

Specific Heat of Thorium at High Temperatures*†

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The specific heat and electrical resistivity of high-purity thorium have been measured from room temperature to 1000°C. The specific heat was measured by an electrical pulse-heating method. The results have been analyzed in terms of additive lattice and electronic specific heats.

APPARATUS AND PROCEDURE

THE specific heat of crystal bar thorium was measured from room temperature to 1000°C by an electrical pulse-heating method. This method has been developed recently and tested thoroughly on high-purity iron. Since a detailed description of the experiment has been given elsewhere,¹ a brief outline will be sufficient here.

The sample was prepared in the form of a wire with diameter of the order of ten mils. A piece of the wire about five cm long was mounted in a sample holder by connecting each end to a copper block or electrode. The sample holder was designed to support these electrodes in the hot zone of a vacuum furnace and also to bring electrical leads from the electrodes out of the vacuum system. The leads were connected into the "unknown" position of a calibrated Kelvin bridge. A calibrated platinum to platinum-13% rhodium thermocouple was attached to one of the copper blocks and served to measure the sample temperature.

The sample was annealed at 1000°C for at least one hour under a pressure of less than 10^{-5} mm of mercury. The furnace was then cooled to room temperature at a rate of about 40°C per hour; during this time the resistance and temperature of the sample were measured at about 5°C intervals. At about 100°C intervals, the sample was pulsed in order to collect specific heat data over a 200°C temperature range.

A pulse was accomplished by connecting a six-volt battery to the battery terminals of the Kelvin bridge for about 30 milliseconds. During this time the sample wire was heated by the large current (of the order of 10 amp) which passed through it, but other parts of the circuit were not heated appreciably. As the temperature of the sample increased during the pulse, its resistance increased and the bridge became unbalanced. The unbalance voltage of the bridge as a function of time throughout the pulse was recorded photographically from the face of a calibrated oscilloscope.

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¹ D. C. Wallace, P. H. Sidles, and G. C. Danielson, *J. Appl. Phys.* **31**, 168 (1960).

The specific heat was calculated throughout each pulse from the ratio of the power delivered to the sample to the time rate of change of the sample temperature. The power delivered was (a) the electrical power dissipated in the sample, calculated from unbalanced Kelvin bridge equations, minus (b) the rate at which heat was lost from the sample by conduction through the wire ends and radiation from the wire surface, calculated with the aid of theoretical expressions obtained by integrating the heat flow equation for the wire. The time rate of change of the sample temperature was obtained by first converting the sample resistance to temperature with the aid of the measured resistance as a function of temperature, and then differentiating the sample temperature with respect to time throughout each pulse. Most of the specific heat computations were carried out with the aid of an IBM-650 computer.

PREPARATION OF THORIUM

Iodide thorium was prepared in this laboratory by the de Boer-van Arkel process.² This method of preparation gave crystal bars of very high-purity thorium. In order to fabricate samples for specific heat measurements, a crystal bar was arc melted into a "button," the button was cut into strips, and the strips were swaged into wires. Without annealing, the wires were further reduced to diameters of 10 to 14 mils by drawing (with lubricant)³ through diamond dies. The wires were cleaned with hot nitric acid in which a little sodium fluosilicate had been dissolved. This cleaning brought out a metallic luster which lasted indefinitely when the wires were stored in air.

TABLE I. Impurities in Ames thorium.

Nonmetallic		Metallic	
C	75 ppm	Fe	<20 ppm
O	58.3 ppm	Mn	<20 ppm
N	3.3 ppm	Al	~30 ppm
H	3.5 ppm	Be	<20 ppm
		Ca	~20 ppm
		Mg	<20 ppm
		Si	<50 ppm
		Zr	<200 ppm
		Ni	<20 ppm

² N. D. Veigel, E. M. Sherwood, and I. E. Campbell, in *The Metal Thorium*, edited by H. A. Wilhelm (American Society for Metals, Cleveland, Ohio, 1958), Chap. 7.

³ *The Reactor Handbook* (Technical Information Service, U. S. Atomic Energy Commission, Washington, D. C., 1955), Vol. 3, Sec. 1, p. 317.

Table I gives a list of impurities which is representative of the thorium used in this experiment; the metallic impurities were present in amounts only of the order of or less than the limit of spectrographic detection.

The thorium wires could not be mounted in direct contact with the copper electrodes of the sample holder, since thorium alloys with copper at high temperatures. It was therefore necessary to separate the thorium from the copper with strips of platinum or of tantalum. The wires were mounted variously by clamping the ends between platinum strips or by spot welding the ends to platinum or tantalum strips.

RESULTS OF MEASUREMENTS

The room-temperature resistivity of thorium is extremely sensitive to small amounts of impurities, especially carbon.⁴ Values greater than $18 \mu\text{ohm-cm}$ have been commonly reported, but the lowest measured value is $12.2 \mu\text{ohm-cm}$ at 23°C .⁵ The thorium wires which were used in the present investigation were found to have a resistivity of $17.4 \mu\text{ohm-cm}$ at 25°C before annealing. The lowest value obtained after annealing was about $16.9 \mu\text{ohm-cm}$ at 25°C .

The curve of the resistance as a function of temperature was reproducible during heating and cooling cycles of the furnace. The apparent resistivity as a function of temperature was calculated from the measured resistance as a function of temperature and the room temperature dimensions. Because of the difficulty of measuring the cross-sectional areas of the fine wires, the accuracy of the resistivity is placed at 1%. These data are listed in Table II.

TABLE II. Electrical resistivity and specific heat of thorium as functions of temperature.

Temperature ($^\circ\text{C}$)	Apparent resistivity ($\mu\text{ohm-cm}$)	Specific heat (cal/mole deg)
25	16.9 _s	6.56
50	18.4 _s	6.63
100	21.4 _s	6.75
150	24.4 _o	6.87
200	27.3 _s	6.99
250	30.3 _o	7.12
300	33.2 _o	7.24
350	36.1 _o	7.36
400	38.8 _s	7.49
450	41.6 _o	7.61
500	44.2 _o	7.73
550	46.7 _s	7.85
600	49.2 _o	7.99
650	51.5 _s	8.13
700	53.8 _o	8.28
750	55.9 _s	8.44
800	58.0 _s	8.62
850	60.0 _s	8.81
900	62.0 _o	9.02
950	63.9 _o	9.26
1000	65.7 _s	9.54

For each sample, the complete set of specific heat data points (about 25 points for each of 10 pulses or 250 points in all) was plotted as a function of temperature, and a smooth curve was fitted graphically to the points. The final results for four samples showed minor discrepancies and these were again smoothed graphically. The results, listed in Table II, are accurate to at least 2% over the entire temperature range.

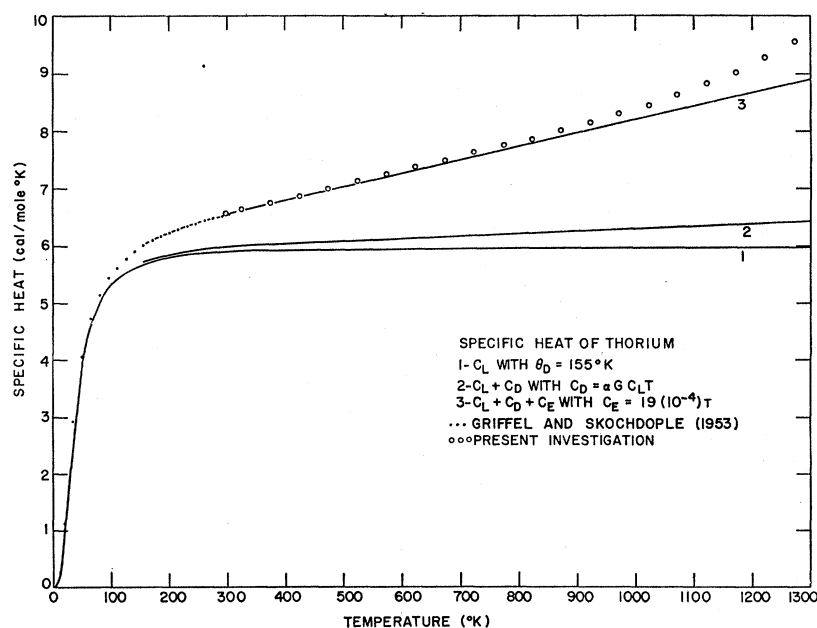
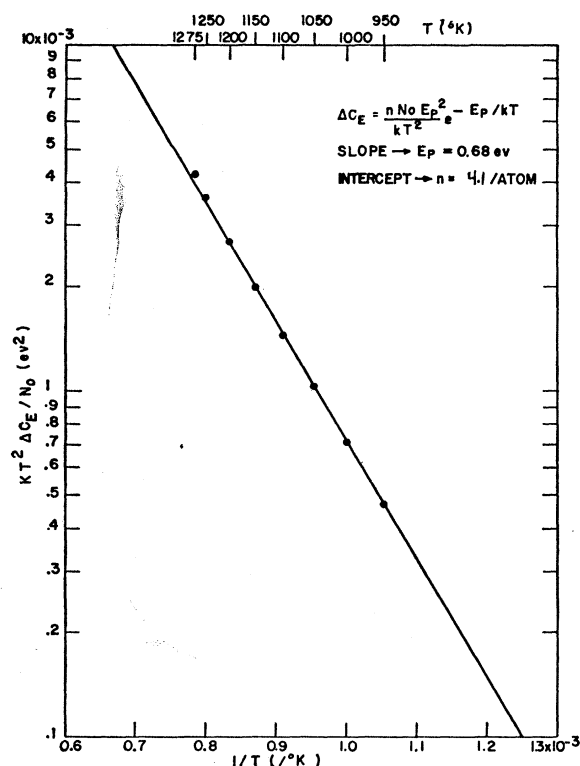


FIG. 1. Theoretical and experimental specific heat curves for thorium.

⁴ J. F. Smith, reference 2, Chap. 10.

⁵ Reference 2, p. 155.

FIG. 2. Treatment of the excess specific heat, ΔC_E , for thorium.

ANALYSIS OF SPECIFIC HEAT

If the interaction between the lattice and electrons in a metal is neglected, the specific heat can be represented by

$$C_P = C_L + C_D + C_E, \quad (1)$$

where C_P is the specific heat at constant pressure, C_L is the lattice specific heat at constant volume, C_D is the specific heat contribution due to the dilatation (thermal expansion) of the crystal, and C_E is the specific heat of the electrons at constant volume.

These contributions have been calculated for α -thorium and the results are shown in Fig. 1. The term C_L was calculated according to the Debye theory, with Debye temperature $\theta_D = 155^\circ\text{K}$. The term C_D was calculated from the Grüneisen formula $C_D = \alpha G C_L T$, where α is the temperature coefficient of volume expansion, G the Grüneisen constant, and T the absolute temperature. The values of α were taken from a curve fitted to the data given by Smith⁴ and the data given by Erfling.⁶ The Grüneisen constant was computed at room temperature from the formula $G = \alpha V / \kappa C_L$, where V is the molar volume and κ the isothermal compressibility. With the aid of Bridgman's⁷ value of $1.85(10^{-12})$ cm²/dyne for κ at 30°C and the room temperature value of $32.4(10^{-6})/^\circ\text{C}$ for α , G was found to be 1.39.

⁶ H. Erfling, Ann. Physik **41**, 467 (1942).

⁷ P. W. Bridgman, *The Physics of High Pressure* (G. Bell and Sons, London, 1949).

A first approximation to the term C_E was calculated from the formula $C_E = \gamma T$ with $\gamma = 19(10^{-4})$ cal/mole $^\circ\text{K}^2$.

The specific heat of thorium has been measured from 1° to 20°K by Smith and Wolcott.⁸ They reported a γ value of $11.2(10^{-4})$ cal/mole $^\circ\text{K}^2$ from their results over the range 1° to 4°K . They also found that the value of θ_D decreased from 170°K at 4°K to a minimum of 138°K at 14°K and then increased as the temperature was further increased. Griffel and Skochdopole⁹ have measured the specific heat of thorium from 18° to 300°K ; their results are shown in Fig. 1. Clusius and Franzosini¹⁰ have analyzed these data in the region 20° to 155°K according to the "intermediate temperature" theory of Clusius and Bühler,¹¹ and found a γ value of $16.4(10^{-4})$ cal/mole $^\circ\text{K}^2$. From 155° to 300°K , however, Clusius and Franzosini found that a γ value of $19(10^{-4})$ cal/mole $^\circ\text{K}^2$ and a θ_D of approximately 155°K gave the best fit to the data of Griffel and Skochdopole. The specific heat of thorium which contained some 6% thorium oxide has been measured from 300° to 1400°C by Jaeger and Veenstra¹²; however, their values are about 10% higher than the results of the present investigation. This discrepancy is probably due to the impurity of the samples used by Jaeger and Veenstra.

The present specific heat data are also shown in Fig. 1. These results are about 0.4% higher than those of Griffel and Skochdopole at room temperature. This discrepancy is within the limit of experimental error of the present investigation, and is small enough to be neglected for purposes of the analysis of the data. Thus, curve 3 not only fits the data of Griffel and Skochdopole from 155° to 300°K , but it also fits the present data quite well up to 550°K .

Above room temperature the calculated C_P does not depend critically upon the choice of θ_D , but is very much affected by the value of γ . It is well known that at high temperatures there should be a specific heat contribution which is proportional to temperature as a result of the anharmonicity of the lattice forces. Since this contribution should be present at temperatures above the Debye temperature, one might suppose that this is the difference between the high-temperature γ value of $19(10^{-4})$ cal/mole $^\circ\text{K}^2$ and the low-temperature γ value of $11.2(10^{-4})$ cal/mole $^\circ\text{K}^2$. However, preliminary calculations which are in progress indicate that such a contribution for a metal should be very small and should be negative. If the anharmonic specific heat is represented by βT , β should be of order $-5(10^{-5})$ cal/mole $^\circ\text{K}^2$ for thorium. At the present time, therefore, no explanation can be offered for the discrepancy

⁸ P. L. Smith and N. M. Wolcott, Suppl. Bull. Intern. Inst. Refrig. **3**, 283 (1955).

⁹ M. Griffel and R. E. Skochdopole, J. Am. Chem. Soc. **75**, 5250 (1953).

¹⁰ K. Clusius and P. Franzosini, Z. Naturforsch. **11a**, 957 (1956).

¹¹ K. Clusius and H. H. Bühler, Z. Naturforsch. **10a**, 930 (1955).

¹² F. M. Jaeger and W. A. Veenstra, Proc. Koninkl. Akad. Wetenschap (Amsterdam) **37**, 327 (1934).

between high- and low-temperature γ values. It should be pointed out that such a discrepancy is quite commonly found in metals.¹³

At high temperatures, the specific heat rises considerably above curve 3. The difference between the measured values and curve 3, the excess specific heat, was found to fit an equation of the standard Schottky type. Friedel¹⁴ has attributed such an excess specific heat to the metallic electrons in the case of uranium. According to Friedel, if there is a very sharp energy level which contains n electron states per atom separated from the Fermi energy by energy E_P (above or below the Fermi energy), then there will be a specific heat contribution due to the thermal excitation of electrons to or from this level. When E_P is large compared to kT , the excess specific heat per mole is given by

$$\Delta C_E = (nN_0 E_P^2 / kT^2) e^{-E_P/kT}, \quad (2)$$

where N_0 is Avogadro's number. A somewhat more general discussion of the approximations involved in arriving at (2) is given in the Appendix.

Figure 2 shows that the excess specific heat for thorium is of the form of (2). A straight line has been fitted to the experimental points, and the slope has given a value of 0.68 eV for E_P and the intercept at $(1/T)=0$ has given a value of 4.1 per atom for n . It should be pointed out that the creation of defects in the lattice should also give rise to a specific heat contribution of the form of (2), but although the value found for E_P is reasonable for a defect creation energy, n is far too large to be reasonable for the number of defects. It is therefore concluded that the observed excess specific heat in thorium is probably an electronic effect, and not due to defect formation.

ACKNOWLEDGMENTS

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APPENDIX: EXCESS ELECTRONIC SPECIFIC HEAT

For a system of electrons which obey the Fermi-Dirac statistics we have

$$n_0 = \int_0^\infty N(E) f dE, \quad \text{the total number of electrons;} \quad (A1)$$

$$U = \int_0^\infty E N(E) f dE, \quad \text{the internal energy of the} \quad (A2)$$

electron system; and

$$f = [e^{(E-\zeta)/kT} + 1]^{-1}, \quad \text{the distribution function;} \quad (A3)$$

¹³ See for example, A. H. Wilson, *Theory of Metals* (Cambridge University Press, New York, 1953), 2nd ed., p. 150.

¹⁴ J. Friedel, *J. Phys. Chem. Solids* **1**, 175 (1956).

where E =electron energy, $N(E)$ =density of electronic states, and ζ =Fermi energy [$\zeta_0 = \zeta(T=0)$]. Since n_0 is strictly constant, we have the condition

$$0 = \frac{\partial n_0}{\partial T} = -\frac{1}{T} \int_0^\infty \frac{\partial f}{\partial E} N(E) [E - \zeta + T\zeta'] dE, \quad (A4)$$

where $\zeta' = d\zeta/dT$. With the aid of (A4) the specific heat at constant volume can be written

$$C = \frac{\partial U}{\partial T} = -\frac{1}{T} \int_0^\infty \frac{\partial f}{\partial E} N(E) [E - \zeta + T\zeta']^2 dE. \quad (A5)$$

To represent the model of a very sharp electron energy level located at energy E_a , where $|E_a - \zeta_0| = E_P$, we write $N(E) = N_1(E) + n\delta(E - E_a)$, where $N_1(E)$ is an analytic function of E for energies within a few kT of ζ_0 , n is the number of electron states in the level at energy E_a and $\delta(E - E_a)$ is a δ function. We consider the limit $kT/\zeta \ll 1$. With the aid of (A1), $\zeta(T)$ is found to be

$$\zeta - \zeta_0 = -\frac{n}{N_1(\zeta_0)} g(E_a) - \frac{\pi^2 (kT)^2}{6 N_1(\zeta_0)} \left[\frac{dN_1(E)}{dE} \right]_{E=\zeta} - \dots, \quad (A6)$$

where $g(E_a) = f(E_a)$, $E_a > \zeta_0$; $g(E_a) = f(E_a) - 1$, $E_a < \zeta_0$. The entire effect of the energy level at E_a is contained in the first term on the right of (A6); the remaining terms form the usual power series in T^2 . Note that $\zeta' \rightarrow 0$ as $T \rightarrow 0$, so that if T is small enough, $\zeta \approx \zeta_0$.

We consider finally the limit $E_P/kT \gg 1$ and investigate the condition that $|E_a - \zeta|$ can be replaced to good approximation by $E_P = |E_a - \zeta_0|$; this condition is $|E_a - \zeta| \gg |\zeta - \zeta_0|$. If $N_1(E)$ is well behaved, the contribution of the power series in T^2 to $(\zeta - \zeta_0)$ is small compared to ζ_0 or compared to E_P . We then obtain the condition $|E_a - \zeta| \gg [n/N_1(\zeta_0)] g(E_a)$, or approximately

$$E_P e^{E_P/kT} \gg n/N_1(\zeta_0). \quad (A7)$$

For the present model, the specific heat is found from (A5) to be

$$C = C_1 + \Delta C,$$

$$C_1 = -\frac{1}{T} \int_0^\infty \frac{\partial f}{\partial E} N_1(E) [E - \zeta + T\zeta']^2 dE,$$

$$\Delta C = -\frac{n}{T} \left[\frac{\partial f}{\partial E} \right]_{E=E_a} [E_a - \zeta + T\zeta']^2.$$

Under the approximations listed above, these ex-

pressions become

$$C_1 \approx \frac{\pi^2}{3} k^2 T N_1(\xi_0) \times \left\{ 1 - \frac{n}{N_1(\xi_0)} e^{-E_p/kT} \left[\frac{1}{N_1} \frac{dN_1}{dE} \right]_{E=\xi_0} \right\} + O(T^3) + \dots, \quad (\text{A8})$$

$$\Delta C \approx (nE_p^2/kT^2) e^{-E_p/kT}. \quad (\text{A9})$$

C_1 is expressed as usual in an odd-power series in T , but the coefficients are modified by the addition of terms in $e^{-E_p/kT}$. These extra terms will in general be small compared to the usual terms, so that the effect of the electron energy level at E_a upon C_1 will be negligible. In the expression for ΔC , $|E_a - \xi + T\xi'|$ has been replaced by E_p ; this approximation is of the same order as the replacement of $|E_a - \xi|$ by E_p .

Critical Fields of Superconducting Tin, Indium, and Tantalum*

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Precise ballistic-induction measurements of the critical field curves of tin, indium, and tantalum are reported. The measurements were made to provide more accurate data on the deviation of the critical field curves from the parabolic law. The resulting deviation functions are generally within the range of uncertainty of earlier measurements. The main experimental error in the observed deviation now arises from uncertainty in the extrapolation of the measurements to 0°K from the present lower limit of 1.1°K. Measurements at lower temperatures which will eliminate some of this uncertainty are to be desired.

I. INTRODUCTION

ALL pure superconductors have critical field curves which approximate the parabolic relation, $H_c = H_0[1 - (T/T_c)^2]$. Experimental measurements have shown¹ (and theory has predicted²) deviations from this relation. Observations on lead³ and mercury⁴ have been of particular interest in showing deviations of the opposite sense from those found in the majority of superconductors and predicted by theory. The present work reports critical field measurements on superconducting elements all of which deviate from the parabolic H_c relation in the sense predicted by the BCS theory. These measurements achieve a significant improvement in accuracy over earlier results and also show differences in detail among the several elements.

II. EXPERIMENTAL

The two tin specimens measured differed both in purity and preparation. Sn-1 was reagent grade material (99.97%) from Allied Chemical Company.

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¹ See, for example, M. A. Biondi, A. T. Forrester, M. P. Garfunkel, and C. B. Satterthwaite, *Revs. Modern Phys.* **30**, 1109 (1958).

² J. Bardeen, L. N. Cooper, and J. R. Schrieffer, *Phys. Rev.* **108**, 1175 (1957).

³ D. L. Decker, D. E. Mapother, and R. W. Shaw, *Phys. Rev.* **112**, 1888 (1958).

⁴ D. K. Finnemore, D. E. Mapother, and R. W. Shaw, *Phys. Rev.* **118**, 127 (1960).

It was cast and grown as a nearly single crystal in a graphite coated Pyrex tube and in a vacuum of 10^{-5} mm Hg. The tube was later etched off in hydrofluoric acid. Sn-2 was formed from 99.9998% pure tin from Vulcan Detinning Company. It was vacuum cast and grown in a carefully cleaned and outgassed crucible of pure graphite. The outside of the crucible was slotted to allow it to be broken away from the specimen with a minimum of damage. This specimen was then vacuum annealed near the melting point to minimize the effects of strains introduced during the removal of the crucible.

Two indium specimens were also prepared, both from high purity indium supplied by the Indium Corporation of America. Sample In-0-8 was prepared in the same manner as Sn-1 and the preparation of In-2 and Sn-2 similarly corresponded. Semiquantitative spectrographic analysis by the Detroit Testing Laboratory indicated a total metallic impurity of 0.03% in In-0-8 and 0.05% in In-2. This difference is thought to result from a higher initial purity of the slug used in forming In-0-8 rather than the difference in fabrication techniques. The dimensions of the tin and indium specimens were approximately the same: cylinders of diameter 0.070 in. and length 1.5 in.

The tantalum was kindly provided by Dr. J. I. Budnick who reported a resistance ratio for the material between 20°C and 0°K of 1400. It was in the form of 0.010-in. diameter wire which was cut with a razor blade into approximately 1.5-in. lengths. No doubt some strained regions with altered super-