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Uranium Mononitride: Heat Capacity and Thermodynamic Properties from 5° to 350°K*

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The low-temperature heat capacity of UN was determined by adiabatic calorimetry and found to have a normal sigmate temperature dependence, except for the presence of an anomaly near 52°K associated with antiferromagnetic ordering of the electron spins. At 298.15°K the heat capacity (C_P), entropy ($S°$), enthalpy function [$(H°-H°_0)/T$], and Gibbs energy function [$-(G°-H°_0)/T$] are, respectively, 11.43, 14.97, 7.309, and 7.664 cal/(gfm·°K).

I. INTRODUCTION

THE existence of three uranium nitrides, UN, U_2N_3, and UN_2, has been well established, but few thermodynamic and thermochemical properties have been reported. Recent redeterminations of the melting point of uranium mononitride have raised the previously reported melting temperature to 2850°C at and above 2.5 atm pressure of nitrogen.[1,2] Interest in UN as a potential reactor fuel has therefore increased. Its high melting point, high enthalpy of formation,[3] high density, high thermal conductivity [0.54 W/(cm·°C) at 298°K compared with 0.03 for UO_2 and 0.25 for UC], appreciable electrical conductivity, and good phase stability (even under neutron irradiation) provide a highly desirable combination of refractory characteristics. Its thermal, electronic, and bonding behaviors are of particular interest in comparison with those of other uranium chalcogenides and pnictides (US, USe, UC, and UP, for example) which also possess the sodium chloride structure. The evaluation of such data may provide explanation of the apparent bulk instability of the UO phase.

II. EXPERIMENTAL

A. Preparation and Characterization of the Sample

Uranium mononitride is usually prepared by hydriding uranium, decomposing it to form powdered metal, and subsequently reacting this with nitrogen or ammonia. However, the uranium metal in this sample was not pulverized by hydriding but reacted directly with ammonia in a vertical Vycor flow furnace at 850°C, using a reaction time of about 24 h to obtain complete reaction of the metal. The uranium dinitride thus produced was converted to mononitride under vacuum (final value 0.23 torr) in a graphite crucible heated within a graphite resistance furnace at a temperature of 1325°C for 2 h. Stanford Research Institute had prepared the sample (N-19) at the request of W. Hubbard of the Argonne National Laboratory. Through his interest and the generosity of the Laboratory, the material was made available for these measurements. The analytical data provided by Stanford Research Institute and the Argonne National Laboratory are given in Table I.

Calculation of the proximate constitution of the sample requires a knowledge of the form in which oxygen is present. The oxygen could well be totally present as UO, which is isostructural with UN, but x-ray-diffraction data taken at Stanford Research Institute utilizing synthesized calibration standards have been interpreted[4] as indicating that oxygen is present partly (0.8 wt%) as a surface contaminant in the form of UO_2 and partly (1.4 wt%) as UO in solid solution with UN. Although we do not endeavor to judge the reliability of the x-ray result without more information on the basis of the calibration, we feel confident in ascribing the oxygen in the sample to uranium monoxide in solid solution in the nitride for several reasons. First, the presence of a separate, fairly pure UO_2 phase would be expected to show the cooperative, antiferromagnetic–paramagnetic transition near 30°K.[5] The absence of any such anomaly in the region of 30° suggests essentially complete absence (i.e., less than 0.1 wt%) of the dioxide phase.

Moreover, the amount of monoxide present is within the limits of its solubility in the mononitride.[6] A further argument in favor of this interpretation is found in the

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[4] Stanford Research Institute, "High Purity Uranium Compounds" (report submitted to Argonne National Laboratory, 1963).

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[6] H. M. Feder (personal communication).

TABLE I. Analysis and characterization of UN calorimetric sample.

Substance	Amount present (wt%)	Source	Average (wt%)
U	94.49, 94.56	SRI[a]	94.52
N	5.41, 5.14 5.31, 5.34[b]	SRI ANL	5.28
O	0.20, 0.20 0.20, 0.21	SRI ANL[c]	0.20
C	0.05 0.066, 0.062, 0.053, 0.053	SRI ANL	0.05
H	(0.04) 0.0002 to 0.0004	SRI ANL	0.0003
Fe	(0.01–0.1) (emission spectrograph) 0.05 (calorimetric)	SRI SRI	0.05
Al	0.003–0.03	SRI	0.01
Mn	0.0003–0.003	SRI	
Total			100.12

[a] SRI, Stanford Research Institute.[4]

[b] These recent nitrogen determinations by Holt of Argonne National Laboratory using an inert-gas fusion manometric method previously described [B. D. Holt and H. T. Goodspeed, Anal. Chem. **35**, 1510 (1963)] are of higher precision and support the previously selected average value.

[c] ANL, Argonne National Laboratory.

proximate analysis given later which, on this basis, shows the uranium nitride in this sample to be stoichiometric. Although a large stoichiometry range at sufficiently high temperatures has been postulated for UN,[7] Olson and Mulford[2] noted no deviation from constancy in the lattice parameter.

To establish the form of the iron in the mononitride, a mixture of UN and enough iron to form U_6Fe was heated at 1400°C for 2 h.[4] The resultant x-ray patterns showed some iron, possibly some UFe_2, and an unidentified compound, but no reduction in the intensity of the UN line. If U_6Fe or UFe_2 had formed, a large fraction of the UN would have decomposed. The x-ray pattern of a sample prepared from uranium hydride plus iron powder at 600°C confirmed U_6Fe to be the predominant compound. Upon nitriding this with ammonia at 850°C, the x-ray pattern showed only the lines for the UN_2 phase. Since Fe_4N is not stable under the conditions used for forming the uranium dinitride phase, the conclusion follows that the iron present is largely elemental iron.

The proximate composition is, therefore, determined as 95.5 mole % uranium mononitride ($UN_{1.00}$), 3.2 mole % uranium monoxide, 1.1 mole % uranium monocarbide, and 0.2 mole % elemental iron.

B. Cryostat and Calorimeter

Determinations on uranium mononitride were made by the quasiadiabatic technique using the Mark III cryostat, Calorimeter W-17A (which has been previously described[8]) and thermometer (laboratory designation A-3) which is believed to reproduce the thermodynamic temperature scale to within 0.03°K above the oxygen point. All determinations of mass, temperature, resistance, voltage, and time are referred to calibrations or standardizations made by the National Bureau of Standards. The heat capacity of the empty calorimeter, thermometer, and heater assembly was determined in a separate series of measurements. Corrections to the data were made for the differing quantities of Apiezon-T grease (used to provide thermal contact between the heater–thermometer–calorimeter assembly), of Cerroseal (In–Sn) solder (used to seal the sample space), and of purified helium gas (used to facilitate thermal equilibration) present in the two series of determinations. For heat-capacity measurements on the sample, 146 torr of helium gas was admitted to the sample space. The calorimetric sample massed 130.902 g (*in vacuo*) and represented more than 55% of the total measured heat capacity at all temperatures. A density of 14.32 g/cc[9] for UN was used to obtain the buoyancy adjustment.

III. RESULTS

The heat capacity of the sample is presented in Table II in chronological sequence so that the temperature increments used in the measurements may usually be deduced from the differences in the adjacent (mean) temperatures. These results are presented in terms of the defined thermochemical calorie of 4.1840 J, an ice-point temperature of 273.15°K, and a gram-formula mass (gfm) of 252.037. These data have been adjusted for curvature and for the presence of 1.1 mole % of uranium monocarbide[10] and 0.2 mole % of elemental iron[11] on the basis of values previously reported. These adjustments total less than 0.2% of the heat capacity above 30°K. Because the 3.2 mole % of uranium monoxide believed to be present in the calorimetric sample is in solid solution, is isostructural, and is reported to have a lattice constant only 0.82% larger than that of uranium mononitride,[9] it was considered to have a heat-capacity contribution equal to that of the mononitride. It is further presumed to have little influence on the temperature or the enthalpy of transition. The data in the region of the transition are presented in Fig. 1.

The smoothed heat capacities and the thermo-

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dynamic functions derived from these data are presented in Table III at selected temperatures. The smoothed heat capacities are obtained by a digital computer program and checked by comparison with large scale plots of the data. In spite of the relatively low purity of the sample, the heat-capacity values are believed to be characterized by a probable error decreasing from 0.3% above 60°K to less than 0.2% above 200°K. The integrations also were performed by a digital computer. These functions are believed to have a probable error of less than 0.3% at temperatures above 100°K. The enthalpy of Runs A, B, C, and D noted in Table II accorded with calculated enthalpy increments to within 0.07%. No adjustment has been made for isotope mixing or nuclear spin contributions to the entropy and Gibbs energy functions; hence, these values are practicable for use in chemical thermodynamic calculations.

TABLE II. Heat capacity of uranium mononitride.[a]

T	C_P	T	C_P	T	C_P
Series I		17.13	0.373	43.67	2.952
		18.87	0.462	46.19	3.240
118.03	7.019	20.78	0.579	48.48	3.503
124.99	7.330	22.85	0.728	50.60	3.756
133.41	7.686	25.06	0.914	52.61	3.666
142.59	8.054	27.64	1.167	54.62	3.537
151.92	8.399	30.48	1.501	56.59	3.667
161.23	8.716	33.66	1.788	58.47	3.804
170.55	9.017	37.36	2.211	60.27	3.937
179.92	9.285	38.62	2.358		
189.16	9.535	42.07	2.759	Series V	
198.10	9.756	46.07	3.222		
206.88	9.962	ΔHt Run A		25.64	0.976
215.56	10.156	ΔHt Run B		28.86	1.348
224.51	10.335	61.97	4.051	ΔHt Run C	
233.79	10.511	68.62	4.482	64.81	4.251
243.07	10.695	75.38	4.879	70.30	4.585
252.21	10.821	82.54	5.299		
261.31	10.958	89.99	5.666	Series VI	
270.37	11.083	98.98	6.115		
279.40	11.199	106.90	6.505	32.08	1.619
288.55	11.319	116.26	6.938	ΔHt Run D	
297.75	11.430			61.80	4.045
306.84	11.532	Series III			
316.34	11.642			Series VII	
325.97	11.736	35.46	2.002		
335.82	11.822	42.55	2.822	44.94	3.096
345.88	11.884	46.44	3.270	46.05	3.223
		49.04	3.570	47.10	3.342
Series II		51.65	3.825	48.12	3.469
		53.67	3.498	49.10	3.574
5.69	0.069	57.53	3.737	49.82	3.658
6.09	0.078	59.37	3.871	50.28	3.703
6.84	0.089	61.14	3.998	50.74	3.744
7.70	0.104	62.84	4.119	51.18	3.828
8.66	0.122			51.62	3.888
9.77	0.149	Series IV		52.06	3.895
11.04	0.172			52.50	3.670
12.41	0.202	33.52	1.780	52.96	3.478
13.89	0.248	37.57	2.243	53.42	3.472
15.46	0.302	40.84	2.623	53.88	3.487

[a] Units: calories, gram-formula mass, Kelvin degrees.

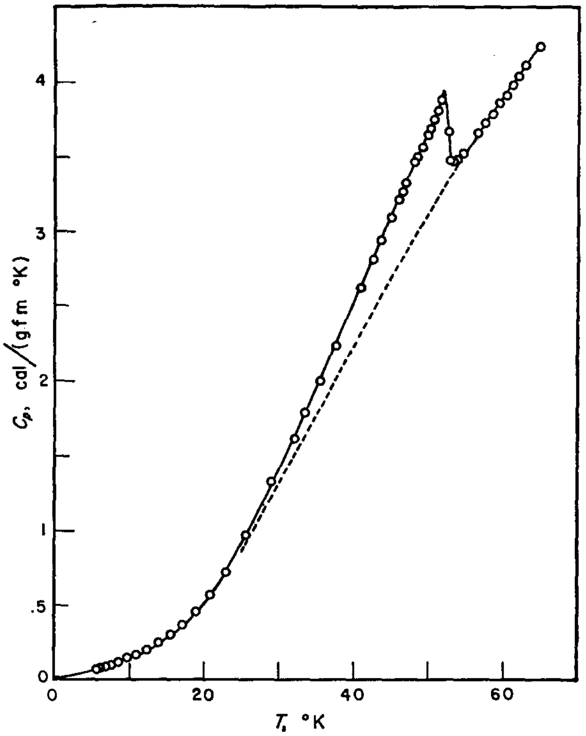

FIG. 1. Heat capacity of UN in the region of the antiferromagnetic–ferromagnetic transition. The points represent individual determinations, and the dashed curve is the estimate of the lattice contribution.

IV. DISCUSSION

The combination of refractory qualities with high electrical and thermal conductivities which characterize uranium nitride is partly a consequence of its electronic configuration. However, an unambiguous assignment of the electron configuration is certainly not possible on the basis of the limited, existing magnetic-susceptibility data.[12–14] Allbutt *et al.*[13] found no field dependence in the susceptibility between 80° and 320°K. Their magnetic-moment values were sensibily constant at 3.11±0.005 Bohr magnetons (μ_B) and corresponded to a Curie–Weiss Θ equal to -325°K. These values accord well with $\Theta = -310$°K and a moment of 3.0 μ_B reported by Trzebiatowski and coworkers,[12] and with that of Didchenko and Gortsema[14] (3.04 μ_B). These are in poor agreement with the theoretical value (3.62 μ_B) for $5f^3$ ions. Comparison with data on PuC suggests that despite the minute differences in interatomic distances a partial quenching of the orbital moment of UN occurs apparently as a consequence of the larger but less stable $5f$ shell of

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TABLE III. Thermodynamic functions of uranium mononitride.[a]

T	C_P	$S°$	$H°-H°_0$	$-(G°-H°_0)/T$
5	0.060	0.056	0.14	0.028
10	0.148	0.123	0.65	0.058
15	0.286	0.207	1.71	0.093
20	0.527	0.319	3.68	0.135
25	0.913	0.476	7.22	0.187
30	1.406	0.685	12.99	0.252
35	1.946	0.942	21.36	0.331
40	2.517	1.238	32.50	0.426
45	3.099	1.568	46.55	0.534
50	3.684	1.925	63.51	0.655
60	3.914	2.599	100.48	0.924
70	4.572	3.253	142.97	1.210
80	5.157	3.902	191.7	1.506
90	5.691	4.541	245.9	1.808
100	6.188	5.166	305.4	2.113
110	6.661	5.779	369.6	2.418
120	7.113	6.378	438.5	2.723
130	7.543	6.964	511.8	3.027
140	7.949	7.538	589.3	3.329
150	8.327	8.100	670.7	3.628
160	8.676	8.648	755.7	3.925
170	8.996	9.184	844.1	4.219
180	9.290	9.707	935.6	4.509
190	9.558	10.216	1029.8	4.796
200	9.806	10.713	1126.7	5.080
210	10.034	11.197	1225.9	5.360
220	10.244	11.669	1327.3	5.636
230	10.439	12.128	1430.7	5.908
240	10.619	12.577	1536.0	6.176
250	10.785	13.014	1643.1	6.441
260	10.937	13.440	1751.7	6.702
270	11.079	13.855	1861.8	6.960
280	11.211	14.260	1973.2	7.213
290	11.336	14.656	2086.0	7.463
300	11.455	15.042	2199.9	7.709
350	11.951	16.848	2785.8	8.888
273.15	11.12	13.98	1897	7.040
298.15	11.43	14.97	2179	7.664

[a] Units: calories, gram-formula mass, Kelvin degrees.

uranium. It is reasonable to predicate the existence of a transition in bond character from UC through UN and UP to US and USe. UC has been postulated as covalent and US as ionic.[13] That UN does indeed have a transitional nature is in some respects demonstrated by the Curie–Weiss magnetic-susceptibility curve, which is intermediate between those of UC and US. Consequently, the bonding and electronic structure in UN may be expected to be significantly different from that in UC. No magnetic transformation has been found for UC either by means of heat-capacity measurements[10,15,16] or by resistivity measurements.[17] As Costa *et al.* have suggested,[18] the difference in behavior between UN and UC may be due to a larger band population in the nitride. This would have the effect of stabilizing the *f* states in this compound.[19,20]

Magnetic-susceptibility and neutron-diffraction data[21] are said to have confirmed the existence of an antiferromagnetic transition in uranium mononitride near 45°K. Moreover, Costa *et al.*[18] observed a change in slope in the thermoelectric power and a large decrease in the resistivity-temperature coefficient near 50°K. The existence of a discontinuity in the heat-capacity curve near 45°K has also been reported by Martin.[22]

Estimation of the entropy and enthalpy associated with the antiferromagnetic anomaly is reasonably difficult. However, utilizing a Debye Θ-versus-temperature plot to assist in drawing a smooth curve beneath the transition for the lattice heat-capacity contribution yields a value for the enthalpy of transition of 7.2 cal/gfm and a corresponding entropy of transition of 0.17 cal/(gfm·°K). This probably minimal value may be compared with the entropy of the US transition [1.17 cal/(gfm·°K) at 179°K][23] and that of the USe transition [1.05 cal/(gfm·°K) at 160.5°K][24] in spite of the significant differences in temperature.

The UN entropy at 298°K has been estimated as 13 cal/(gfm·°K) in the compilation of Rand and Kubascheweski.[25]

The high electrical conductivity of UN accords with the appearance of a component of heat capacity linear in temperature below 23°K. Analysis of the data on a C_P/T-vs-T^2 plot shows that the low-temperature heat capacity is well represented as $C_V \approx C_P = 0.0110T + (3.86\times10^{-5})T^3$. This equation was used for the extrapolation of the thermal data to 0°K. The coefficient ($\gamma = 0.011$) of the linear or electronic term is directly related to the density of states:

$$\gamma = (2\Pi^2 k^2/3q)(d\nu'/d\epsilon')_{\epsilon_0},$$

in which q is the number of electrons in the band per atom, ϵ_0 is the Fermi level in electron volts, and $(d\nu'/d\epsilon')_{\epsilon_0}$ is the density of states per atom.[26] By Stoner's method, the density of states for UN [expressed as the number of states *per atom per electron volt*, $(d\nu'/d\epsilon')$] is

$$(d\nu'/d\epsilon') = 8.8788\times10^{-2}(\gamma\times10^4) = 9.73.$$

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Although relatively large, this value is comparable to those for other isostructural uranium compounds.[10,16,23,24]

In addition to establishing an approximate value for the coefficient of the electronic heat-capacity contributions and revealing the thermal and magnetic anomalies near 52°K, the present results provide definitive thermodynamic data at higher temperatures. Although the impurity content of the sample is relatively high and the proximate composition is limited by the precision of the nitrogen analyses, the close similarity of heat capacities of the impurities (UC, UO) with that of UN minimizes the uncertainty in the adjusted results as may be seen in the analogous case of heat-capacity measurements in two laboratories[10,15,16] on impure but well-characterized samples of uranium carbides from three independent sources. Nevertheless, further measurements on pure uranium mononitride are an obvious desideratum in the regions where the effect of impurities on the heat capacity cannot be accurately assessed, i.e., near the thermal anomaly and below 20°K.

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Exchange Effects in the $^3A_2\rightarrow{}^1E$ Absorption Transition of the Ni^{2+} Ion in Fluoride Compounds*

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The effect of the exchange interaction between nickel ions on the structure and position of the $^3A_2\rightarrow{}^1E$ Ni^{2+} ion absorption transition has been studied experimentally in fluoride compounds. The spectra observed in these materials are found to depend on the concentration of the nickel ion component and the crystal structure.

INTRODUCTION

Structure has been reported in the low-temperature absorption spectra of the $^3A_2\rightarrow{}^1E$ transition of the Ni^{2+} ion in NiF_2,[1] $KNiF_3$,[2] and $RbNiF_3$,[3] which has been attributed to the exchange interaction between nickel-ion pairs. The splitting of the major lines of this structure in NiF_2 and $KNiF_3$ have been found to be proportional to the magnetic ordering temperature of the crystal.[1,2] In this publication, we report effects on the spectra of the $^3A_2\rightarrow{}^1E$ Ni^{2+} transition in several fluoride hosts due to variations in the composition and structure of the crystals. The ion–ion exchange interaction and the crystal structure are found to be very important in determining the spectrum of this transition.

EXPERIMENTAL

Crystal specimens for the fluoride materials used in these experiments were prepared by the horizontal Bridgman technique in an HF or inert-gas atmosphere. High purity of the starting materials, particularly the NiF_2, was found to be essential to good crystal growth. Samples 0.5 cm on a side were typically obtained. X-ray photographs revealed that these materials contained less than 1% of secondary phases. In the mixed crystals prepared, the concentrations reported are those of the starting materials.

The crystal samples were mounted on a copper cold finger which was attached to the coolant reservoir of an optical vacuum Dewar. Temperature measurements were made with a thermocouple fixed to the sample. The absorption spectra reported here were measured on a Perkin–Elmer 112 recording spectrometer equipped with a tungsten-filament lamp light source and an S–20 response photomultiplier detector. The resolution of the present experimental arrangement was estimated

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