

DISCUSSION

Four different phenomena in KD_2PO_4 have been explained quantitatively in terms of deuteron intrabond jumps associated with the effective motion of the thermally created DPO_4 and D_3PO_4 groups postulated by Takagi⁷ in his modification of the Slater² theory of KH_2PO_4 -type crystals. These phenomena are the deuteron magnetic resonance splitting below the ferroelectric transition temperature T_c , the deuteron spin-lattice relaxation due to intrabond motion both above and below T_c , the dielectric relaxation at high frequency, and the ferroelectric domain-wall mobility. The mean time T_w found for motion of a deuteron along its bond has been used together with the fractional population of the Takagi groups to calculate the mean time T_0 per effective move of a Takagi group. The result that T_0 is comparable to \hbar/kT implies little correlation between successive deuteron jumps associ-

ated with Takagi group motion. This is in interesting contrast to the intrabond motion in KH_2PO_4 , which Blinc and Svetina¹² describe as correlated proton tunneling associated with effective motion of HPO_4 and H_3PO_4 groups, in order to explain the result of Bjorkstam and Oettel¹¹ that domain-wall mobility in KH_2PO_4 is several orders of magnitude greater than in KD_2PO_4 .

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β -Uranium Hydride: Heat Capacities from 1.4 to 23°K and Some Derived Properties*

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The heat capacity of the metallic, ferromagnetic compound $\beta\text{-UH}_3$ was determined from 1.4 to 23°K. An attempt was made to fit the data at the lowest temperatures by an equation of the form $C_p = \gamma T + AT^3 + BT^{3/2}$, where γT is the contribution of the conduction electrons, AT^3 is the lattice contribution, and $BT^{3/2}$ is the magnetic contribution. The coefficient γ is $29 \pm 1 \text{ mJ } ^\circ\text{K}^{-2} \text{ mole}^{-1}$. Because of uncertainty in the magnetic contribution, no reliable estimate of A or of the Debye Θ could be made. The thermodynamic functions S° , $(H^\circ - H_0^\circ)/T$ and $(G^\circ - H_0^\circ)/T$ were reevaluated as 63.67 ± 0.13 , 30.24 ± 0.06 , and $-33.43 \pm 0.07 \text{ J } (^\circ\text{K mole})^{-1}$, respectively, at 298.15°K.

INTRODUCTION

THE β crystalline modification of UH_3 is the usual phase formed when the hydride is prepared from the elements at 200°C or higher temperatures. The unit cell has cubic symmetry with $a_0 = 6.644 \text{ \AA}$, and contains eight uranium atoms arranged as in α tungsten, i.e., 2U_I at $(0, 0, 0)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and 6U_{II} at $\pm(\frac{1}{4}, 0, \frac{1}{2})$.^{1,2} Each U_{II} atom has two U_{II} atoms as nearest neighbors at 3.322 Å and four U_I atoms as next-nearest neighbors at 3.714 Å; each U_I atom has twelve U_{II} atoms as nearest neighbors at 3.714 Å. According to the neutron-diffraction study reported by Rundle,² the hydrogen atoms in $\beta\text{-UD}_3$ are in the center of a deformed tetrahedron and are equidistant (2.32 Å) from four uranium atoms. It was concluded by Rundle^{1,2} that the $\beta\text{-UD}_3$ structure is held together principally by U-D bonds rather than U-U bonds.

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

¹ R. E. Rundle, *J. Am. Chem. Soc.* **69**, 1719 (1947).

² R. E. Rundle, *J. Am. Chem. Soc.* **73**, 4172 (1951).

The additional information that $\beta\text{-UH}_3$ has an electrical conductivity of the same order of magnitude as that of uranium metal³ and that it is ferromagnetic below about 173°K^{4,5} increases the interest in the low-temperature properties of this unusual compound.

The heat capacities of $\beta\text{-UH}_3$ ⁶ and $\beta\text{-UD}_3$ ⁷ have been previously determined from 5 to 350°K in this laboratory. From these results⁷ the entropy associated with the ferromagnetic transitions of $\beta\text{-UH}_3$ and $\beta\text{-UD}_3$ were found to be 1.19 and 1.18 cal deg⁻¹ mole⁻¹, respectively. These heat capacities were known to be increasingly uncertain below 20°K due to adsorption of He⁴ exchange gas on the samples. In this paper we report

³ F. H. Spedding, A. S. Newton, J. C. Warf, O. Johnson, R. W. Nottorf, I. B. Johns, and A. H. Daane, *Nucleonics* **4**, 4 (1949).

⁴ (a) W. Trzebiatowski, A. Sliwa, and B. Stalinski, *Roczniki Chem.* **26**, 110 (1952); (b) **28**, 12 (1954).

⁵ M. K. Wilkinson, C. G. Shull, and R. E. Rundle, *Phys. Rev.* **99**, 627 (1955).

⁶ H. E. Flotow, H. R. Lohr, B. M. Abraham, and D. W. Osborne, *J. Am. Chem. Soc.* **81**, 3529 (1959).

⁷ B. M. Abraham, D. W. Osborne, H. E. Flotow, and R. B. Marcus, *J. Am. Chem. Soc.* **82**, 1064 (1960).

TABLE I. Experimental heat-capacity values for β -UH₃. Molecular wt.=241.06. The units are mJ, °K, and mole.

\bar{T}	C_p	\bar{T}	C_p
1.469	43.81	5.420	179.3
1.582	47.06	5.925	201.2
1.653	49.33	6.540	230.2
1.764	52.62	7.222	265.4
1.869	55.78	7.952	307.2
1.986	59.35	8.741	359.1
2.070	61.95	9.615	425.3
2.197	65.85	10.530	506.9
2.286	68.60	11.504	609.5
2.431	73.20	12.632	754.4
2.678	80.87	13.861	949.9
2.944	89.30	15.184	1206
3.240	98.83	16.647	1551
3.562	109.5	17.293	1724
3.927	122.0	18.969	2229
4.332	136.5	20.759	2853
4.767	152.9	22.650	3611
4.987	161.7		

more precise measurements of the heat capacity of β -UH₃ from 1.4 to 23°K made in another apparatus without the use of exchange gas in the calorimeter. It was anticipated that the new results could be used to evaluate quantitatively the contributions of the conduction electrons, the lattice, and possibly the ferromagnetism to the measured heat capacities near 0°K.

EXPERIMENTAL

β -UH₃ Sample

The sample was prepared by the reaction of uranium metal with hydrogen at 200°C and then cooled slowly to room temperature in the presence of hydrogen at one atmosphere pressure. The uranium metal was high-purity metal as described in previous publications.^{6,8} Pure hydrogen gas was obtained from another sample of UH₃ by thermal decomposition near 400°C.

The H/U atomic ratio was determined by two methods. A value of H/U = 2.999 ± 0.001 was calculated from the weight of the uranium metal and the weight of the β -UH₃ formed from the reaction with hydrogen. A second average value of H/U = 3.000 ± 0.002 was calculated from the volumes of hydrogen obtained from three weighed samples of the β -UH₃ taken from the calorimeter after the measurements. A spectrochemical analysis for impurities indicated the following impurities in parts per million with a factor of 2 uncertainty: Ag, 1; B, 15; Cr, 10; Cu, 5; Fe, 20; Mg, 8; Mn, 1; Na, 8; Ni, 8; Pb, 1; Sn, 5. The following elements were looked for but not detected within the limits of detection given, in parts per million: Al, 5; As, 20; Be, 0.2; Bi, 1; Ca, 100; Co, 5; K, 50; Li, 5; Mo, 50; P, 100; Sb, 5; Si, 100; Ti, 200; V, 100; Zn, 50. Finally, the sample was found to contain 23 and 30 ppm of oxygen and nitrogen, respectively. The isotopic composition of the uranium in the sample was 99.599 at.

⁸ H. E. Flotow and D. W. Osborne, Phys. Rev. **151**, 564 (1966).

% U²³⁸, 0.398 ± 0.003 at. % U²³⁵, and 0.0022 ± 0.0002 at. % U²³⁴.⁸

Although the method of preparation was known to produce only the β phase of UH₃ (α -UH₃ forms in varying fractional amounts when the reaction is carried out below 200°C)⁹ an x-ray analysis was performed for positive identification. As expected, the structure was determined as cubic with $a_0 = 6.644$ Å, in agreement with the results of Rundle.²

The β -UH₃ powdered sample was prepared for loading into the calorimeter in a helium-filled dry box by pouring the sample into each of two right annular thin (0.006-cm wall) copper cylinders which were then pressed at one kbar pressure in a special hardened steel die.¹⁰ The copper-encapsulated sample specimens were slipped over a reentrant well in the calorimeter.¹¹ A few mg of Apiezon T grease were used to effect thermal contact between the copper capsule and the reentrant well of the calorimeter. The pressed specimens had adequate thermal conductivity throughout¹⁰ and therefore the use of helium exchange gas in the calorimeter sample space was not required. The calorimeter was soldered shut on a high vacuum line. The mass of the sample was 38.245 g.

Calorimetric Techniques

A detailed description of the calorimetric apparatus, measurement techniques, calibration of the germanium resistance thermometer, and method of calculation used for the present measurements has been given in recent publications^{8,11} from this laboratory. In brief, the heat-capacity determinations were made by an isothermal technique wherein the temperature of a copper ring to which the leads and supporting tubes are thermally

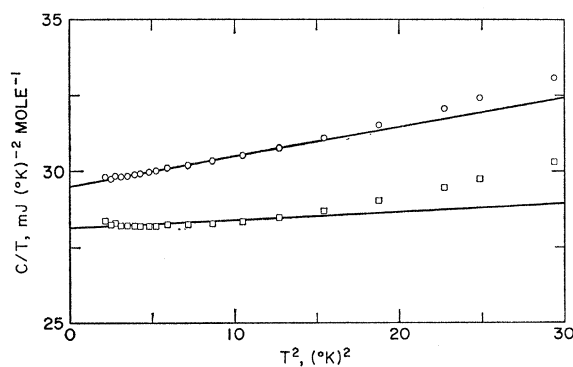


FIG. 1. Plot of C_p/T and of $(C_p - C_M)/T$ versus T^2 . C_M is the magnetic contribution, estimated from spin-wave theory to be $1.190 T^{3/2}$ mJ(°K mole)⁻¹. \circ : $C =$ uncorrected C_p . \square : $C = C_p - C_M$. The bottom line represents Eq. (6) and the top line Eq. (7) of the text.

⁹ R. N. R. Mulford, F. H. Ellinger, and W. H. Zachariasen, J. Am. Chem. Soc. **76**, 297 (1954).

¹⁰ H. E. Flotow and D. W. Osborne, Rev. Sci. Instr. **37**, 1414 (1966).

¹¹ D. W. Osborne, H. E. Flotow, and F. Schreiner, Rev. Sci. Instr. **38**, 159 (1967).

TABLE II. Thermodynamic properties of β -UH₃ at selected temperatures. The units for the thermodynamic quantities are J(°K mole)⁻¹.

T	C_p	S°	$(H^\circ - H_0^\circ)/T$	$-(G^\circ - H_0^\circ)/T$
2	0.0598	0.0586	0.0295	0.0291
5	0.1621	0.1512	0.0770	0.0742
10	0.4579	0.3411	0.1837	0.1574
15	1.167	0.6405	0.3764	0.2641
20	2.583	1.1524	0.7356	0.4168
298.15	49.29±0.10	63.67±0.13	30.24±0.06	33.43±0.07

anchored was held constant by automatic control circuits to better than $\pm 0.001^\circ\text{K}$ during a heat-capacity measurement. The calibration of the germanium resistance thermometer (laboratory designation Ge No. 3) is based upon the vapor pressure of He³ (T₆₂ scale) from 0.85 to 2.3°K, upon the vapor pressure of He⁴ (T₅₈ scale) from 2.1 to 4.2°K, upon a He⁴-filled gas thermometer from 4.2 to 25°K, and on the vapor pressure of liquid hydrogen near 20°K.¹¹

The temperature drift of the calorimeter was followed for about 10 min, then the calorimeter was heated electrically for 3 min, and finally the temperature drift was again followed for about 10 min. The drifts before and after the heating periods were constant. Because of the radioactive self-heating, the lowest temperature for the measurements was only 1.4°K.⁸ The temperature rises were approximately equal to 10% of the initial temperature of each run. The heat capacity of the empty calorimeter was determined experimentally in a separate series of measurements. Small adjustments were made to the measured heat capacities for differences in the amounts of copper, Apiezon T-grease, and 50-50 lead-tin solder between the empty and full calorimeter heat capacity runs. These adjustments were calculated with sufficient accuracy from the reported heat capacities of copper,¹¹ Apiezon T-grease,¹² and solder,^{13,14} so that an uncertainty from this source of less than 0.1% was introduced into the reported molal heat capacities. No corrections were made for impurities in the sample.

The probable error of the results is estimated to be $\pm 0.2\%$ over the entire temperature range. This estimate is based in part upon the heat-capacity results obtained in this apparatus for a sample of the 1965 Calorimetry Conference Copper Standard.¹¹

RESULTS AND DISCUSSION

The experimental heat-capacity values are presented in order of increasing temperature in Table I. These results agree with previous data⁸ obtained for β -UH₃ in this Laboratory to $\pm 0.3\%$ near 20°K. However, at lower temperatures the earlier results tend to be somewhat higher than the present results ($+5\%$ at 15°K

and $+14\%$ at 10°K), and this disagreement is undoubtedly caused by adsorption and desorption of the He⁴ exchange gas on the finely powdered sample in the calorimeter below 20°K during the prior experiment.⁶

A listing of the heat-capacity values of β -UH₃ at selected temperatures is given in Table II. These values were obtained from a least-squares polynomial fit of the data given in Table I together with the earlier data⁶ from 20 to 38°K. Also given in Table II are values for the entropy S° , the enthalpy function $(H^\circ - H_0^\circ)/T$, and the Gibbs energy function $(G^\circ - H_0^\circ)/T$, which were calculated from the heat-capacity data and an extrapolation from 2 to 0°K by means of Eq. (6). The values at 298.15°K for the entropy and Gibbs energy function are slightly lower (but within the estimated probable errors) than the previous values because of the lower heat capacities obtained below 20°K in the present experiment.

It was expected that from the lowest temperature of the present experiment up to 4 or 5°K the heat capacity of the β -UH₃ sample could be represented by an equation of the following form:

$$C_p = \gamma T + AT^3 + BT^{3/2}; \quad (1)$$

(C_p is indistinguishable from C_v at these temperatures). In this equation, γT is the contribution of the conduction electrons, AT^3 is the lattice contribution, and $BT^{3/2}$ is the magnetic contribution according to spin-wave theory. At still lower temperatures there should be a term in T^{-2} arising from the nuclear spin hyperfine contribution of the U²³⁵ in the sample. If the T^{-2} term is of the same magnitude as in U²³⁵ metal,¹⁵ after correction for the U²³⁵ content of the present sample it would amount to only 0.04% of the total heat capacity at 1.5°K. Perhaps this term would be larger in a ferromagnetic compound of U²³⁵, but since no evidence of a T^{-2} term can be seen in measurements¹⁶ on a sample of the ferromagnetic compound uranium monosulfide containing 0.7 at. % U²³⁵, we believe that it can be neglected here.

An attempt to determine all three coefficients in Eq. (1) by a least-squares fit of the data from 1.4 to

¹² E. F. Westrum, Jr., C. Chou, D. W. Osborne, and H. E. Flotow, *Cryogenics* **7**, 43 (1967).

¹³ J. de Nobel and F. J. du Chatenier, *Physica* **29**, 1231 (1963).

¹⁴ W. J. Ziegler and J. C. Mullins, *Cryogenics* **4**, 39 (1964).

¹⁵ C. W. Dempsy, J. E. Gordon, and R. H. Romer, *Phys. Rev. Letters* **11**, 547 (1963).

¹⁶ E. F. Westrum, Jr., R. R. Walters, H. E. Flotow, and D. W. Osborne, *J. Chem. Phys.* (to be published).

4°K was unsatisfactory, because the coefficient B obtained in this way was negative, which is physically impossible. The coefficients and standard errors found by this method were $\gamma = 30.23 \pm 0.18 \text{ mJ}(\text{°K})^{-2} \text{ mole}^{-1}$, $A = 0.131 \pm 0.009 \text{ mJ}(\text{°K})^{-4} \text{ mole}^{-1}$, and $B = -0.60 \pm 0.16 \text{ mJ}(\text{°K})^{-5/2} \text{ mole}^{-1}$, and the standard deviation of an individual point was 0.09%.

Another method of treating the data is to obtain an approximate value of B from spin-wave theory and then to evaluate γ and A by a least-squares fit of $(C_p - BT^{3/2})$ to the equation

$$(C_p - BT^{3/2}) = \gamma T + AT^3. \quad (2)$$

According to Dyson¹⁷ the magnetic contribution, C_M , for sc, bcc, or fcc ideal Heisenberg ferromagnets is

$$C_M = 5.029 R \theta^{3/2} + O(\theta^{5/2}), \quad (3)$$

where

$$\theta = T / (2\pi T_c). \quad (4)$$

T_c in Eq. (4) is approximately equal to the Curie temperature. The structure of $\beta\text{-UH}_3$ is cubic but is more complicated than sc, bcc, or fcc. Also, $\beta\text{-UH}_3$ is electrically conducting, and therefore its behavior may deviate appreciably from that of an ideal Heisenberg ferromagnet, in which the spins are assumed to be localized. However, if we make the assumption that Eqs. (3) and (4) are nevertheless applicable we obtain, from $T_c = 170.7 \text{°K}$,

$$C_M = 1.19 T^{3/2} \text{ mJ}(\text{°K mole})^{-1}. \quad (5)$$

Using the data from 1.4 to 4°K and assuming $B = 1.19 \text{ mJ}(\text{°K})^{-5/2} \text{ mole}^{-1}$, we obtain

$$C_p = (28.14 \pm 0.04) T + (0.0269 \pm 0.0060) T^3 + 1.19 T^{3/2} \text{ mJ}(\text{°K mole})^{-1}, \quad (6)$$

with a standard deviation of 0.32% for an individual

¹⁷ F. J. Dyson, Phys. Rev. **102**, 1230 (1956).

point. The standard deviation is approximately equal to that expected from the estimated experimental error, but as can be seen from the squares in Fig. 1 the deviations show a systematic trend with temperature. This trend suggests that the magnetic contribution given by Eq. (5) is too large.

On the other hand, if the magnetic contribution is considered to be negligible, a least-squares fit from 1.4 to 4°K gives

$$C_p = (29.53 \pm 0.02) T + (0.0959 \pm 0.0026) T^3 \text{ mJ}(\text{°K mole})^{-1} \quad (7)$$

with a standard deviation of 0.13% for an individual point. The circles in Fig. 1 show the fit to this equation. The fact that Eq. (7) fits the data better than Eq. (6) is another indication that the magnetic contribution may be less than that given by Eq. (5).

Because of the uncertainty in the magnetic contribution it is not possible to derive a reliable value of the coefficient A or Debye Θ for the lattice contribution. However, γ is fairly independent of B , changing only from $\gamma = 28.14 \text{ mJ}(\text{°K})^{-2} \text{ mole}^{-1}$ for $B = 1.19 \text{ mJ}(\text{°K})^{-5/2} \text{ mole}^{-1}$ to $\gamma = 29.53$ for $B = 0$. We conclude that for $\beta\text{-UH}_3$, $\gamma = 29 \pm 1 \text{ mJ}(\text{°K})^{-2} \text{ mole}^{-1}$. This value may be compared with $\gamma = 9.88 \text{ mJ}(\text{°K})^{-2} \text{ mole}^{-1}$ found for uranium metal⁸ and $\gamma = 23.4 \text{ mJ}(\text{°K})^{-2} \text{ mole}^{-1}$ for US.¹⁶

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