

Maslakovets¹⁰ upon heating and cooling crystals. They, however, only observe such effects in *p*-type crystals of PbTe with practically no effect being observed in *n*-type crystals. Our results, on the other hand, show precipitation effects in both *n* and *p*-type crystals. In the *n*-type crystals, much longer annealing times at a given temperature were required for the effects to be observed than in *p*-type crystals.

¹⁰T. L. Kovalchik and Iu. P. Maslakovets, *J. Tech. Phys.* (U. S. S. R.) **26**, 2417 (1956) [*Soviet Phys.—Tech. Phys.* **1**, 2337 (1957)].

From Hall effect data on *n*-type PbTe crystals, the intrinsic carrier concentration and resistivity at room temperature are estimated to be $n_i = 2 \times 10^{16}/\text{cm}^3$ and $\rho_i = 0.2 \text{ ohm cm}$.

ACKNOWLEDGMENTS

The author is most grateful to Dr. B. Houston for providing the *p*-type PbTe crystal and the information on dislocation densities, and to Dr. R. Brebrick for providing the *n*-type material used in these experiments.

Anomalous Lattice Specific Heat of Gold and Zinc at Liquid Helium Temperatures

J. E. ZIMMERMAN AND L. T. CRANE

Scientific Laboratory, Ford Motor Company, Dearborn, Michigan

(Received December 1, 1961)

The heat capacities of both single-crystal and polycrystalline samples of gold and of zinc have been measured between 1.5 and 4.2°K. For gold the results may be represented accurately by an equation of the form $C = \gamma T + \beta T^3$, but the coefficient β of the cubic term is significantly smaller than the value derived from low-temperature elastic constants measured on the same specimen. For zinc a polynomial expression of the results requires a T^5 term in addition to the usual linear and cubic terms. The T^5 term is positive, as in most other solids upon which measurements have been made, but is very large in magnitude, amounting to about one-fifth of the total heat capacity at 4°K. The agreement between the Debye temperatures near 0°K calculated from heat capacity and from low-temperature elastic constants measured on the same specimen may be within experimental error.

INTRODUCTION

THE work reported in this paper was undertaken in an effort to resolve some of the inconsistencies between the lattice specific heats of certain metals as determined directly by heat capacity measurements and as derived from low-temperature elastic constants. An impetus was provided by the availability of the large single-crystal specimens of gold and zinc used by Alers and Neighbours^{1,2} for elastic constant determinations. We were thus able to eliminate one source of experimental uncertainty by making both of the essential measurements on the same set of specimens. Since these measurements did nothing to resolve the inconsistencies, heat capacity measurements were made later on polycrystalline specimens to see if this sort of change of macrostructure might affect the lattice specific heat, unlikely though it seemed.

The measurements reported here on gold are largely in agreement with previous accurate helium temperature results. On zinc, our measurements show some detail not apparent in earlier work.

It is assumed that in these two metals, gold and

zinc, the specific heat C is the sum of an electronic component linear in temperature and denoted by γT , and a lattice component making up the remainder. Conventionally at low temperatures one assumes also that the lattice component is cubic and may be denoted by βT^3 , where theoretically $\beta = 1943(1/\theta_0)^3 \times 10^{-6}$ joules per mole deg⁴ and T is small compared to θ_0 , the "Debye characteristic temperature." Thus, if one plots experimental values of C/T vs T^2 , the points are expected to fall on a straight line of the form $C/T = \gamma + \beta T^2$, from which the coefficients γ and β , and θ_0 , are determined. The Debye temperature θ_0 is also calculable from low-temperature elastic constants. Alers and Neighbours³ in a review article have given a comprehensive discussion of various ways of doing this and have made a comparison between Debye temperatures derived from heat capacities and from elastic constants for all the solids for which data were available.

As we shall see, the specific heat of zinc cannot be fitted by linear plus cubic terms alone even at temperatures below $\theta_0/100$. Empirically, therefore, we have added a term δT^5 to the specific heat equation. Qualitatively this is justified by much theoretical and

¹G. A. Alers and J. Neighbours, *J. Phys. Chem. Solids* **7**, 58 (1958).

²J. Neighbours and G. A. Alers, *Phys. Rev.* **111**, 707 (1958).

³G. A. Alers and J. Neighbours, *Revs. Modern Phys.* **31**, 675 (1959).

experimental evidence.⁴ Quantitatively, however, we cannot account for the magnitude of the T^5 term actually observed.

EXPERIMENTAL

Heat capacity measurements on the single-crystal specimens were made in a previously described calorimeter⁵ which used helium exchange gas during calibration of the carbon-resistance thermometer. The only variation in technique was to use a manganin-wire heat leak between the zinc specimen and the helium bath. After calibration the exchange gas was pumped out at 4.2°K and the bath temperature then was lowered to 1.5°K. The wire heat leak was small enough that several hours were required for the specimen to cool to the latter temperature. This procedure was adopted to avoid the troublesome adsorption of helium by the zinc, an effect apparently also observed by Keesom and Kok.⁶ The polycrystalline specimens were measured in an entirely different calorimeter which utilized a mechanical heat switch for thermometer calibration. This calorimeter also has been described in the literature.⁷ Both calorimeters embodied vapor bulbs for the primary determination of temperature.

The single-crystal specimens were cut from the same large single-crystal ingots used by Alers and Neighbours for elastic-constant measurements. The properties of

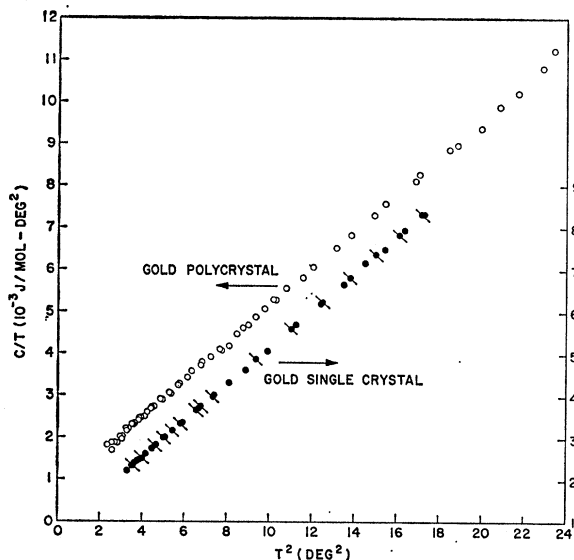


FIG. 1. Specific heats of single-crystal and polycrystalline gold, plotted as C/T vs T^2 . The two sets of points indicated for the single crystal are results from two different runs. Right- and left-hand ordinates are displaced to avoid confusion.

⁴ J. de Launay, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1956), Vol. 2, p. 257.

⁵ J. E. Zimmerman and F. E. Hoare, *J. Phys. Chem. Solids* **17**, 52 (1960).

⁶ W. H. Keesom and J. A. Kok, *Physica* **1**, 770 (1933).

⁷ L. T. Crane and J. E. Zimmerman, *Phys. Rev.* **123**, 113 (1961).

TABLE I. Description of specimens.

		Analysis	Treatment	Weight
Zn	Single-crystal	99.98	See reference 1	103.0
Zn	Polycrystal	99.999 ⁺	Vacuum melted and slow cooled	46.6
Au	Single-crystal	99.99 ⁺	See reference 2	270.5
Au	Polycrystal	99.999 ⁺ ^a	Vacuum chill-cast	72.3

^a According to the supplier, the only detectable impurities were: Ag, 3 parts per million (ppm); and Cu, Fe, Si, Pb, and Mg, each less than 1 ppm.

these and the polycrystalline specimens are summarized in Table I.

In fitting polynomials in T to our specific heat data, least squares analyses have been employed. Coefficients derived by this method are given along with standard deviations. Owing to rather small scatter of our experimental points and to the rather large number of points taken, these standard deviations probably represent a minor, though not insignificant, part of the total experimental error.

Gold

Our data for gold, both single-crystal and polycrystalline, are shown in Fig. 1. A least squares analysis of the single-crystal data gives $C = (767 \pm 13)T + (439 \pm 1)T^3$, from which we get a Debye temperature of 164.2. Least squares analysis of the polycrystalline data gives $C = (740 \pm 10)T + (440.5 \sim 0.8)T^3$ and a Debye temperature of 164.0. For comparison, measurements made by Corak *et al.*⁸ lead to an equation $C = (740 \pm 13)T + (436 \pm 3)T^3$,⁹ in good agreement with our results.

The Debye temperature of 164.2 obtained for the single-crystal specimen is thus about 1½% larger than the value 161.6 derived by Alers and Neighbours from elastic constant measurements on pieces cut from the same ingot. This inconsistency could be accounted for by an error of about five percent in lattice specific heat determination, or by a three percent error in elastic constant measurement. Since both sets of measurements are believed to be considerably more accurate than this, the two percent inconsistency in Debye temperature appears to be inherent in the gold specimen itself. Note that the calorimetric Debye temperature is larger than the elastic constant value, rather than smaller as in most other solids. Magnesium is the only other solid which has been observed to exhibit this phenomenon.¹⁰

In view of the relatively large lattice contribution to the specific heat of gold, it would be interesting to make accurate measurements at still lower temperatures. A very small higher order term in the specific heat might

⁸ Corak, Garfunkel, Satterthwaite, and Wexler, *Phys. Rev.* **98**, 1699 (1955).

⁹ Calculated by J. Skalyo and A. Arrott using Corak's data and the 1955 temperature scale. Units used throughout this paper are microjoules, unless otherwise stated.

¹⁰ J. Rayne, *J. Phys. Chem Solids* **7**, 268 (1958).

bring the calorimetric and elastic constant results into coincidence at slightly lower temperatures. In magnesium the lattice contribution is already relatively small at helium temperatures, so the prospect of making significant measurements at lower temperatures is less appealing. A difficulty with the hypothesis of a higher order term in gold is the fact that all available experimental evidence indicates that the lattice heat capacity at all temperatures above 2°K is in the form of a Debye function with $\theta=165^\circ\text{K}$.¹¹ The higher order term must therefore be of rather special form.

Zinc

Recent measurements^{12,13} of the specific heat of zinc have given Debye temperatures of the order of 300°K, in relatively wide disagreement with the elastic constant

TABLE II. Specific heat of zinc single crystal.

T^2 (°K) ²	C/T (10 ⁻⁶ joule/mole deg ²)	e_1	e_3	
3.43	850	-4	-8	
3.68	861	0	-3	
3.92	874	1	-1	
4.16	890	0	-2	
4.43	908	-2	-3	
4.66	911	9	8	
5.03	944	-1	-1	
5.39	974	-8	-7	
5.74	989	-1	0	
6.06	1008	1	3	
6.35	1023	4	7	
6.65	1045	2	5	
6.94	1066	0	4	
7.28	1082	7	11	
7.86	1130	-1	3	
8.41	1173	-6	-1	
9.02	1210	0	5	
9.68	1259	-1	4	
10.39	1310	0	5	
11.13	1372	-6	-2	
11.82	1418	1	5	
12.60	1485	-5	-2	
13.76	1570	4	5	
15.10	1682	4	1	
15.94	1760	-2	-7	
16.27	1776	11	5	
16.72	1832	-5	-13	
17.26	1869	6	-3	
17.33	1891	-10	-19	
17.49	1890	6	-4	
		rms=4.8	rms=6.3	
	γ	β	δ	θ_0
Method 1	658	51.0	1.13	336
Method 1 (least squares)	656±8	51.5±1.7	1.11±0.07	
Method 3 Zavaritskii (reference 14)	641	(55.6)	0.89	(327)
Seidel and Keesom (reference 12)	652			340±20
	640	66	0.39	309

¹¹ P. H. Keesom and N. Pearlman, *Handbuch der Physik* (Springer-Verlag, Berlin, 1956), Vol. XIV, p. 282.

¹² P. L. Smith, *Phil. Mag.* **46**, 744 (1955).

¹³ G. Seidel and P. H. Keesom, *Phys. Rev.* **112**, 1083 (1958).

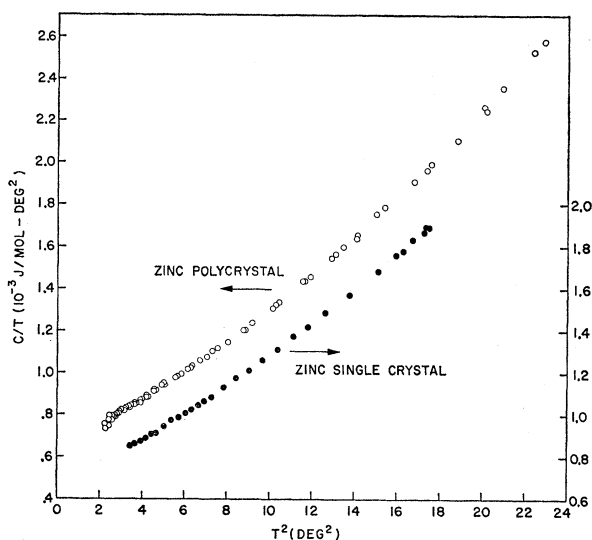


Fig. 2. Specific heats of single-crystal and polycrystalline zinc plotted as C/T vs T^2 . Right- and left-hand ordinates are displaced to avoid confusion.

value of^{3,14} 327°K in spite of the fact that the measurements were made at temperatures of the order of 1/100 of the Debye temperature. Results of the present measurements are shown in Table II and in Fig. 2. It is immediately obvious that these data are not to be fitted by the usual linear plus cubic terms. An equation of the form $C=\gamma T+\beta T^3+\delta T^5$ can be made to fit very well, however, as is shown by what follows.

In view of the elastic constant and other specific heat data already available, several methods of treating these data suggest themselves, namely: (1) to derive all three coefficients, γ , β , and δ by least squares or visual curve fitting; (2) to take the value of γ from published work and derive the coefficients of T^3 and T^5 from our data; (3) to take the coefficient of T^3 derived from elastic constants and derive γ and δ from the present data; and (4) to take both γ and β from the sources mentioned and derive only the coefficient of T^5 .

If we concentrate on the single crystal data, since this was the specimen with which the elastic constants were determined, the first method leads to an equation $C=658T+51.0T^3+1.13T^5$, derived by visual curve fitting. The Debye temperature corresponding to this coefficient of T^3 is 337°. The first two terms in the equation are very close to those obtained by Zavaritskii¹⁵ from measurements between 0.5 and 2.0°K. The mean result of measurements on two different samples was $\gamma=652\pm 40$, and measurements on one sample only gave $\theta_0=340\pm 20$. Thus, if we use his value of γ , method (2) would give an equation almost the same as method (1). Seidel and Keesom,¹³ on the other hand, obtained $\gamma=640$ by fitting their data between 0.4 and

¹⁴ C. W. Garland and R. Dalven, *Phys. Rev.* **111**, 1232 (1958).

¹⁵ N. V. Zavaritskii, *Zhur. Eksp. i Teoret. Fiz.* **34**, 1116 (1958).

4.2°K with a three-constant equation. This should be a reliable value of γ in spite of the fact that above 3°K, as the authors themselves point out, the scatter in the results is unusually large. Turning to method (3), the coefficient β derived from a Debye temperature of 327° is 55.6, and the complete set of coefficients, obtained by visual curve fitting, is 641, 55.6 and 0.89. It appears, therefore, that if we use the γ -value found by Seidel and Keesom, methods (2), (3), and (4) all give essentially the same result. The two sets of coefficients derived by methods (1) and (3) are included in Table II, along with a table of differences, calculated minus measured values in columns headed e_1 and e_3 . The result of a least squares analysis by method (1) is also included.

As Table II shows, the equation with three adjustable coefficients gives an excellent fit to the experimental data; the deviations appear to be random, with an rms value of 4.8 microjoules per mole deg². The equation derived by method (3) gives deviations of noticeably nonrandom character; however, the rms value of 6.3 is still so small that it is tempting to conclude that the elastic constant value of Debye temperature does indeed fit the calorimetric facts near absolute zero. One might also conclude that it will require a very refined specific heat measurement to determine the limiting value of Debye temperature to much better than 2 or 3%.

It is interesting to compare an extrapolation of our results with those of Eichenauer and Schulze¹⁶ at higher temperatures. At 12°K, their low-temperature limit, the equation $641T + 55.6T^3 + 0.89T^5$ derived by method (3) yields $C = 0.078$ cal per mole deg, compared to their value of 0.088. This is better agreement than one might expect, considering the length of the extrapolation and the magnitude of the T^5 term at this temperature. Eichenauer and Schulze derive a Debye temperature of 209 at 12°K, compared to the low-temperature value of around 330. This change in Debye temperature is considerably larger than has been observed in most other solids, though the change in cadmium is nearly the same,¹⁷ and there are indications of a similar effect in gallium.¹³ The extrapolation of our results agrees

even more closely with measurements made by Smith¹² above 4°K. For example, Smith gives effective Debye temperatures of 300, 280, 250 and 235 at 4, 6, 8, and 10°K, respectively. Our method (3) equation gives 303, 281, 254, and 238.

Garland and Silverman¹⁸ have recently reconsidered the data of Seidel and Keesom together with that of Phillips.¹⁹ They show that a limiting Debye temperature of 322°K ($\gamma = 653$, $\beta = 58.2$, $\delta = 1.02$) gives a reasonable fit to the experimental data and conclude also that the disagreement between calorimetric and elastic constant is probably not significant.

Although our single-crystal and polycrystal zinc results agree very closely—within one percent—below 3°K, above that temperature there is appreciable divergence, amounting to 4% at 4°K. In view of the fact that all other measurements that we have made in both calorimeters, including those on gold reported in this paper, agree much more closely than this, it appears that there is an essential difference between the lattice dynamics of the two specimens. Whether or not this difference is a consequence of the different crystallite sizes is open to speculation. Least-squares analysis of the polycrystal data gives the relation $C = (643 \pm 4)T + (51.8 \pm 0.1)T^3 + (1.40 \pm 0.04)T^5$. The disagreement at the higher temperatures appears mainly as a disagreement in the coefficients of T^5 , as expected.

Note Added in Proof. Du Chatenier and De Nobel [Physica 28 (to be published)] have recently measured specific heats of the noble metals of 99.9999% purity between 1 and 30°K. For gold they give $\gamma = 0.74_0$ and $\theta_0 = 165.9$, in good agreement with results given in this paper. Their measurements confirm another unique feature of the physical properties of gold, namely that the effective Debye temperature θ_D is practically independent of temperature, or perhaps even increases slightly with temperature.

ACKNOWLEDGMENT

The authors are greatly indebted to Dr. G. A. Alers for his stimulating interest in this work and for many informative discussions.

¹⁶ W. Eichenauer and M. Schulze, Z. Naturforsch. **14a**, 28 (1959).

¹⁷ P. L. Smith and N. M. Wolcott, Phil. Mag. **1**, 854 (1956).

¹⁸ C. W. Garland and J. Silverman, J. Chem. Phys. **34**, 781 (1961).

¹⁹ N. E. Phillips, Phys. Rev. Letters **1**, 363 (1958).