q_0 .

Our results are in good agreement with recent studies of Austin¹⁵ and of Esser and Euster-

brock,¹⁶ in the region from room temperature to 1000°K. The low temperature region has been previously studied by Ebert;¹⁷ Dorsey,^{10,18} and Grueneisen.¹⁹

Aluminum

The specimens were cut from a block of high purity aluminum containing 99.997 percent Al.

TABLE III. Thermal expansion of aluminum.

T °C	$\Delta l/l_0 \times 10^4$	T °C	$\Delta l/l_0 \times 10^4$	T °C	$\Delta l/l_0 \times 10^4$
-191.0	-34.358	43.0	10.273	233.2	57.073
-184.5	-33.891	47.5	11.209	237.1	58.009
-176.5	-32.932	50.7	12.145	240.2	58.945
-169.5	-31.996	55.0	13.104	244.1	59.881
-161.5	-31.061	59.0	14.017	247.9	60.817
-156.0	-30.125	62.8	14.953	251.0	61.753
-148.0	-29.189	67.0	15.889	254.7	62.889
-142.7	-28.277	70.3	16.825	258.0	63.625
-137.0	-27.342	75.9	17.761	261.1	64.561
-130.5	-26.406	79.0	18.697	264.6	65.497
-126.0	-25.517	82.8	19.633	268.0	66.433
-120.0	-24.512	87.0	20.615	271.0	67.369
-115.0	-23.576	91.0	21.505	275.0	68.305
-109.0	-22.664	95.0	22.441	277.9	69.241
-104.0	-21.775	97.6	23.377	281.0	70.177
-99.5	-20.816	102.8	24.359	284.5	71.113
-93.6	-19.834	106.4	25.272	287.5	72.049
-89.0	-18.898	110.5	26.231	291.0	72.985
-84.0	-17.963	114.0	27.121	294.0	73.921
-79.5	-17.027	117.8	28.057	297.1	74.857
-75.3	-16.092	122.5	29.086	300.6	75.793
-70.5	-15.156	126.0	29.929	303.7	76.729
-66.0	-14.225	130.0	30.888	307.0	77.665
-61.3	-13.285	134.4	31.801	310.0	78.601
-56.5	-12.349	138.0	32.760	313.0	79.537
-52.5	-11.413	142.0	33.673	316.0	80.473
-48.0	-10.478	145.1	34.632	319.7	81.409
-43.5	-9.543	149.0	35.545	322.8	82.345
-37.5	-8.607	153.0	36.481	326.1	83.281
-34.6	-7.672	157.0	37.417	329.2	84.217
-30.1	-6.736	160.0	38.353	333.0	85.153
-26.0	-5.800	162.5	38.938	336.0	86.089
-22.0	-4.865	163.0	39.289	339.0	87.025
-17.0	-3.929	167.2	40.225	341.9	87.961
-13.2	-2.994	171.0	41.161	345.0	88.897
-9.0	-2.058	175.0	42.097	348.0	89.833
-5.0	-1.123	178.6	43.033	351.0	90.815
0	0	182.0	43.969	354.1	91.705
3.5	.7484	185.9	44.905	357.0	92.641
7.6	1.684	189.9	45.841	360.0	93.577
11.0	2.620	193.0	46.777	363.0	94.513
15.1	3.555	196.7	47.713	366.1	95.449
19.2	4.491	200.8	48.649	369.4	96.385
21.0	4.958	204.0	49.585	372.8	97.321
23.0	5.426	208.0	50.521	375.5	98.280
25.0	5.894	211.5	51.457	379.0	99.193
28.0	6.646	215.0	52.393	381.6	100.13
29.0	6.997	218.9	53.329	384.7	101.06
31.0	7.465	222.5	54.265	387.5	102.00
35.0	8.401	226.0	55.201	391.0	102.96
39.0	9.337	229.7	56.137	393.8	103.87

¹² G. Borelius and C. H. Johansson, *Ann. d. Physik* **75**, 23 (1924).

¹³ F. Simon and R. Bergmann, *Zeits. f. physik. Chemie* **B8**, 255 (1930).

¹⁴ S. Aoyama and T. Ito, *Tohoku Imp. Univ. Sci. Rep.* **27**, 348 (1939).

¹⁵ J. B. Austin, *Physics* **3**, 240 (1932).

¹⁶ H. Esser and H. Eusterbrock, *Arch. f. Eisenhüttenwesen* **14**, 341 (1941).

¹⁷ H. Ebert, *Zeits. f. Physik* **47**, 712 (1928).

¹⁸ H. G. Dorsey, *Phys. Rev.* **27**, 1 (1908).

¹⁹ E. Grueneisen, *Ann. d. Physik* **33**, 33 (1910).

The heating rate from room temperature to 500°C was 30° per hour. The cooling rate from room temperature to -191°C was 20°C per hour. Helium gas at a pressure of 3 mm of Hg was used in low temperature test, and also in the high temperature test up to +170°C, at which point the system was evacuated to a pressure of 10^{-5} mm of Hg for the remainder of the high temperature test. Table III contains the data tabulated as before. There is a small amount of scattering from 160 to 300°C caused by the lack of thermal equilibrium between specimens and refraction thermometer on evacuation of the gas. A plot of the true linear coefficient of thermal expansion *versus* temperature in degrees Kelvin is given in Fig. 3. The dots represent the data with the solid line giving the Grueneisen plot. This excellent fit between the Grueneisen equation and the experimental data was obtained using a characteristic Debye temperature of 400, a value of 2.7 for $\frac{1}{6}(m+n+3)$, and a value of 83.6×10^3 cal for Q_0 .

Previous measurements in the temperature region from room temperature to 700°K have been made by Hidnert,²⁰ Uffelman,⁷ Henning,⁶ and by Taylor, Willey, Smith and Edwards.²¹ The low temperature region from room temperature to -191°C has been studied by Buffington and Latimer,⁹ Henning,⁶ and Ebert.¹⁷ A comparison of our values of mean coefficient of thermal expansion with values reported by Hidnert; and Taylor, Willey, Smith, and Edwards is fairly good. We are also in fairly good agreement in the low temperature region with the results of Buffington and Latimer.

Nickel

The nickel used for the specimens, obtained from the International Nickel Company, contained 99.90 percent Ni, the impurities consisting of 0.03 percent Fe, 0.0035 percent Mg, 0.0005 percent Cu, 0.05 percent C, <0.001 percent Mn, 0.0043 percent Al, 0.011 percent SiO₂. Table IV contains the experimental data tabulated as before. The true coefficient of thermal expansion *versus* temperature in degrees Kelvin is given in Fig. 4. The dots again represent the experi-

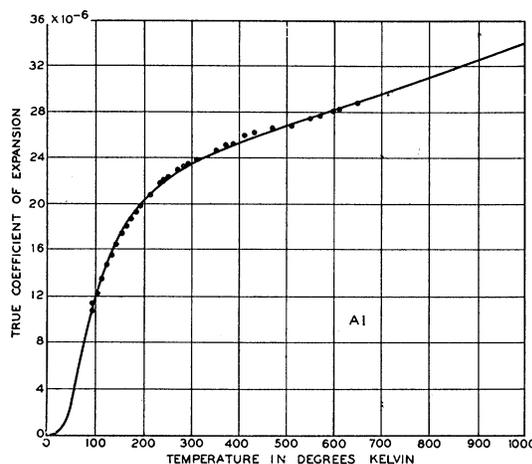


FIG. 3. True coefficient of thermal expansion *vs.* temperature for Al. The dots are experimentally derived coefficients. The solid curve is the Grueneisen plot with $\theta = 400$, $\frac{1}{6}(m+n+3) = 2.7$, $Q_0 = 83.6 \times 10^3$ cal.

mentally derived coefficients with the theoretical Grueneisen plot given by the full drawn curve. The Grueneisen curve was obtained by using a characteristic Debye temperature θ , of 410, the value of 4 for $\frac{1}{6}(m+n+3)$, and the value of 151.5×10^3 cal for Q_0 . In the case of nickel, in contrast to the metals Au, Cu, and Al, the behavior of the thermal coefficient of expansion is obscured by the presence of a volume change accompanying the vanishing of ferromagnetism. The peak in the β *vs.* T plot occurs at 635°K, which is the Curie point. In view of the excellent agreement between experiment and theory for the cases of Cu, Au, and Al, we feel that the Grueneisen curve of Fig. 4 represents the course of β *vs.* T insofar as controlled by thermal vibrations, while the deviation beginning at about 320°K is due to the volume change of magnetic origin. It is also of interest to note that the experimental points do not again coincide with the theoretical curve until a temperature of about 780°K is reached, which is some 145° above the Curie point, the peak in the β *vs.* T plot.

A detailed plot of temperature coefficient of electrical resistivity *vs.* temperature of nickel of the same purity, from unpublished data, shows a peak in the identical position on the temperature scale. The temperature coefficient of resistivity does not again become constant at higher temperatures until a temperature of about 800°K,

²⁰ P. Hidnert, Sci. Pap. Bur. Stand. **19**, 697 (1924).

²¹ C. S. Taylor, L. A. Willey, D. W. Smith, and J. D. Edwards, Metals and Alloys **9**, 189 (1938).

TABLE IV. *Thermal expansion of nickel.*

T °C	$\Delta l/l_0 \times 10^4$	T °C	$\Delta l/l_0 \times 10^4$	T °C	$\Delta l/l_0 \times 10^4$
-192.0	-18.830	99.0	12.930	308.0	44.528
-191.0	-18.579	101.0	13.243	311.6	45.018
-184.5	-18.127	104.0	13.684	314.0	45.507
-174.0	-17.575	107.0	14.174	317.0	45.997
-165.5	-17.072	111.1	14.663	320.2	46.487
-158.2	-16.570	115.5	15.202	322.8	47.001
-152.0	-16.068	118.3	15.642	326.0	47.515
-145.0	-15.616	122.6	16.156	329.0	47.980
-139.8	-15.139	125.1	16.622	331.8	48.494
-133.1	-14.562	129.6	17.136	334.8	49.008
-128.0	-14.060	133.8	17.650	337.1	49.473
-122.5	-13.558	137.0	18.090	340.5	49.963
-117.5	-13.080	140.5	18.604	343.0	50.403
-112.0	-12.553	144.0	19.143	344.7	50.648
-107.0	-12.126	147.5	19.559	346.0	50.893
-101.0	-11.549	151.0	20.073	347.5	51.138
-96.0	-11.047	154.0	20.538	348.1	51.382
-92.0	-10.545	157.8	21.101	349.6	51.627
-87.0	-10.043	160.1	21.566	350.9	51.872
-82.2	-9.591	163.5	22.007	352.8	52.192
-78.0	-9.089	167.0	22.546	354.0	52.362
-74.0	-8.536	170.0	22.986	355.0	52.606
-69.0	-8.034	173.4	23.476	357.0	52.900
-64.6	-7.582	176.2	23.990	358.1	53.096
-60.0	-7.030	180.0	24.480	359.5	53.390
-55.6	-6.528	182.8	24.945	360.8	53.586
-51.2	-6.026	186.0	25.483	362.0	53.830
-47.0	-5.574	189.1	25.924	363.4	54.075
-42.3	-5.021	192.6	26.462	364.0	54.320
-38.2	-4.569	196.2	26.927	366.2	54.565
-33.3	-4.017	199.4	27.393	367.8	54.834
-29.7	-3.540	203.0	27.931	369.0	55.054
-25.4	-3.013	206.0	28.372	370.6	55.299
-21.1	-2.460	209.2	28.886	372.4	55.617
-17.0	-2.009	213.0	29.424	373.7	55.813
-13.0	-1.506	216.0	29.914	375.0	56.034
-9.0	-1.004	219.0	30.330	376.7	56.278
-4.5	-.502	222.7	30.869	378.0	56.572
0	0	226.5	31.383	379.1	56.768
2.0	.351	229.6	31.823	381.2	57.013
8.1	1.004	233.3	32.362	382.5	57.282
12.0	1.506	236.0	32.803	385.3	57.747
15.1	2.009	239.0	33.292	388.0	58.237
20.1	2.511	243.0	33.806	391.6	58.726
23.2	3.013	246.0	34.271	394.6	59.216
28.0	3.590	249.0	34.785	397.8	59.706
31.2	4.017	252.1	35.299	400.8	60.195
36.0	4.519	255.0	36.009	404.5	60.734
39.4	5.021	258.3	36.205	407.0	61.223
43.0	5.523	261.3	36.768	409.0	61.664
47.0	6.026	264.5	37.184	413.0	62.153
51.0	6.528	268.0	37.723	415.5	62.668
55.0	7.030	270.3	38.164	418.5	63.133
58.8	7.532	273.6	38.678	422.0	63.647
62.2	8.034	279.2	39.657	424.0	64.112
66.0	8.536	282.3	40.146	427.1	64.601
69.8	9.038	285.0	40.611	430.0	65.140
74.0	9.540	288.8	41.126	434.0	65.630
77.7	10.043	291.2	41.591	442.7	67.049
81.5	10.545	294.0	42.080	454.0	69.008
85.4	11.047	297.0	42.643	467.2	70.966
89.1	11.549	299.0	43.108	477.5	72.924
93.4	12.051	303.0	43.574	486.2	74.491
97.1	12.553	305.7	44.039	488.5	74.883

a behavior very like that of the expansion coefficient. Mott and Potter explain such "tails" extending over a rather wide range by the assumption that at the Curie point the large Weiss domains break up, leaving something of the nature of short range order to vanish gradually as T is further increased.

The Heisenberg theory of ferromagnetism, as pointed out by Fowler and Kapitza²² and later demonstrated by Powell,²³ can account in a rough quantitative way for the change in volume which ferromagnetic substances undergo as the ferromagnetism vanishes on heating. The first careful experimental attempt to obtain the ferromagnetic change in length was made by Williams²⁴ on quite pure nickel. In order to obtain the area under the Curie peak Williams used as a base line his own data at temperatures from room temperature to about 300°C and those of Hidnert²⁵ for temperatures considerably above the Curie point. We feel in view of the excellent agreement obtained between theory and experiment for Cu, Au, and Al that a theoretical Grueneisen curve which fits the experimental points at temperatures around room temperature and below would serve as a much more accurate base line than the experimental curve used by Williams. The increase in volume due to the vanishing of ferromagnetism begins as low as 325°K in Fig. 4 whereas in Fig. 5 of Williams' paper it is not perceptible until about 525°K is attained.

A careful measurement of the area between the Grueneisen and the experimental curves gives the value 3.65×10^{-4} for the ferromagnetic change in length per unit length, compared with Williams' value of 0.92×10^{-4} for nickel of comparable purity.

We are in quite good agreement with the previous experimental values of Williams.²⁴ Other work at temperatures above room temperature includes the studies of Hidnert;²⁵ Henning;⁶ Disch;²⁶ Uffelman;⁷ Eucken and Dannoehl;⁴ Rosenbohm;⁵ Colby,²⁷ and x-ray studies at high

²² R. H. Fowler and P. Kapitza, Proc. Roy. Soc. **124**, 1 (1929).

²³ F. C. Powell, Proc. Phys. Soc. London **42**, 390 (1930).

²⁴ C. Williams, Phys. Rev. **46**, 1011 (1934).

²⁵ P. Hidnert, J. Research Nat. Bur. Stand. **5**, 1305 (1930).

²⁶ J. Disch, Zeits. f. Physik **5**, 173 (1921).

²⁷ W. F. Colby, Phys. Rev. **30**, 506 (1910).

temperatures by Owen and Yates²⁸ and also by Jesse.²⁹ We are in good agreement with recent low temperature work of Adenstedt.⁸ Other low temperature work includes that of Henning;⁶ Disch;²⁶ Aoyama and Ito,¹⁴ and also of Simon and Bergmann.¹³ We do not confirm the existence of a flat plateau in the β vs. T plot for the temperature region from 175 to 235°K reported by Simon and Bergmann, nor do we agree with the value of β at any temperature.

Iron

The iron used in this investigation was kindly furnished by Dr. J. G. Thompson of the United States Bureau of Standards. He reports the impurities to be

Cu—<0.002 percent	P—0.0005 percent
Si—0.001 percent	O ₂ —0.0003 percent
Be—<0.001 percent	N ₂ —0.0002 percent
Al—Nil	H ₂ —0.0002 percent
C—0.001 percent	Fe—99.992 (by difference)
S—0.0023 percent	

The iron specimens were heated in He gas at a pressure of 3 mm of Hg up to 100°C at a rate of 10°C per hour, then in a vacuum of 10⁻⁵ mm of Hg up to 800°C. The low temperature test was made in an atmosphere of He at 3 mm of Hg at a cooling rate of 20°C per hour. Table V contains data on the expansion at different temperatures. The dots in Fig. 5 again give the graphically derived true coefficients of thermal expansion as a function of temperature in degrees Kelvin, with the solid curve giving the Grueneisen plot. We note that the fit is much worse than in the case of Ni and we are forced to the conclusion that deviations from the Grueneisen curve at temperatures above 200°K are to be attributed to disturbances arising from the slow disappearance of ferromagnetism with increasing temperature. The Grueneisen curve was obtained with the characteristic Debye temperature of 420, the value of 3.7 for $\frac{1}{6}(m+n+3)$, and the Q_0 value of 166.67×10^3 cal.

In the temperature region above room temperature we find ourselves in rather good qualitative agreement with the results of Austin and

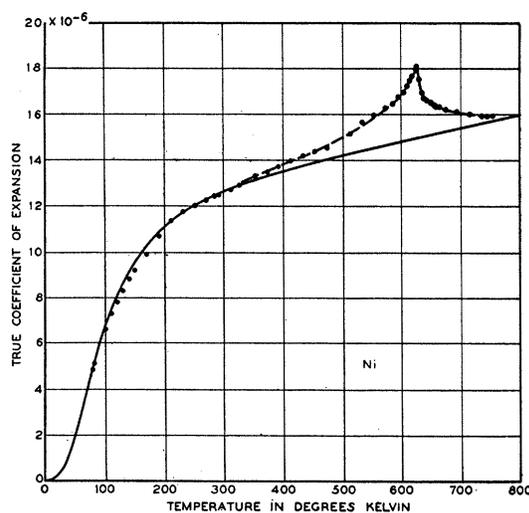


FIG. 4. True coefficient of thermal expansion vs. temperature for Ni. The dots are experimentally derived coefficients. The solid curve is the Grueneisen plot with $\theta = 410$, $\frac{1}{6}(m+n+3) = 4.0$, $Q_0 = 151.5 \times 10^3$ cal.

Pierce,³⁰ and with those of Esser and Eusterbrock.¹⁶ The variations from sample to sample are quite considerable in the region above room temperature where presumably the effects of extremely small amounts of impurities can materially affect the ferromagnetic change in length. In the low temperature region we are in rather good agreement with the results of Adenstedt⁸ and somewhat in poorer agreement with the results of Dorsey¹⁰ and of Ebert.¹⁷ Again, as in the case of Ni we fail to find any evidence of the flat plateau extending from 195 to 235°K as reported by Simon and Bergmann. Furthermore we fail to agree with them as to values of the coefficient throughout the region.

DISCUSSION OF RESULTS

The agreement between our experimental results and the Grueneisen theory is excellent in the cases of the metals Cu, Au and Al, i.e., in metals free of complications arising from volume changes due to slow disappearance of ferromagnetism with increasing temperature. In the case of Ni the fit is good below 325°K which indicates that the thermal expansion is to be attributed solely to the normal lattice vibrations

²⁸ E. A. Owen and E. L. Yates, *Phil. Mag.* **21**, 809 (1936).

²⁹ W. P. Jesse, *Physics* **5**, 147 (1934).

³⁰ J. B. Austin and R. H. H. Pierce, Jr., *Physics* **4**, 409 (1933).

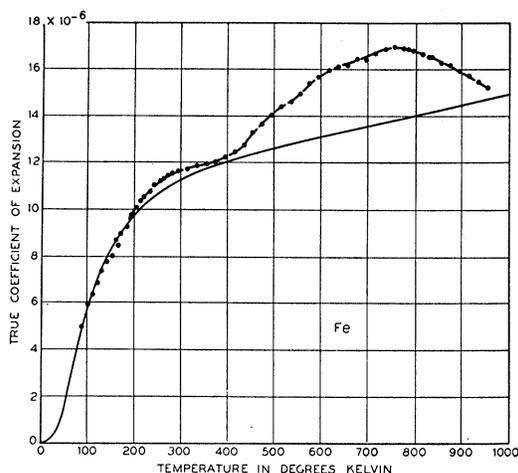


FIG. 5. True coefficient of thermal expansion vs. temperature for Fe. The dots are experimentally derived coefficients. The solid curve is the Grueneisen plot with $\theta = 420$, $\frac{1}{6}(m+n+3) = 3.7$, $Q_0 = 166.67 \times 10^8$ cal.

considered in the Grueneisen theory. Above this temperature, where the disappearance of ferromagnetism produces an increase in volume, the total thermal expansion is much greater up to a temperature some 135° above the peak or Curie point. Since such considerations are not involved in the basis of the Grueneisen theory, we should not expect the latter to agree with the experimental results. For the same reasons we should also expect no agreement between theory and experiment for the case of Fe.

The theoretically expected values for $\frac{1}{6}(m+n+3)$,—obtained by assuming $m=3$ along with values of n taken from the Grueneisen constant γ with the aid of Eq. (4)—are 2.68, 3.70, 2.83, 2.55, and 2.26 for Cu, Au, Al, Ni, and Fe, respectively. These values are in moderately good agreement with the values used in order to obtain a good fit between the theoretical Grueneisen curve and the data of 2.8, 3.4, 2.7, 3.7 and 4.0, respectively.

It is of interest to note that small amounts of impurities appear to play only a minor role in the thermal expansion of non-ferromagnetic metals, and also a vanishingly small role in the ferromagnetic metals at temperatures sufficiently low for the temperature dependence of the ferromagnetism to play a small part in the thermal expansion. The good agreement obtained between our results and those of Taylor, Willey,

Smith, and Edwards²¹ on the very pure Al at high temperatures compared with results obtained by Hidnert²⁰ using Al of a substantially less degree of purity indicate that the small amounts of impurities do not play a very important role. The same can be said for the agreement between our results on Al at low temperatures and those of Buffington and Latimer⁹ obtained with rather impure material.

TABLE V. Thermal expansion of iron.

$T^\circ\text{C}$	$\Delta l/l_0 \times 10^4$	$T^\circ\text{C}$	$\Delta l/l_0 \times 10^4$	$T^\circ\text{C}$	$\Delta l/l_0 \times 10^4$
-181.5	-16.607	81.0	9.710	385.1	53.830
-176.0	-16.109	85.2	10.210	392.0	54.806
-166.0	-15.241	90.0	10.711	398.5	55.757
-159.0	-14.740	93.0	11.211	405.2	56.808
-148.0	-14.240	97.1	11.712	410.7	57.759
-142.0	-13.739	102.9	12.262	417.1	58.760
-134.0	-13.289	106.2	12.713	423.2	59.761
-127.0	-12.738	111.6	13.213	430.0	60.837
-121.0	-12.237	115.2	13.714	435.3	61.788
-114.5	-11.737	119.9	14.265	441.3	62.764
-109.5	-11.236	123.0	14.715	447.0	63.765
-103.5	-10.786	127.9	15.241	453.0	64.766
-98.0	-10.235	132.0	15.716	459.0	65.767
-92.5	-9.735	136.0	16.267	465.0	66.768
-87.0	-9.234	141.0	16.767	471.0	67.769
-81.2	-8.734	144.0	17.218	477.0	68.770
-77.0	-8.233	147.2	17.768	483.5	69.771
-73.0	-7.783	151.0	18.219	488.8	70.772
-67.1	-7.232	155.1	18.769	495.0	71.773
-62.8	-6.732	161.6	19.720	501.0	72.774
-57.8	-6.231	169.2	20.721	507.0	73.775
-53.3	-5.806	176.5	21.797	513.0	74.776
-48.0	-5.230	183.0	22.723	519.0	75.777
-42.2	-4.730	190.0	23.724	525.0	76.778
-38.0	-4.229	197.0	24.800	531.5	77.779
-33.2	-3.729	205.0	25.726	537.0	78.780
-29.0	-3.228	212.0	26.802	543.0	79.781
-25.0	-2.728	218.1	27.728	549.0	80.882
-20.5	-2.227	226.1	28.804	555.2	81.883
-16.0	-1.727	232.3	29.730	561.0	82.784
-11.0	-1.226	239.6	30.731	567.0	83.785
-6.7	-.7257	246.2	31.732	573.0	84.786
-2.7	-.2252	252.9	32.733	579.0	85.787
0	0	260.0	33.734	582.8	86.438
2.5	.3504	266.0	34.735	584.2	86.788
5.8	.7758	272.7	35.736	590.5	87.789
10.5	1.276	279.0	36.737	597.9	88.841
14.0	1.777	285.2	37.738	602.8	89.842
18.0	2.277	292.1	38.739	609.0	90.793
22.0	2.778	298.1	39.740	615.8	91.844
28.0	3.304	304.5	40.742	622.1	92.795
32.5	3.454	310.8	41.793	627.5	93.796
36.0	4.204	317.0	42.794	635.2	94.797
40.3	4.705	323.8	43.770	641.2	95.798
45.1	5.205	329.8	44.796	648.5	96.899
48.8	5.706	336.0	45.822	655.0	97.900
53.0	6.206	342.0	46.748	660.1	98.801
57.0	6.707	348.0	47.774	667.0	99.802
61.5	7.207	354.1	48.800	674.3	100.90
65.0	7.708	360.5	49.801	678.0	101.30
68.9	8.208	362.2	50.752	681.0	101.91
73.0	8.709	373.0	51.753	684.8	102.90
77.8	9.209	379.8	52.804		

In ferromagnetic metals such as Ni and Fe, on the other hand, the presence of small amounts of impurities can play a dominating role in determining the total thermal expansion for certain temperature regions. This is clearly indicated for the case of Fe by a comparison of our results with those of Austin and Pierce³⁰ and of Esser and Eusterbrock,¹⁶ as well as results obtained by these workers on irons of slightly different purity. For the temperature region between room temperature and the temperature of liquid nitrogen the role played by small amounts of impurities in Fe is much smaller than in the high

temperature region, as evidenced by the rather good agreement between our results and those of Adenstedt⁸ and also the older results of Dorsey.¹⁰ Williams²⁴ demonstrated rather clearly the influence of small amounts of impurities on the thermal expansion for the case of nickel near the Curie temperature.

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Rigidity Modulus of Beta-Brass Single Crystals

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The rigidity modulus of ten beta-brass single crystals has been measured as a function of crystal orientation and of temperature from 25° to 500°C by the method of the composite piezoelectric oscillator. The reciprocal of the rigidity modulus, $1/G'$, is linearly related to the orientation function. When these data are combined with Rinehart's previous measurements of Young's modulus, the principal elastic parameters are found to be 3.88, -1.52 and 0.578×10^{-12} cm²/dyne, respectively, at room temperature. Curves and tables give them as functions of temperature up to and slightly beyond the critical temperature for order-disorder. At room temperature, the rigidity modulus is a maximum in the [100] direction, $G'_{[100]} = 17.3 \times 10^{11}$ dyne/cm², and a minimum in the [111] direction, $G'_{[111]} = 1.35 \times 10^{11}$ dyne/cm², and at the critical temperature, $G'_{[100]} = 13.5 \times 10^{11}$ dyne/cm² and $G'_{[111]} = 1.06 \times 10^{11}$ dyne/cm². The elastic anisotropy as given by $G'_{[100]}/G'_{[111]}$ is 12.8 at room temperature, decreases to 12.3 at 250°C and has a value of 13.0 at the critical temperature. The bending-torsion effect was found to be large and in agreement with theory.

INTRODUCTION

THE transition from "order" to "disorder" in certain binary alloys has been studied in terms of changes in various physical properties during this transition.¹ The study of the elasticity of single crystals has been particularly interesting, although a complete theoretical treatment has not been given. Siegel² has determined all the principal elastic constants (and corresponding elastic parameters) for Cu₃Au single crystals, from room temperature up to and beyond the critical temperature for order-

disorder. Both Webb³ and Rinehart⁴ have worked with single crystals of beta-brass. The former's work included a preliminary study of Young's modulus at room temperature and as a function of the orientation of the crystals. A static method was used. Rinehart, using a more accurate dynamic method extended the work on Young's modulus from about -80° to 500°C (about 30° above the critical temperature). The dependence on orientation was very precisely determined. Rinehart's data established, throughout the temperature range, the elastic parameter, s_{11} , and a

¹ F. Nix and W. Shockley, *Rev. Mod. Phys.* **10**, 1 (1938).

² S. Siegel, *Phys. Rev.* **57**, 537 (1940).

³ W. Webb, *Phys. Rev.* **55**, 297 (1939).

⁴ J. Rinehart, *Phys. Rev.* **58**, 385 (1940) and **59**, 308 (1941).