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Heat Capacity of Alpha Uranium from 1.7 to 25°K*

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The heat capacity of high-purity alpha uranium has been determined from 1.7 to 23°K and smoothed into previous data at 25°K. These heat capacities are significantly lower than the values reported by other investigators. The values for γ, the coefficient of the electronic contribution to heat capacity, and for the Debye Θ at 0°K, were determined to be 9.88 ± 0.05 mJ deg^{-2} (g at.)$^{-1}$ and 222 ± 2°K, respectively. The C_p-C_v correction was evaluated between 15 and 80°K to show the effect of the anomalous expansive and compressive behavior of uranium between 20 and 45°K on the lattice heat capacity. Tabular values of C_p, C_v, Θ, and other thermodynamic quantities are presented up to 25°K.

INTRODUCTION

IN a previous paper from this laboratory[1] the heat capacity and other thermodynamic properties of high-purity uranium between 5 and 350°K were reported. Those results were obtained with an adiabatic calorimeter employing a platinum resistance thermometer. Mainly because of the decreased sensitivity of the thermometer at the lower end of the temperature range, the estimated probable error in the heat capacity was 5% at 5°K and 1% at 14°K, although it was only 0.2% at temperatures of 30°K or more. The poor accuracy at the lowest temperatures and the lower temperature limit of 5°K made it impossible to estimate γ and Θ_0 in Eq. (1),

$$C_v=\gamma T+(12R\pi^4/5\Theta_0^3)T^3, \qquad (1)$$

which should be valid at sufficiently low temperatures (but not so low that the hyperfine contribution of U^{235} is appreciable nor so low that the uranium becomes superconducting).

A number of other investigators[2–6] have measured the heat capacity of uranium below 25°K. The measurements of Jones *et al.*[2] and of Clusius and Piesbergen[4] extended down to 15° and 10°K, respectively. These temperatures are not sufficiently low for estimating γ and Θ_0. Both γ and Θ_0 were obtained by Smith and Wolcott[3] and by Goodman *et al.*,[5] and γ was reported by Dempesy *et al.*[6] However, from 5 to 20°K the heat capacities obtained by Smith and Wolcott are generally higher than those obtained by Flotow and Lohr.[1] They agree at 5°K, are 19% higher at 10°K, are 6% higher at 15°K, and are 4% higher at 20°K, relative to the results of Flotow and Lohr. At 4°K the heat capacity calculated from the γ and Θ_0 reported by Goodman *et al.* is 4% lower than that calculated from the values reported by Smith and Wolcott. The γ determined by Dempesy *et al.*[6] from measurements below 0.75°K is about 11% higher than the average of the other γ values.[3,5]

In view of these somewhat discordant results it seemed worthwhile for the present authors to remeasure the heat capacity of uranium in a different apparatus, which is capable of more accurate measurements down to lower temperatures. This paper presents the results for a sample of high-purity alpha uranium from 1.7 to 23°K. Calculations of γ, of the Debye Θ at various temperatures, and of some thermodynamic properties of uranium are given.

EXPERIMENTAL

Uranium Sample

The sample consisted of 11 uranium rods which were 0.32 cm in diameter and 4.4 cm long. The metal was the high-purity, polycrystalline, alpha uranium produced by the metallurgical division of this laboratory[7] by the electrolysis of UF_4 in a fused mixture of KCl and LiCl, followed by vacuum casting into billets and swaging of the billets into rods. Spectrographic analysis showed 2 ppm Mg and 15 ppm Si; chemical analysis for C, N, and O gave 15, <10, and 12 ppm, respectively. The following impurities were looked for but were not detected (within the indicated limits of spectroscopic sensitivities, in ppm): Ag, 1; Al, 5; As, 10; B, 0.1; Be, 0.5; Bi, 1; Ca, 20; Co, 5; Cr, 1; Cu, 1; Fe, 2; K, 50; Li, 1; Mn, 1; Mo, 20; Na, 10; Ni, 5; P, 50; Pb, 1; Sn, 5; Ti, 50; Zr, 50. Isotopic analyses showed that the uranium sample was somewhat depleted in U^{234} and U^{235} compared with the natural isotopic abundances. The mass spectrometer gave 99.599 at.% U^{238}, 0.398 ± 0.003 at.% U^{235}, and 0.0022 ± 0.0002 at.% U^{234}. Alpha pulse analysis gave 0.38 ± 0.07 at.% U^{235} and 0.00213 ± 0.00005 at.% U^{234}.

Surface oxide was removed with dilute HNO_3, and the rods were annealed *in vacuo* at 600°C for 2 h. At the end

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* Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[1] H. E. Flotow and H. R. Lohr, J. Phys. Chem. **64**, 904 (1960).

[2] W. M. Jones, J. Gordon, and E. A. Long, J. Chem. Phys. **20**, 695 (1952).

[3] P. L. Smith and N. M. Wolcott, Bull. Inst. Intern. Froid, Annexe, 283 (1955).

[4] K. Clusius and U. Piesbergen, Helv. Phys. Acta **31**, 302 (1958).

[5] B. B. Goodman, J. Hillairet, J. J. Veyssié, and L. Weil, in *Proceedings of the Seventh International Conference on Low Temperature Physics, Toronto, 1960* edited by G. M. Graham and A. C. Hollis (University of Toronto Press, Toronto, Canada, 1961), pp. 350–356.

[6] C. W. Dempesy, J. E. Gordon, and R. H. Romer, Phys. Rev. Letters **11**, 547 (1963).

[7] B. Blumenthal and R. A. Noland, *Progress in Nuclear Energy* (Pergamon Press, Inc., New York, 1956), Series V, Vol. 1, pp. 62–80.

of this time the pressure was 1×10^{-6} mm Hg, and the sample was then cooled to room temperature *in situ*. The sample had a mass of 74.685 g. It was sealed in the calorimeter with 6.65×10^{-7} moles of He^4 to facilitate rapid thermal equilibrium. This amount of He^4 gave a pressure of less than 3×10^{-3} mm Hg in the calorimeter at 1.2°K, and since the pressure was much less than the vapor pressure of He^4 at all temperatures down to the lowest reached in these experiments (about 1.4°K) no condensation could occur. Because of the low pressure and because of the small specific surface area of the sample it is believed that adsorption of the He^4 in the calorimeter was completely negligible.

Cryostat and Calorimeter

The cryostat consisted of two coaxial glass Dewars, the inner one for liquid helium and the outer one for liquid nitrogen. The essential features of the apparatus have been described elsewhere.[8] The calorimeter and its support have been modified as depicted in Fig. 1, and the size of the calorimeter has been reduced (to an internal volume of 6.1 cm³) to permit the study of smaller samples. Three stainless steel tubes (0.5 mm i.d., 0.06 mm wall), only one of which is shown in Fig. 1, extend from an isothermal guard block (not shown) to small copper support arms. One of the tubes leads from the vapor pressure volume (2.6 cm³) in the top of the calorimeter support to mercury and oil manometers outside the cryostat, so that vapor pressure measurements can be made to verify the calibration of the germanium resistance thermometer. The other two tubes are for support only. Three spring-loaded nylon cords lead from the eyelets on the bottom of the calorimeter to the surrounding vacuum jacket. The lower part of the copper support is a bifilarly threaded tube with an 1170-Ω heater of Evanohm wire, which is cemented in place with GE 7031 varnish. The gold-plated copper calorimeter is slipped over the heater tube and clamped in position as shown in Fig. 1. A small amount of Apiezon T grease is used for thermal contact between the heater tube and the re-entrant well of the calorimeter and for thermal contact of the clamp with the support and the calorimeter.

The contacting cone on the bottom of the calorimeter is not used in this apparatus but is used for a cooling contact in another apparatus for heat-capacity measurements from 5 to 350°K.[9,10] The contacting cones near the top of the support are used to cool below 77°K, and no helium exchange gas is used in cooling the calorimeter when liquid helium is in the Dewar.

The electrical leads from the calorimeter support to the isothermal guard block are about 10 cm long and are double silk covered constantan, 0.13 mm in diam for the two current leads to the heater and 0.08 mm in diam for the other leads. The wires are wound twice around the top of the vapor pressure volume, to which they are cemented with GE 7031 varnish, and twice around the isothermal guard block, to which they are affixed with baked Formvar varnish. One potential lead to the heater branches from a current lead just before it leaves the calorimeter support, and the other branch point is located where the other current lead reaches the isothermal guard block. This method of connecting the potential leads is used in order to compensate automatically for the heat developed in the current leads, half of which goes to the calorimeter and half to the isothermal guard block.

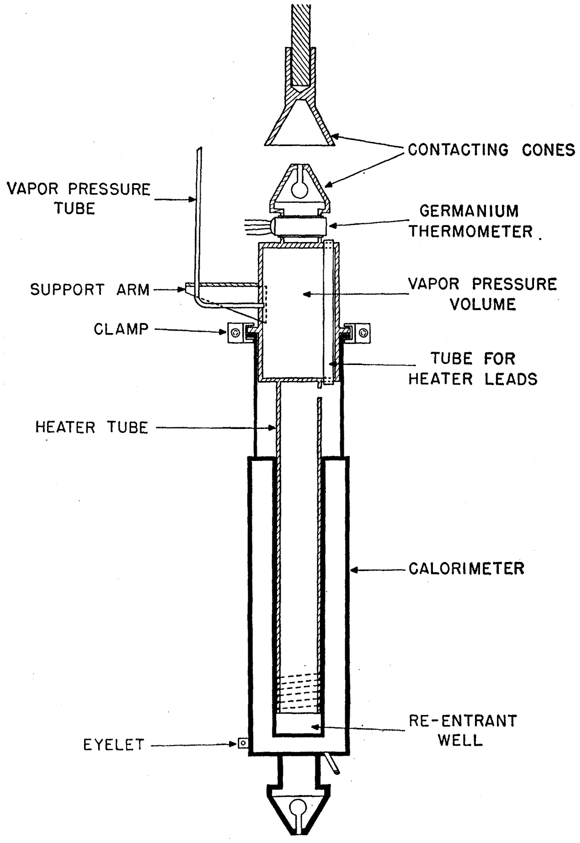

FIG. 1. Calorimeter and calorimeter support used for measurement of the heat capacity of alpha uranium. The calorimeter support includes a contacting cone, a germanium resistance thermometer, a vapor-pressure volume, and a heater. It is suspended by three small, thin-walled stainless-steel tubes from an isothermal guard block (not shown). The calorimeter is clamped to the support and is brought into thermal contact with it by means of a weighed amount of Apiezon T grease. Spring-loaded nylon cords are attached to three eyelets at the bottom of the calorimeter and to the surrounding vacuum jacket (not shown). The cone on the bottom of the calorimeter is for cooling in another apparatus.

Thermometry

The calorimeter thermometer (laboratory designation Ge No. 3) is a four-lead, platinum-encapsulated ger-

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[8] J. H. Burns, D. W. Osborne, and E. F. Westrum, Jr., J. Chem. Phys. 33, 387 (1960).

[9] E. F. Westrum, Jr., J. B. Hatcher, and D. W. Osborne, J. Chem. Phys. 21, 419 (1953).

[10] D. W. Osborne and E. F. Westrum, Jr., J. Chem. Phys. 21, 1884 (1953).

manium resistor (Radiation Research Corporation, type CG-1). It is located in a copper sleeve in the neck of the contacting cone of the calorimeter support, as shown in Fig. 1, with Apiezon T grease for thermal contact between the capsule and the sleeve. The platinum capsule as received contained an atmosphere of He^4; however, in order to avoid a bump in the heat-capacity curve due to the evaporation of condensed He^4 near 2°K the He^4 was allowed to escape through a small hole drilled in the bottom of the capsule, which was subsequently soldered shut in air. Excellent thermal contact between the germanium crystal and the calorimeter support is achieved through the two 0.25-mm diam platinum leads which are used to supply the measuring current. These leads are connected to the current supply by means of manganin wires, and in addition they are soldered to 0.25-mm diam Formvar insulated copper wires, which are wound two times around the top of the support and held in thermal contact with the support by GE 7031 varnish.

The calibration of the germanium resistance thermometer will be described elsewhere.[11] In brief, it was calibrated against the vapor pressure of n-H_2 near the boiling point, against a He^4 gas thermometer at many temperatures between 4.2 and 25°K, against the vapor pressure of liquid He^4 between 2.1 and 4.2°K,[12] and against the vapor pressure of liquid He^3 between 0.85 and 2.3°K.[13] The boiling point of n-H_2 was taken to be 20.384°K.[14]

The resistance of the germanium thermometer was measured with a Rubicon Model 2773 double six-dial potentiometer and a Rubicon Model 3550 photoelectric galvanometer. The thermometer current was reversed at intervals to permit evaluation of the thermal emf in the potential leads. With the thermometer currents used in the present experiments (2.8 to 38 μA, depending on the temperature) the temperature sensitivity was approximately 1×10^{-5} deg at 1.6°K, 2×10^{-5} deg at 4.2°K, 6×10^{-5} deg at 12°K, and 4×10^{-5} deg at 23°K.

Operation of the Calorimeter

The calorimeter was cooled from room temperature to 77°K by means of liquid nitrogen, with nitrogen exchange gas in the vacuum jacket. The exchange gas was evacuated at 77°K, and the calorimeter was further cooled to 1.4°K by means of the contacting cones and liquid helium. Upon decontacting the cones the calorimeter warmed rapidly because of the radioactive decay of the uranium, and as a consequence it was not possible to make measurements on uranium below 1.6°K with the present apparatus. Although the sample was depleted in U^{234} and U^{235}, a calculation from the isotopic analysis shows that the radioactive heating is 3.0×10^{-6} W (g at.)$^{-1}$, of which 67% is due to U^{238}, 2% due to U^{235}, and 31% due to U^{234}. This energy release caused the calorimeter to warm about 9.5×10^{-3} deg min^{-1} at 1.6°K, 2.7×10^{-3} deg min^{-1} at 4.2°K, 3.8×10^{-4} deg min^{-1} at 10°K, and 4.7×10^{-5} deg min^{-1} at 20°K, when the isothermal guard block was at the same temperature as the calorimeter.

During each heat-capacity determination the temperature of the isothermal guard block was maintained constant to better than ±0.001°K by means of a carbon resistance thermometer, a heater on the guard block, and an automatic control circuit. The germanium resistance thermometer was followed for a period of 10 min or more, then the calorimeter was heated electrically for 3 min, at a rate such that the temperature rise would be about $0.1T$, and finally the thermometer was observed for another 10 min or so. Whenever possible the temperature of the isothermal guard block was chosen so that the drift rates of the calorimeter before and after the heating period would be approximately equal in magnitude and opposite in sign. Owing to the radioactive heating this could not be achieved below 2.5°K.

The heat supplied electrically was measured with a White double potentiometer and an accurate timer. The uncertainty in this quantity was at most 0.05%.

Correction for Heat Interchange

For most of the heat-capacity determinations, the temperature drifts before and after the heating period were relatively small and essentially constant. In such cases the correction for heat interchange between the calorimeter and its surroundings and for any constant influx of heat (e.g., from the thermometer current as well as from radioactive decay) could be made by the usual method of extrapolating the temperatures observed in the fore period and in the after period to the middle of the heating period. That is, the mean heat capacity $\bar{C}$ at the mean temperature $\bar{T}$ was calculated from

$$C=Q/(T_2'-T_1'), \tag{2}$$

where Q is the heat supplied electrically, and T_1' and T_2' are the temperatures obtained by linear extrapolation to the middle of the heating period. The mean of T_1' and T_2' was taken as $\bar{T}$, for this can be shown to be preferable to using the mean of the temperatures at the start and end of the heating period when Eq. (2) is employed.

For the determinations at the lowest temperatures the drifts changed appreciably during the time of observation, and therefore a computer was used to obtain a least-squares fit of the temperature-time data with exponential equations of the form

$$T=a+b\exp(-\lambda t), \tag{3}$$

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[11] D. W. Osborne, H. E. Flotow, and F. Schreiner, Rev. Sci. Instr. (to be published).

[12] F. G. Brickwedde, H. van Dijk, M. Durieux, J. R. Clement, and J. K. Logan, J. Res. Natl. Bur. Std. (U. S.) **64A**, 1 (1960).

[13] R. H. Sherman, S. G. Sydoriak, and T. R. Roberts, J. Res. Natl. Bur. Std. (U. S.) **68A**, 579 (1964).

[14] F. G. Brickwedde, Phys. Today **16**, No. 5, 24 (1963).

where a, b, and λ are constants, and λ is positive. These equations were used to calculate the temperatures T_1 and T_2 at the start and end of the heating period and the drifts $(dT/dt)_1$ and $(dT/dt)_2$ at the same times. The mean heat capacity was then calculated from Eq. (2) with the following values for T_1' and T_2':

$$T_1'=T_1+(dT/dt)_1 t_h/2\,, \tag{4}$$

$$T_2'=T_2-(dT/dt)_2 t_h/2\,, \tag{5}$$

where t_h is the heating interval. The main assumptions in this method of calculation are that Newton's law of cooling holds for the heat interchange and that the temperature rises linearly with time during the heating period.

A practically equivalent method of calculation is to use the exponential fits and preliminary values for the heat capacity C_1 at T_1 and C_2 at T_2 in the relation

$$\bar{C}=\{Q+[C_1(dT/dt)_1+C_2(dT/dt)_2]t_h/2\}/(T_2-T_1)\,. \tag{6}$$

When Eq. (6) was used, $\bar{T}$ was taken to be the mean of T_1 and T_2.

All three methods of calculation of the present data gave the same answer within 0.1%, after making allowance for the slight differences in $\bar{T}$.

RESULTS AND DISCUSSION

Heat-Capacity Results

The experimental heat-capacity points for alpha uranium metal are given in Table I. The heat capacity of the empty calorimeter and its support, which was about 12% of the total heat capacity at 1.7°K and about 20% of the total above 6°K, was determined in a separate series of experiments and was subtracted from the total. The amount of Apiezon T grease was the same within 0.1 mg in the measurements on the empty and on the full calorimeter. A small correction has been made for curvature, equal to $-(d^2C_p/dT^2)(\Delta T)^2/24$, and also a correction has been made for the heat capacity of the small amount of He^4 exchange gas in the calorimeter.

TABLE I. Experimental values of the heat capacity of alpha-uranium metal. At. wt=238.04.

$\bar{T}$ (°K)	C_p [mJ deg^{-1} (g at.)$^{-1}$]	$\bar{T}$ (°K)	C_p [mJ deg^{-1} (g at.)$^{-1}$]
Series I		6.827	133.2
1.702	17.56	7.504	165.6
1.949	20.56	8.257	210.8
2.129	22.78	9.091	274.4
2.405	26.34	10.020	364.9
2.661	29.80	11.025	489.0
2.920	33.50	12.099	654.8
3.206	37.80	13.267	878.2
3.518	42.81	Series III	
3.849	48.54	12.924	807.5
4.215	55.42	14.185	1086
4.639	64.30	15.480	1429
Series II		16.950	1887
4.649	64.82	18.556	2470
5.128	76.26	20.308	3197
5.648	90.60	22.228	4094
6.208	108.9		

TABLE II. Smooth values of the heat capacities and Debye Θ of alpha-uranium metal. In calculating Θ, the coefficient γ was taken to be 9.88_2 mJ deg^{-2} (g at.)$^{-1}$.

T (°K)	C_p [mJ deg^{-1} (g at.)$^{-1}$]	C_v [mJ deg^{-1} (g at.)$^{-1}$]	Θ (°K)
0	0	0	(221.9)
1	(10.06)	(10.06)	(221.8)
2	21.20	21.20	221.3
3	34.54	34.54	220.5
4	51.34	51.34	219.2
5	73.12	73.12	217.2
6	101.9	101.9	214.4
7	140.8	140.8	210.4
8	194.5	194.5	205.1
9	267.0	267.0	199.6
10	362.6	362.6	194.6
11	485.1	485.1	190.1
12	637.6	637.6	186.3
13	822.6	822.6	183.1
14	1042	1042	180.5
15	1295	1294	178.4
16	1583	1581	176.7
17	1905	1900	175.4
18	2260	2249	174.3
19	2646	2626	173.4
20	3062	3030	172.6
21	3505	3456	171.9
22	3973	3898	171.5
23	4462	4351	171.1
24	4969	4819	170.8
25	5489	5306	170.4

The accuracy of the heat-capacity measurements is almost entirely dependent on the accuracy with which the temperature rise and the correction for heat interchange can be determined, since the uncertainty in the heat supplied electrically is at most 0.05%. For almost all of the present measurements the precision (probable error) of the corrected temperature rise is estimated to be 0.2%. However, because of uncertainties in the temperature scale the estimated probable error in the heat capacities is 0.4% for all of the points above 2°K. At the lowest mean temperature, 1.7°K, the accuracy may be only 1%, because of the large temperature drift caused by the radioactive decay. The estimate of 0.4% probable error for the heat capacities determined in this apparatus is reinforced by the excellent agreement between our results on 99.99+% copper[11] and those obtained by Martin[15] and by Ahlers.[16]

Values of the heat capacity C_p at 1°K intervals up to 25°K are given in Table II. These were obtained from smooth curves through the present experimental points and through the earlier[1] experimental points above 20°K. The deviation of the smooth curve reported by Flotow and Lohr[1] from the present curve is negligible at 25°K, −0.7% at 20°K, −0.5% at 15°K, −3.1% at 10°K, and +14.4% at 5°K. The agreement is within the

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[15] D. L. Martin, Phys. Rev. **141**, 576 (1966).

[16] G. Ahlers, Rev. Sci. Instr. **37**, 477 (1966).

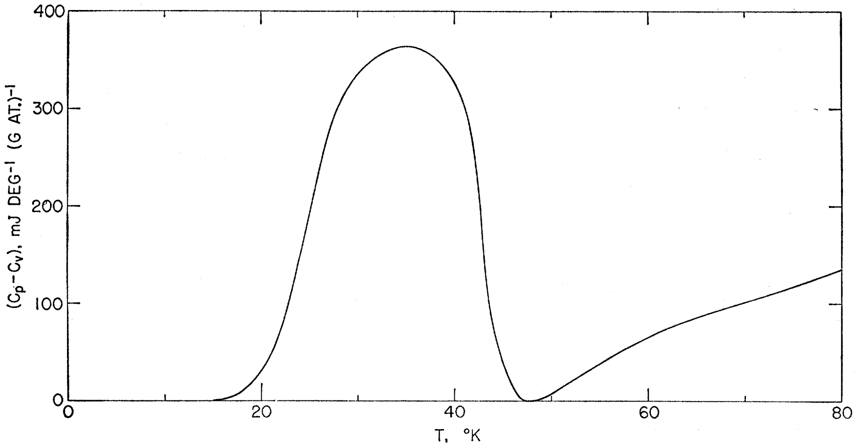

FIG. 2. $C_p - C_v$ for alpha-uranium metal.

sum of the estimated experimental errors, except at 5°K, but the present values are considered to be much more accurate than the earlier ones below 20°K and of comparable accuracy from 20 to 23°K.

The present C_p values are appreciably lower than those obtained by Jones *et al.*[2] from 15 to 25°K, by Smith and Wolcott[3] from 1.2 to 20°K, by Clusius and Piesbergen[4] from 10 to 18°K, and by Goodman *et al.*[5] from 1 to 4°K. In view of our concordant results on 99.99+% copper as mentioned above, it seems unlikely that the differences are due to some unsuspected error in our temperature scale or measuring technique. The differences are much too large to be explained by varying strains developed in the polycrystalline samples on cooling through the region of anomalous expansivity near 43°K.[17] Instead we believe that the differences are in some cases due to the use of less accurate measuring techniques by the other observers and in some cases due to the use of less pure samples of uranium. In most cases, unfortunately, adequate details concerning the measuring techniques and the purity and physical state of the samples are lacking.

$C_p - C_v$ Correction

The correction of C_p to C_v was calculated from the thermodynamic relation

$$C_p/C_v = 1 + (\alpha_v^2 VT)/(\beta_v C_p)\,, \qquad (7)$$

where α_v is the volume coefficient of thermal expansion, V is the molal volume, and β_v is the volume coefficient of adiabatic compressibility. The molal volume of uranium goes through a minimum near 43°K,[17] and therefore α_v passes through zero near this temperature and becomes negative below it, eventually approaching zero at lower temperatures in accordance with the third law of thermodynamics. Lloyd and Barrett[18] have evaluated the average α_v between 20 and 40°K, but for the purpose of correcting C_p to C_v a more detailed analysis was required. Large plots of the lattice constants a, b, and c of the orthorhombic unit cell versus temperature were made from the data shown in Fig. 1 of the paper by Barrett, Mueller, and Hitterman,[17,19] and smooth curves were drawn through the points. From readings of a, b, and c at close temperature intervals a large plot of the volume of the unit cell versus temperature, an enlargement of Fig. 2 in the aforementioned paper,[17] was made, and a smooth curve was drawn. This curve was differentiated numerically by making readings at intervals of 2.5°K and calculating

$$\alpha_v = (\Delta V/\Delta T)/V\,. \qquad (8)$$

A plot of these values of α_v, plots of β_v from the data of Fisher,[20,21] our plot of the volume of the unit cell, and our C_p curve were then used to calculate C_p/C_v from Eq. (7). Although the data on β_v do not extend below 23°K, β_v is not a strong function of temperature and could, therefore, be extrapolated with sufficient accuracy for the $C_p - C_v$ correction to 15°K, where α_v becomes negligible. The resultant $C_p - C_v$ correction is shown in Fig. 2, and this difference has been subtracted from the C_p values in Table II to obtain the tabulated values of C_v.

γ and Θ

The usual method of calculating γ and Θ_0 is to fit Eq. (1) to the heat-capacity data up to 4.2°K, either by least squares or by means of a plot of C_v/T versus T^2. Application of this method to the present data gives $\gamma = 9.83$ mJ deg^{-2} (g at.)$^{-1}$ and $\Theta_0 = 217.6$°K.

However, a plot of Θ for the experimental points above 4.2°K (see Fig. 3), calculated by subtracting γT from each C_v and fitting each residual with a Debye heat-capacity function, shows that Θ for uranium changes rapidly with temperature. It seems unlikely,

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[17] C. S. Barrett, M. H. Mueller, and R. L. Hitterman, Phys. Rev. **129**, 625 (1963).

[18] L. T. Lloyd and C. S. Barrett, J. Nucl. Mater. **18**, 55 (1966).

[19] A copy of the original data was obtained through the courtesy of L. T. Lloyd.

[20] E. S. Fisher, J. Nucl. Mater. **18**, 39 (1966).

[21] E. S. Fisher (private communication).

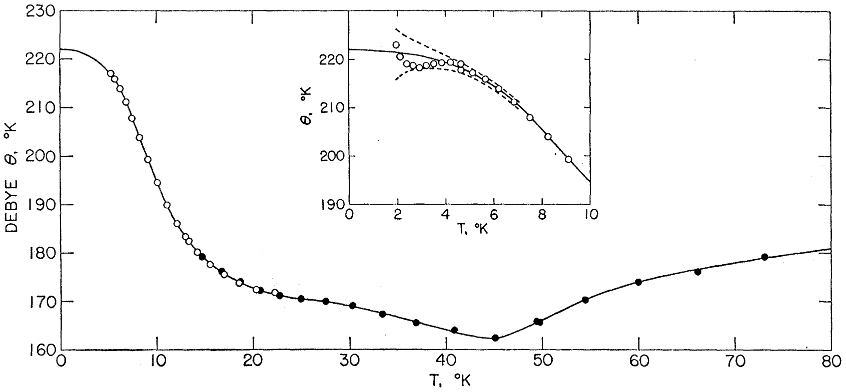

FIG. 3. Debye Θ for alpha-uranium metal as a function of temperature. The experimental C_p measurements were corrected for the difference between C_p and C_v and for the electronic contribution, $9.882T$ mJ deg^{-1} (g at.)$^{-1}$. The dashed curves show the effect of ±0.5% error in C_p. ○: present work; ●: Flotow and Lohr, Ref. 1.

therefore, that Θ is constant from 0 to 4.2°K. To allow for a change of Θ with temperature the experimental data between 1.7 and 9.1°K were fitted with a power series of the form

$$C_v = \sum_{i=1}^{n} A_i T^{2i-1} \qquad (9)$$

with $n=4$. Then γ equals A_1, and the Debye Θ at 0°K is given by

$$\Theta_0 = (12R\pi^4/5A_2)^{1/3}. \qquad (10)$$

The values obtained by this method were $\gamma = 9.88_2 \pm 0.05$ mJ deg^{-2} (g at.)$^{-1}$ and $\Theta_0 = 221.9 \pm 2$°K. Almost identical values were obtained by fitting the data from 1.7 to 6.2°K to Eq. (9) with $n=3$.

A comparison of γ and Θ_0 obtained calorimetrically by various investigators is given in Table III. A value of Θ_0 for α-uranium based on single-crystal moduli at sufficiently low temperatures is not available for comparison at the present time. However, recent measurements on ultrasonic wave velocities extending to 4°K are expected to yield all nine principal elastic moduli, and a value of Θ_0 will be calculated from these results.[21]

Values of the Debye Θ calculated from the experimental points determined in the present investigation and in previous work above 14°K at this laboratory[1] are shown in Fig. 3. The experimental C_p results were corrected to C_v by means of the plot shown in Fig. 2, the electronic contribution γT was subtracted, and the remainder (i.e., the lattice heat capacity at constant volume) was used to calculate the Debye Θ. The value of γ used in the calculations was 9.88_2 mJ deg^{-2} (g at.)$^{-1}$.

TABLE III. Comparison of values of γ and Θ_0 obtained calorimetrically for alpha uranium. Units are mJ deg^{-2} (g at.)$^{-1}$ for γ and °K for Θ_0.

Authors	γ	Θ_0
Smith and Wolcott[a]	10.9	200
Goodman *et al.*[b]	10.6 ±0.2	206±5
Dempesy *et al.*[c]	12.1 ±0.3	...
Present work	9.88±0.05	222±2

[a] Reference 3. [b] Reference 5. [c] Reference 6.

The solid curve (see insert, Fig. 3) up to 7°K is from the fit according to Eq. (9) with $n=4$, and above 7°K it was drawn through the experimental points.

It is interesting to note that a minimum in Θ occurs near 45°K. As pointed out by Fisher and McSkimin,[22] C_p/T has a maximum near this temperature, and several other properties such as the coefficient of thermal expansion,[17,23] the elastic moduli,[22] the temperature dependence of the thermoelectric power,[24] the Hall coefficient,[25] the electrical resistivity divided by T,[22,25] and the thermal conductivity[26] also have anomalies in this temperature region. Another unusual feature of the Θ-versus-T curve is that there is a noticeable "shoulder" between 25 and 30°K.

The unusual shape of the Θ-versus-T curve (Fig. 3) may possibly be caused in part by a variation of γ, which we assumed to be constant. Geballe *et al.*[27] have speculated that the volume increase below 43°K is due to a shift of electrons from the $6d-7sp$ band to the $5f$ band. It is not possible to establish definitely the behavior of γ as a function of temperature from the information available at this time.

TABLE IV. Thermodynamic properties of alpha-uranium metal up to 25°K.

T (°K)	C_p [cal deg^{-1} (g at.)$^{-1}$]	$S°$ [cal deg^{-1} (g at.)$^{-1}$]	$H°-H_0°$ [cal (g at.)$^{-1}$]	$-\left(\frac{G°-H_0°}{T}\right)$ [cal deg^{-1} (g at.)$^{-1}$]
5	0.0175	0.0136	0.0364	0.0064
10	0.0867	0.0413	0.2551	0.0159
15	0.3095	0.1121	1.164	0.0345
20	0.7318	0.2544	3.688	0.0700
25	1.312	0.4779	8.749	0.1279

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Thermodynamic Functions

Several thermodynamic functions for alpha-uranium metal have been calculated by suitable integrations of the smooth C_p curve given in Table I, and these are tabulated in Table IV at 5°K intervals up to 25°K. The latter table is in cal deg^{-1} (g at.)$^{-1}$ with 1 cal$=4.184$ J, for comparison with, and use with, Table II of Flotow and Lohr.[1] The agreement at 25°K is close enough so that the entries above 25°K can be used without change. In particular, at 298.15°K the values are $S^\circ = 12.00\pm0.02$ cal deg^{-1} (g at.)$^{-1}$, $H^\circ - H_0^\circ = 1521\pm3$ cal (g at.)$^{-1}$, and $(G^\circ - H_0^\circ)/T = -6.893$ cal deg^{-1} (g at.)$^{-1}$.

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Model Hamiltonian for Paraelectric Impurities in Alkali Halides*

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Certain dipolar impurities in alkali halides, such as OH$^-$ in KCl, are free to reorient themselves among the six ⟨100⟩ directions of the crystal. A one-parameter model Hamiltonian is introduced to describe the properties of such an impurity in the presence of electric and strain fields. Wave functions and energy levels are calculated for fields along the [100], [110], and [111] directions. The susceptibility is calculated for frequencies much smaller or much larger than τ_1^{-1}, the rate of relaxation to the lattice. Resonance transitions between different energy levels are described and the matrix elements for such transitions are tabulated for several orientations of dc and rf electric fields. A simple theory of line broadening due to inhomogeneous strains is presented and compared with experimental results.

I. INTRODUCTION

There has been a great deal of recent experimental and theoretical interest in the properties of dipolar impurities in alkali halides. Two general types of impurities have been investigated. One type consists of diatomic ions with a permanent dipole moment; examples are OH$^-$ or CN$^-$ substituted for Cl$^-$ in KCl.[1–12] The second type consists of atomic ions, such as Li$^+$ substituted for K$^+$ in KCl.[13–16] In this type the dipole moment arises because the substituted ion can occupy a different position in the unit cell than the ion it replaces. The most interesting property of both types of impurities is that they are free to reorient themselves along several equilibrium directions of the host lattice; and this reorientation can be influenced by external or internal electric fields and strains. This property makes possible the observation of many of the phenomena that were first observed in connection with paramagnetic impurities in insulating crystals; such as a temperature and field-dependent susceptibility, paraelectric cooling, and paraelectric resonance. All of these have now been observed.

In much of the theoretical work on paraelectric impurities and their interactions with each other and with their environment[10–12] it has been possible to treat the impurity as a classical electric dipole pointing along one of several possible equilibrium directions, each de-

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