Inorganic Chemistry

ARTICLE

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Low Temperature Heat Capacity and Magnetic Properties of UF_3

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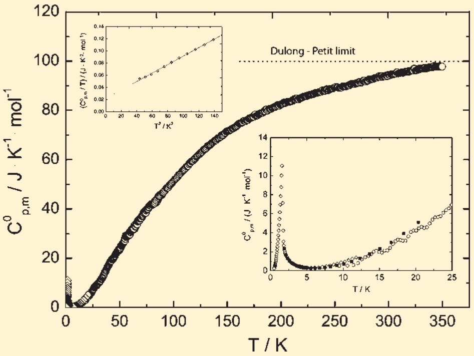
ABSTRACT: The low temperature heat capacity of UF_3 has been measured using an adiabatic low temperature calorimeter in the temperature range from 10 to 350 K. These data are complemented at the lowest temperature region with data obtained with a Quantum Design PPMS-14 device in the temperature range from 0.5 to 20 K. Good agreement between both techniques has been found, and from these experimental results the absolute entropy of UF_3 at 298.15 K has been determined as $126.8 \pm 2.5\ \mathrm{J\ K^{-1}\ mol^{-1}}$. On the basis of the specific heat data and the magnetization measurements performed on a SQUID device, a transition at 1.59 K attributed to Curie temperature of a ferromagnetic transition has been found in this study. This observation makes UF_3 a unique compound with an unusually low ferromagnetic ordering temperature.



1. INTRODUCTION

In the molten salt reactor (MSR) the fissile material is dissolved in the form of fluorides in an inorganic matrix which is in the liquid state during the reactor operation. The main characteristics and developments of this reactor type have been reported, e.g., in an overview paper by MacPherson,[1] by Grimes,[2] and recently by Beneš and Konings in a book chapter.[3] For more details, we refer to those studies. One of the concepts of the MSR which is being investigated is the thorium breeder reactor which produces more fuel than it consumes. Such a concept is based on the conversion of fertile ^{232}Th into fissile ^{233}U by neutron capture and two consecutive β decays of ^{233}Th and ^{233}Pa. In the MSR the uranium is in the form of tetrafluoride (UF_4), but a small addition of UF_3 is necessary in order to control the redox potential of the fluoride salt to avoid corrosion, e.g., leaching of chromium from the structural material. Therefore, a careful investigation on the properties of the UF_3 compound is of great relevance for the development of the MSR.

One of the key physical properties that needs to be investigated is the heat capacity. Its knowledge is not only important from the reactor safety point of view, but also because the fuel of the MSR serves as a heat transfer medium that delivers the energy from the reactor core to the heat exchanger through the primary circuit. In this study, we present the low temperature heat capacity data of UF_3 measured using two different techniques, namely, the adiabatic and the thermal relaxation methods, and the results obtained from both techniques are compared.

In this study the low temperature heat capacity of UF_3 is measured from 0.5 to 350 K. The measurement is important not only to give direct quantitative data, but also to know the heat capacity from 0 K as a function of temperature so that the absolute entropy at 298.15 K, $S°_{298.15}$, can be calculated, bringing one of the key thermodynamic data which determines the stability of UF_3. Furthermore, if a studied compound undergoes a transition (phase transition, excitation to higher energy levels due to crystal field splitting, magnetic, etc.) at the temperature range of the experiment, the heat capacity measurement is a usual method to identify this change, as it is always accompanied with a latent heat.

2. EXPERIMENTAL WORK

The UF_3 sample that was measured in this study was synthesized in The Netherlands Energy Research Foundation (ECN) in Petten and delivered to the Institute of Transuranium Elements (ITU) in 1978. As reported in Cordfunke and Ouweltjes,[4] the sample was prepared by the reaction of UF_4 with a stoichiometric amount of uranium hydride (obtained by a hydrogenation and dehydrogenation cycle of uranium metal repeated several times) in a slow stream of argon at temperatures which slowly increase from 700 to 900 K over 5 h. The sample was of the same batch as used in the enthalpy of formation determination of UF_3 performed by Cordfunke and Ouweltjes;[4] its purity was checked by XRD and chemical analysis based on potentiometric titration determining 99.5% of UF_3. The delivered sample was of a very fine powder form, and before the transportation, it was encapsulated in a quartz ampule under argon atmosphere. Thus, oxidation or water absorption of this sample was avoided in the transient period. The opening of the ampule, the filling of the measuring cell of the adiabatic calorimeter, and the sample encapsulation for the PPMS and SQUID measurements using Stycast and a plexiglass cuvette, respectively, were performed in the glovebox under argon atmosphere which is connected to the purifier keeping the oxygen concentration at the level of less than 5 ppm and the water content less than 1 ppm. Thus, the UF_3 sample was always kept at inert conditions, avoiding any risk of parasitic reactions.

2.1. Adiabatic Calorimetry. The adiabatic calorimeter used in this study was the Cal V type transferred to ITU from the State University of Utrecht in 2007. The medium used as a coolant is either

Received: May 18, 2011
Published: September 13, 2011

liquid nitrogen or liquid helium, depending on the temperature range of the measurement. Hence, the lowest achievable temperature is the boiling point of helium at atmospheric pressure, 4.2 K. The upper limit of the apparatus is 380 K.

The sample vessel is made of copper metal with a volume of 10 cm^3, and the typical mass of a measured sample is between 5 and 10 g. In case of UF_3 measurement, 10.0154 g of fine powder were used. The sample vessel is hermetically closed during the measurement, and prior to insertion in the calorimeter, it is filled with helium gas to maintain better thermal contact within the vessel and to avoid argon condensation at very low temperatures. A small heater is inserted into this vessel which is used to deliver a known amount of heat (exactly measured knowing the electrical current and the resistivity of the heater). In order to keep adiabatic conditions the whole vessel is put in a high-vacuum environment (10^{-6} mbar) to avoid heat losses by convection. However, the heat losses through conduction and radiation are still possible, and therefore, three thermal shields are installed around the sample vessel to maintain adiabatic conditions. Two are radiation shields, cylindrical gold plates surrounding the sample, and one is the wire heater that balances the temperature on the parts of the calorimeter that are in direct contact with the sample vessel through wires that deliver the heat to the sample and measure the temperature. For more information about the device we refer to the study by van Miltenburg et al.[5] where detailed description of the used adiabatic calorimeter is given.

Once the adiabatic conditions are maintained the heat capacity is determined according to

$$C_p = \frac{Q}{\Delta T} \tag{1}$$

where Q is the total amount of heat delivered to the sample vessel and ΔT is the temperature increase taken as a difference of the temperature measured at the end of the stabilization period before and after the heating sequence. In the present case the stabilization period was 300 s for the temperature range from 4.2 to 90 K and 600 s for higher temperature ranges. The shorter stabilization time was used in the lower region as the heat capacity at this range is much lower allowing faster thermal equilibrium. Both stabilization times applied in our experiment were found sufficient to re-equilibrate the temperature, checked by the measurement of sapphire, performed prior to the UF_3 measurement. The total amount of the heat delivered to the sample vessel at each step was set automatically by the controlling software in such a way that the temperature increase was 1 K, respecting the time of the heating sequence at 150 s.

Using this method not only is the heat capacity of a sample measured, but also a contribution of the sample vessel. Therefore, prior to the experiment it is necessary to perform a measurement of the empty vessel (blank run), and this is then subtracted from the signal of the sample measurement.

2.2. PPMS. For the investigation of the behavior of specific heat of UF_3 below 4.2 K (lower limit of our adiabatic calorimeter), the PPMS-14 (physical property measurement system, Quantum Design) instrument installed at ITU was used. It is based on a relaxation method that uses relatively small samples, typically with a mass of a few milligrams, and allows measurements of the specific heat below 1 K.

The UF_3 samples measured in this study were in a form of small solid pieces of weights of 20.1 and 1.8 mg, and prior to the experiment they were encapsulated in the argon glovebox using Stycast which prevented the UF_3 oxidation during the loading procedure. The thus prepared samples were mounted using a standard cryogenic grease (Apiezon) onto a small microcalorimeter platform of the PPMS-14 device suspended by eight thin wires. These wires serve as electrical leads for an embedded heater and thermometer and also provide a well-defined thermal connection. High vacuum conditions prevented any heat loss via exchange gas. The raw measured signal was corrected for an addenda due to Apiezon grease whose heat capacity was measured independently. The experiments were performed in the temperature range 1.7−20 K on a 20.1 mg sample and in the temperature range 0.5−12 K on a 1.8 mg sample using a ^3He cooling system. These measurements discovered a transition below 5 K. In order to determine the nature of the transition several measurements in magnetic fields up to 13 T were performed.

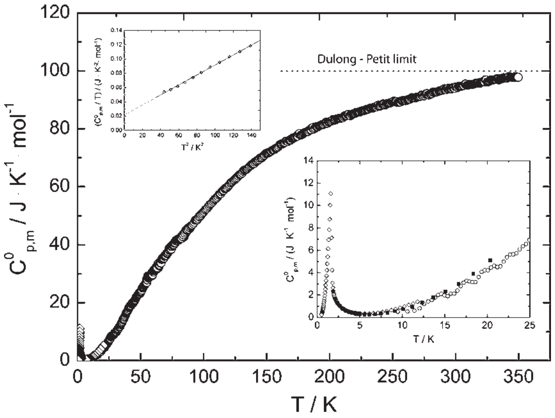


Figure 1. Low temperature heat capacity data obtained in this study: ○ data obtained from Cal V adiabatic calorimeter; ◊ data obtained from the PPMS device. Upper left inset graph shows the measured C_p/T data obtained from PPMS plotted versus T^2. The line is the fit of these data according to eq 2. Bottom right inset graph shows the heat capacity below 25 K indicating a transition at 1.59 K: ◊ 1.8 mg sample, ■ 20.1 mg sample.

2.3. SQUID. As a (ferromagnetic-like) magnetic transition was observed on the basis of the specific heat data, magnetization measurements were performed using a SQUID magnetometer in order to confirm this phenomenon. A solid piece of UF_3 of a cylindrical form and total weight of 157.4 mg was encapsulated in a plexiglass cuvette sealed with epoxy glue and measured from room temperature down to 2 K with applied magnetic fields up to 7 T.

3. RESULTS

3.1. Heat Capacity. As described in section 2.1 the operating temperature range of the Cal V adiabatic calorimeter is from 4.2 to 380 K. However, during the experiment, relatively large scatter of the data was observed for temperatures below 9 K which was explained by evaporation of condensed helium gas which is used, prior to the experiment, to equilibrate the temperature between coolant and sample vessels. Therefore, only the results above 9 K were considered in this study, while the remaining data below 9 K were measured by the PPMS-14 device. The total range covered by the adiabatic calorimeter was thus 9−350 K, and the total range covered by PPMS-14 was 0.5−20 K, allowing a small range of overlap in order to correlate both sets of results. The measurement of the UF_3 heat capacity performed on adiabatic calorimeter was done in five temperature regimes: (1) 9−42 K, (2) 42−64 K, (3) 62−72 K, (4) 72−90 K, and (5) 83−350 K, reaching the Dulong−Petit limit at high temperature. In all cases a smooth transition between the data from different runs was observed as shown in Figure 1. Furthermore, the figure demonstrates a good agreement between the adiabatic and PPMS-14 results, given in the inset graph of the figure.

The measurement on the PPMS-14 device revealed a λ-type anomaly at 1.59 K which is due to the ferromagnetic ordering of U atom as discussed later in section 4.

Table 1. Molar Thermodynamic Functions of UF_3 Obtained in This Study

T/K	$C^0_{p,m}$, J K^{-1} mol^{-1}	S^0_m, J K^{-1} mol^{-1}	$H^T_m - H^0_m$, J mol^{-1}
5	0.27	5.81	8.8
10	0.92	6.13	11.3
15	2.69	6.80	20.3
20	3.95	7.61	36.9
25	6.95	8.80	64.2
30	10.3	10.36	107.3
35	13.74	12.20	167.4
40	17.18	14.25	244.7
45	20.58	16.47	339.1
50	23.9	18.81	450.3
60	30.28	23.72	721.2
70	36.25	28.83	1053.8
80	41.79	34.03	1444.0
90	46.9	39.25	1887.5
100	51.56	44.43	2379.8
110	56.14	49.56	2918.3
120	60.45	54.63	3501.2
130	64.54	59.64	4126.2
140	68.26	64.56	4790.2
150	71.41	69.37	5488.5
160	74.13	74.07	6216.2
170	76.51	78.64	6969.4
180	78.62	83.07	7745.1
190	80.52	87.38	8540.8
200	82.24	91.55	9354.6
210	83.82	95.60	10 184.9
220	85.28	99.54	11 030.4
230	86.63	103.36	11 889.9
240	87.9	107.07	12 762.6
250	89.09	110.68	13 647.5
260	90.21	114.20	14 544.0
270	91.28	117.63	15 451.5
280	92.29	120.96	16 369.3
290	93.26	124.22	17 297.1
298.15	94.01	126.82	18 060.2
300	94.18	127.40	18 234.3
310	95.07	130.50	19 180.5
320	95.92	133.53	20 135.5
330	96.74	136.50	21 098.8
340	97.53	139.40	22 070.1
350	98.29	142.24	23 049.2

For the absolute entropy of UF_3 at 298.15 K to be obtained, all measured low temperature data above 12 K (from Figure 1) were fitted using two polynomial equations which intersect at 115 K, while the data between 7 and 12 K were fitted according to the following law

$$\frac{C_p}{T} = A \cdot T^2 + \gamma_{el} \tag{2}$$

where A is a coefficient to be optimized and γ_{el} is the Sommerfeld coefficient determined as 22 mJ K^{-2} mol^{-1}. The upper inset graph of Figure 1 shows a linear fit of the measured C_p/T data plotted versus T^2 in the temperature range above the transition and below 12 K extrapolated to 0 K. In this case only the data from PPMS were considered as they show much lower scatter than the ones from the adiabatic calorimeter. Furthermore, the transition peak has been fitted as a spline function.

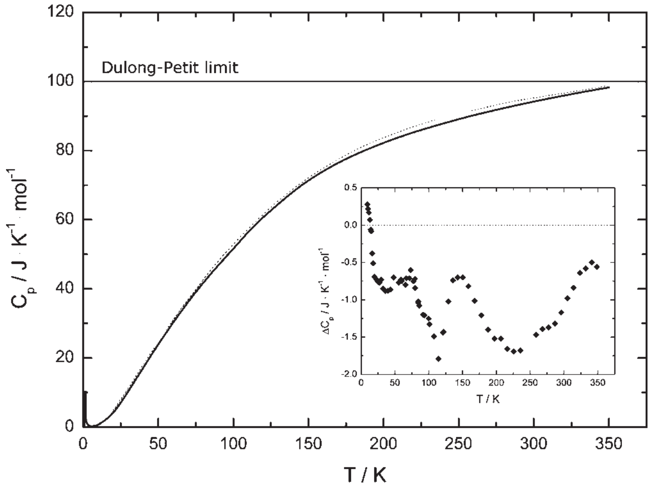


Figure 2. Low temperature heat capacity of UF_3: solid line represents the smoothed data obtained in this study, and the dotted line is the spline function of the data measured by Westrum et al. (as reported in ref 6). Inset graph shows the difference between the data measured in this study and the data by Westrum et al.

The smoothed values of the molar heat capacity of UF_3 obtained by this analysis and its thermodynamic functions calculated by integrations with respect to temperature are listed in Table 1 while the smoothed curve of the molar heat capacity is plotted in Figure 2.

Integrating the obtained $C_p(T)/T$ functions with respect to temperature from 0 to 298.15 K, the absolute entropy is calculated as

$$S°(298.15\ K) = 126.8 \pm 2.5\ J\ K^{-1}\ mol^{-1} \tag{3}$$

and the entropy contribution of the magnetic transition at 1.59 K was determined (after subtraction of electronic contributions) as

$$\Delta S°_{transition} = 5.68\ \ J\ K^{-1}\ mol^{-1} \tag{4}$$

Furthermore, Figure 2 shows our heat capacity data compared with the unpublished experimental data reported by Cordfunke et al.[6] They showed the low temperature heat capacity data of UF_3 measured from 9 to 350 K using adiabatic calorimetry. As shown in the figure, good agreement between their results and ours has been found; the difference is reported in the inset graph of Figure 2. The comparison gives scattered data as non-smoothed values by Cordfunke et al.[6] were used.

3.2. Magnetic Properties. Magnetization of UF_3 was measured at 10 and 2 K in increasing and decreasing magnetic fields from −7 to 7 T, as indicated by arrows in Figure 3. At 10 K a rather linear increase of the magnetization was observed, whereas at 2 K a magnetization loop indicating ferromagnetic ordering (as discussed in the next section) was found. The upper inset graph of Figure 3 shows the Arrott plots where the Curie temperature T_C = 1.6(1) K is inferred by extrapolating the isotherms below 2 K (lower experimental limit). The lower inset graph of the same figure shows the inverse magnetic susceptibility (○) and a Curie−Weiss fit at high temperature, yielding the effective moment 3.68 μ_B and the paramagnetic Curie temperature

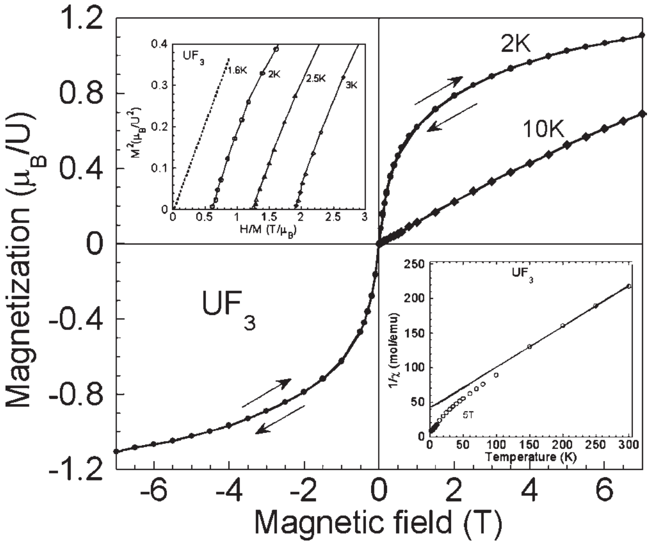


Figure 3. Magnetization of UF_3 measured at 2 K (in increasing and decreasing magnetic fields, as indicated by arrows) and 10 K. Upper inset graph shows Arrott plots. Bottom inset graph shows inverse magnetic susceptibility (○) and a Curie−Weiss fit.

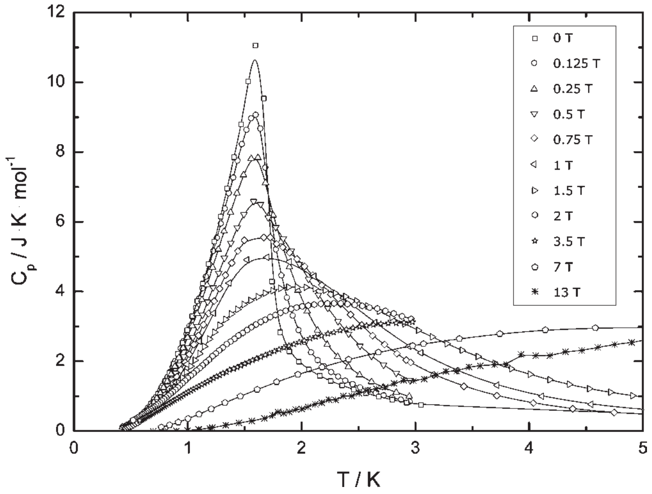


Figure 4. Temperature dependence of the heat capacity of UF_3 under different magnetic fields.

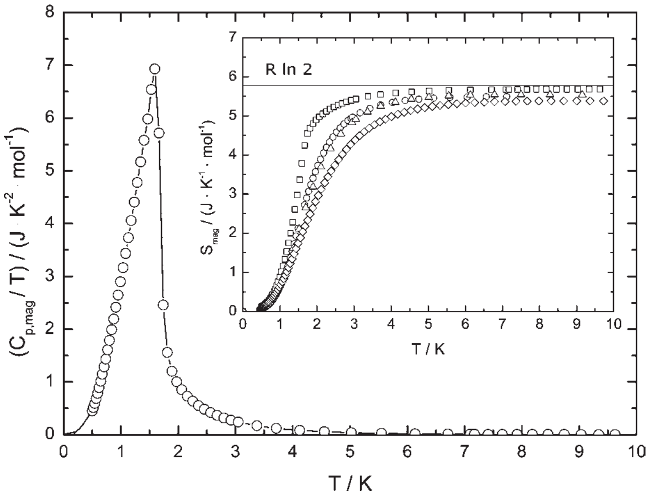


Figure 5. Excess heat capacity of the ferromagnetic transition at 0 T magnetic field. Inset graph shows the entropy of the ferromagnetic transition calculated for different magnetic fields: □ 0 T; ○ 0.75 T; △ 1 T; ◊ 1.5 T.

$\Theta_p = -70$ K. These latter results are very similar to the one reported in a previous study by Berger and Sienko[8] ($\mu_{eff} = 3.67\ \mu_B$ and $\Theta_p = -110$ K).

4. DISCUSSION

The heat capacity measurement of UF_3 showed that a λ-type anomaly occurs at 1.59 K which is typical of a magnetic transition. In order to identify the nature of the transition, the heat capacity was measured in several different magnetic fields up to 13 T, as demonstrated in Figure 4. The figure shows an increase of the transition temperature (T_C) with increasing magnetic field strongly suggesting a ferromagnetic ordering of the U atoms.

The ferromagnetic type of the transition was confirmed by measuring and comparing the magnetization at 10 and 2 K. As demonstrated in Figure 3, no hysteresis (a paramagnetic field dependence) was found at 10 K, whereas at 2 K a magnetization loop, close to saturation at 7 T, indicates the vicinity of ferromagnetic ordering. If we apply a fit using the Brillouin function on the magnetization data at 2 K, we get the values of Landé factor $g = 0.66 \pm 0.02$, and total angular quantum number $J = 1.7 \pm 0.2$, which result in the critical temperature $T_C = 1.66 \pm 0.02$. These freely fitted values are in good agreement with experimental data: The g-value is close to the value expected for the U^{3+} free ion ($g = 0.74$ in intermediate coupling), the J-coefficient is close to the one expected for a doublet ground state ($J = 2$), and the T_C-value is close to the values inferred from magnetization and specific heat measurements.

The extrapolation of Arrott plots (see the inset in Figure 3) indeed provides a similar value, $T_C = 1.6 \pm 0.1$, in excellent agreement with the heat capacity data. For comparison, other uranium based halogenides all undergo antiferromagnetic ordering transitions, such as UCl_3 ($T_N = 6.5$ K), UBr_3 ($T_N = 5.3$ K),[8] and UI_3 ($T_N = 2.6$ K).[9,10]

In the paramagnetic state, UF_3 follows a Curie−Weiss law with an effective magnetic moment very close to that expected for U^{3+} (~3.68 μ_B, although also very close to U^{4+}) in intermediate coupling. The strongly negative paramagnetic Curie temperature ($\Theta_p = -70$ K) suggests the presence of antiferromagnetic interactions; however, the ground state of the system turns out to be ferromagnetic as manifested by the observed and fitted values of T_C.

In Figure 2 we have compared the specific heat curve obtained in this study with the data reported by Cordfunke et al.[6] As discussed earlier, there is a good agreement between both sets of data, our data being slightly lower as shown in the inset graph of Figure 2. This small discrepancy has also an effect on the absolute entropy at 298.15 K which results in 123.4 J K^{-1} mol^{-1} in the case of the work of Cordfunke et al.[6] and 126.8 J K^{-1} mol^{-1} in the present case (eq 3). Although slightly lower values of specific heat were found in this study, the higher entropy is caused by the magnetic transition at 1.59 K which was not considered in the case of Cordfunke et al.[6] The value obtained in our study was compared with the calculation made by Konings[7] who correctly predicted that a low temperature transition with *Rln*2 contribution to the entropy should be considered, confirmed by our experiment. His estimate of the absolute entropy at 298.15 K was 130.58 J K^{-1} mol^{-1} based on the measurements by Cordfunke et al.,[6] somewhat higher than our measured value.

The excess heat capacity, $C_{p,mag}$, related to the ferromagnetic ordering was obtained by the subtraction of electronic and lattice contributions ($C_{p,lat}$; $C_{p,el}$) from the total heat capacity. The lattice contribution in the range of the transition is described by $C_{p,lat} = 7.0 \times 10^{-4} \cdot T^3$ whereas $C_{p,el} = \gamma_{el} \cdot T$, and it was assumed that both contributions are independent of the applied magnetic field. An example of thus obtained $C_{p,mag}/T$ as a function of temperature at 0 T field is shown in Figure 5. The inset graph of the figure shows the magnetic entropy obtained from the integral of the $C_{p,mag}/T$ curve calculated for several different magnetic fields.

Furthermore, the same graph shows that the excess entropy caused by the ferromagnetic transition saturates at 5.68 J K^{-1} mol^{-1}, very close to the theoretical value of U^{3+} ion corresponding to the $R \ln 2 = 5.76$ J K^{-1} mol^{-1}. This indicates that the ground state of UF_3 is a doublet which is corroborated by the Brillouin fit of the magnetization (yielding an effective J close to 2). This confirms what has been shown by Karbowiak and Drozdzynski[11] that the $_4I^{9/2}$ configuration of U^{3+} splitting by the crystal field results in a doublet ground state well separated (~142 K) from the first excited doublet.

5. CONCLUSIONS

In summary, three different experimental techniques have been used in this study to understand thermodynamic and magnetic properties of the UF_3 compound. For the first time, exact values of the specific heat are provided over a broad range of temperature (0.5−350 K). From the very low temperature results ($T < 15$ K) the Sommerfeld coefficient was determined as $\gamma_{el} = 22$ mJ K^{-2} mol^{-1}. Furthermore, the specific heat results revealed a λ-type transition at 1.59 K which is due to the ferromagnetic ordering as confirmed by measuring magnetization and specific heat in the field up to 13 T. The experimentally determined magnetic entropy was found 5.68 J K^{-1} mol^{-1} suggesting that the ground state of UF_3 is a ferromagnetic doublet. With this contribution taken into account, the absolute entropy at 298.15 K was determined as 126.8 J K^{-1} mol^{-1}.

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■ ACKNOWLEDGMENT

The authors wish to thank Dr. van Genderen for a fruitful discussion about the low temperature adiabatic calorimeters as well as M. Sierig for the technical support provided for the heat capacity measurements. N.R.G. Petten is thanked for providing us the sample.

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