# HEAT CAPACITY AND CRYSTAL FIELD MODEL FOR THE URANIUM AND THORIUM OXYCHALCOGENIDES ANOY (An = Th, U - Y = S, Se)

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Heat capacity of the oxychalcogenides UOS and UOSe (low temperature antiferromagnets) has been measured as well as heat capacity of the non-magnetic isomorphous ThOS and ThOSe. From these data, values of the entropy of ordering (close to  $R \ln 2$ ) and Schottky contributions have been calculated for the uranium compounds. These results as well as previously observed magnetic properties are interpreted in a point charge crystal field model for  $U^{4+}$  ions. This model has been extended to UOTe. The electric charges considered in the model are – either limited to the first neighbour polyedron only – or extended to the whole lattice.

## 1. Introduction

The uranium oxychalcogenides UOY (Y = S, Se, Te) form a class of compounds with similar structural and magnetic properties (fig. 1). They all belong to the tetragonal PbFCl-type crystal structure (space group P4/nmm) and become antiferromagnetic at low temperatures [1-3]. The magnetic moments of the U atoms in all three compounds are aligned with the *c*-axis with a type 1A stacking order (+ + - -) in UOS and UOSe [1-2] whereas the order is type 1 (+ - + -) in UOTe [4].

Scientific and Technical Fellowship of the EEC, Brussels, Belgium; on leave from the University of Lièges, Belgium. The effective moment values in the high temperature range are in good agreement with a 4 + valency for the U atoms:  $5f^2$  configuration and  ${}^{3}H_{4}$  ground term (*R*-*S* coupling). But the ordered moment values deduced from neutron diffraction and the curvatures observed in the Curie-Weiss plots of the susceptibility have been interpreted by crystal field splitting with a quasi triplet ground state [5]. On the other hand, specific heat measurements on UOTe by Stalinski et al. [6] result in a magnetic ordering entropy of 4.48 J/mol K, smaller even than the entropy of ordering for a doublet.

The present work was undertaken to provide comparison and further check of the ground-state

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Fig. 1. Coordination polyedron for the AnOY series.

multiplicity by low temperature measurements of the heat capacity for UOS and UOSe. In order to get a more reliable value of their magnetic entropy, heat capacities of the non-magnetic isomorphous ThOS and ThOSe were measured to be used as references for the lattice contributions. Based on the point charge model and molecular field approximation, the crystal field splitting of the uranium compounds was then calculated. The resulting Schottky anomalies and magnetic entropies of ordering are compared to the experimental results in the discussion of this paper.

## 2. Experimental

The preparation of the samples was carried out at Wroclaw.

All of the compounds were prepared by mixing stoichiometric amounts of the suitable dioxides and dichalcogenides. The mixtures were then placed in aluminium crucibles and annealed at 1000 °C for three days in evacuated quartz tubes.

The resulting products were observed by Debye-Scherrer X-ray diffraction and belonged all to the PbFCl structure with parameters close to the literature values.

A more detailed analysis was carried out at the "Laboratoire de Chimie Analytique et Radiochimie", University of Liège (Belgium) for three compounds (UOS, ThOS, ThOSe). The X-Ray diagram showed for UOS three weak extra lines belonging to UC<sub>2</sub> and US<sub>2</sub> spectra, for ThOS a weak extra line belonging to ThO<sub>2</sub>, and for ThOSe several non-identified very weak extra lines.

Spark mass spectroscopy resulted in the total impurity contents per molecule of the compound: 1 at% for UOS, 1.3 at% for ThOS, 0.3 at% for ThOSe. The individual impurity contents were less than 0.1 at% per molecule except for: Si: 0.3% for all compounds, Al: 0.8% in ThOS, Zn and Ca: 0.2% of each in UOS.

Three samples (UOS, UOSe, ThOSe) were sent to Harwell and one (ThOS) to Grenoble for the heat capacity measurements. All samples were in powder form and were kept in evacuated glass ampoules till the final conditioning which took place in helium atmosphere.

For Harwell, the compound was carefully mixed with very pure silver powder in the approximate weight ratio 2:1. A kind of silver cage made up from two silver plates linked by silver wires was then placed in a die and filled up with the above mixture. The whole thing was cold pressed under 4 tons and resulted in a pellet with a total weight of about 6 g and a weight ratio: silver 1: compound 1.

For Grenoble, no silver cage was used but a powder mixture with an equal amount of Ag and ThOS and a total weight of around 3 g.

The apparatus used at Harwell and Grenoble were different but their accuracy is similar and close to 1%: taking into account the ratios of the relative masses of the sample and silver, the final errors on the samples must be about  $\pm 2\%$ .

At Harwell, the equipment for the temperature range 1.5 to 20 K relies upon a transient method using a brass strip to connect the sample to the cold source [7]. From 8 to 300 K, the device is a dynamic calorimeter described in ref. [8]. At Grenoble, a single differential dynamic adiabatic calorimeter covers the range 5 to 300 K [9].

#### 3. Results and analysis of the data

Several runs were made on each compound. The data were smoothed into a single set of ther-

Table 2

Thermodynamic functions for ThOS

Table 1Thermodynamic functions for UOS

Ī	C <sub>p</sub>	S	
(K)	(J/mol K)	(J/mol K)	(K)
5.0	0.03	0.02	5.0
10.0	0.23	0.09	10.0
15.0	0.96	0.30	15.0
20.0	2.27	0.73	20.0
25.0	4.59	1.47	25.0
30.0	7.54	2.56	30.0
35.0	11.04	3.98	35.0
40.0	15.01	5.71	40.0
45.0	19.48	7.73	45.0
50.0	25.00	10.05	50.0
60.0	22.22	15.04	60.0
70.0	25.47	18.68	70.0
80.0	29.62	22.35	80.0
90.0	33.82	26.09	90.0
100.0	37.77	29.86	100.0
110.0	41.58	33.64	110.0
120.0	44.93	37.40	120.0
130.0	47.99	41.12	130.0
140.0	50.99	44.79	140.0
150.0	53.89	48.40	150.0
160.0	56.53	51.97	160.0
170.0	58.95	55.47	170.0
180.0	61.23	58.90	180.0
190.0	63.41	62.27	190.0
200.0	65.46	65.58	200.0
210.0	67.33	68.82	210.0
220.0	68.98	71.99	220.0
230.0	70.37	75.09	230.0
240.0	71.54	78.11	240.0
250.0	72.62	81.05	250.0
260.0	73.63	83.92	260.0
270.0	74.44	86.71	270.0
280.0	75.15	89.43	280.0
290.0	75.79	92.08	290.0
300.0	76.31	94.66	300.0

Т	$C_{n}$	S
(K)	(J/mol K)	(J/mol K)
5.0	0.00	0.00
10.0	0.13	0.03
15.0	0.66	0.17
20.0	1.59	0.48
25.0	2.86	0.96
30.0	4.41	1.62
35.0	6.17	2.43
40.0	8.09	3.38
45.0	10.09	4.44
50.0	12.15	5.61
60.0	16.37	8.20
70.0	20.61	11.04
80.0	24.76	14.07
90.0	28.70	17.21
100.0	32.41	20.43
110.0	35.86	23.68
120.0	39.04	26.94
130.0	41.95	30.18
140.0	44.60	33.39
150.0	47.03	36.55
160.0	49.25	39.66
170.0	51.29	42.71
180.0	53.17	45.69
190.0	54.92	48.62
200.0	56.55	51.47
210.0	58.08	54.27
220.0	59.50	57.01
230.0	60.82	59.68
240.0	62.01	62.29
250.0	63.10	64.85
260.0	64.09	67.34
270.0	65.01	69.78
280.0	65.85	71.92
290.0	66.64	74.24
300.0	67.37	76.52

modynamical values. The four sets are given in tables 1 to 4. In fig. 2  $C_p(T)$  for UOS is compared to the curve for ThOS whereas the corresponding plots for the selenides are given in fig. 3.

All four curves show the normal sigmoid form with superimposed  $\lambda$ -shaped peaks for UOS and UOSe. The temperatures of  $C_{p\max}$  are compared to the temperatures of the maximum susceptibilities in table 5 (together with  $T(\rho\max)$  for UOSe). The values of  $C_p$  and the entropy S at the standard room temperature 298.15 K are equally listed in table 5.

## 3.1. Low temperature analysis

Below 13 K, the usual  $(C_p/T)(T^2)$  curves were plotted for the Harwell data. The electronic heat capacity coefficients  $\gamma(0)$  and Debye temperatures  $\theta_D$  obtained from the intercepts and slopes of the straight line low temperature extrapolations are given in table 5.

The uranium oxychalcogenides are generally considered as semi-conductors according to electrical conductivity measurements on pressed powder samples [2,10] and the thorium oxychalcogenides

Table 4

Thermodynamic functions for ThOSe

 Table 3

 Thermodynamic functions for UOSe

T	C <sub>n</sub>	S	<i>T</i>
(K)	(J/mol K)	(J/mol K)	(K)
5.0	0.04	0.02	5.0
10.0	0.26	0.09	10.0
15.0	1.18	0.34	15.0
20.0	3.09	0.94	20.0
25.0	5.71	1.89	25.0
30.0	8.70	3.20	30.0
35.0	11.91	4.76	35.0
40.0	15.96	6.62	40.0
45.0	19.91	8.72	45.0
50.0	24.30	11.05	50.0
60.0	34.22	16.32	60.0
70.0	48.66	22.57	70.0
80.0	39.01	27.84	80.0
90.0	42.33	32.63	90.0
100.0	45.90	37.28	100.0
110.0	48.94	41.80	110.0
120.0	51.92	46.19	120.0
130.0	54.62	50.45	130.0
140.0	57.38	54.60	140.0
150.0	59.92	58.64	150.0
160.0	62.39	62.59	160.0
170.0	64.62	66.44	170.0
180.0	66.65	70.19	180.0
190.0	68.73	73.85	190.0
200.0	70.58	77.43	200.0
210.0	72.23	80.91	210.0
220.0	73.72	84.30	220.0
230.0	75.09	87.61	230.0
240.0	76.35	90.83	240.0
250.0	77.52	93.98	250.0
260.0	78.60	97.04	260.0
270.0	79.59	100.02	270.0
280.0	80.52	102.93	280.0
290.0	81.40	105.77	290.0
300.0	82.24	108.55	300.0

Т	$C_{p}$	S
(K)	(J/mol K)	(J/mol K)
5.0	0.02	0.01
10.0	0.17	0.05
15.0	0.81	0.22
20.0	2.13	0.62
25.0	4.08	1.29
30.0	6.53	2.24
35.0	9.36	3.46
40.0	12.41	4.90
45.0	15.57	6.55
50.0	18.72	8.35
60.0	24.71	12.30
70.0	29.93	16.52
80.0	34.46	20.81
90.0	38.47	25.11
100.0	42.07	29.35
110.0	45.32	33.52
120.0	48.21	37.59
130.0	50.79	41.55
140.0	53.14	45.40
150.0	55.28	49.14
160.0	57.15	52.77
170.0	58.87	56.29
180.0	60.58	59.70
190.0	62.17	63.02
200.0	63.53	66.24
210.0	64.88	69.37
220.0	65.96	72.42
230.0	67.03	75.37
240.0	67.94	78.25
250.0	68.84	81.04
260.0	69.64	83.76
270.0	70.45	86.40
280.0	71.33	88.98
290.0	72.13	91.49
300.0	72.75	93.95

are likely insulators. The interpretation of the non-zero  $\gamma(0)$  values is thus not obvious. Going back to the measurement method, one must consider that, at very low temperature only 17% of the measured heat capacity is due to the sample. The rest is cryostat addenda (46%) and silver (37%). Because they are mainly metallic, they have an electronic coefficient and dominate the total. A small error in the addenda could reduce the  $\gamma$  value for ThOSe to zero as expected and reduce the values for UOS and UOSe by 1 to 2 mJ/molK<sup>2</sup>. However, this reduction can certainly not reduce

all the  $\gamma$  values to zero. There remains probably in UOS and UOSe some impurity effects although few metallic impurities have been detected in the former.

The  $\theta_D$  values were calculated assuming that 9NDebye modes contribute to the phonon term of the heat capacity. No comparison can be made with the data of ref. [6] who worked on UOTe in the temperature range 21-326 K. The Grenoble data on ThOS are too imprecise below 10 K to allow any kind of evaluation of  $\gamma(0)$  and  $\theta_D$ . The  $\theta_D$ values for both uranium compounds are compara-



Fig. 2. Specific heat of UOS and ThOS.

ble to one another (306 and 316 K, respectively) but far smaller than  $\theta_D$  (ThOSe) (368 K). Bearing in mind the low Néel temperatures of UOS and UOSe, this feature reflects the existence of a nonnegligible magnetic contribution to the low temperature specific heat.

We have tried to calculate this contribution



Fig. 3. Specific heat of UOSe and ThOSe.

 $C_{\text{mag}}$  in UOSe by simply assuming:

$$C_p(\text{UOSe}) - C_p(\text{ThOSe}) = C_{\text{mag}} + CT, \qquad (1)$$

with C a constant.

The theoretical low temperature approximations to  $C_{\text{mag}}$  lead: for Heisenberg models, to a  $T^3$ 

Table 5

Characteristic values for the heat capacity and entropy of UOS, UOSe, ThOSe and ThOS

	UOS	ThOS	UOSe	ThOSe	
$\frac{\overline{C_p \max}}{(J/\operatorname{mol} K)}$	35.6	_	49.5		
$T(C_p \max)$ (K)	55.35	-	69.80	_	
$T(\chi \max)(\mathbf{K})$	55.0 56.5 [1] [14]	-	74.0 [14]	_	
$T(\rho \max)(\mathbf{K})$	-	-	90.0 [2]	-	
$C_p(298.15)$ (J/mol K)	76.23	67.25	82.10	72.65	
S(298.15) (J/mol K)	94.20	76.34	108.04	93.50	
$\gamma(0)$ (mJ/mol K <sup>2</sup> )	2.0	-	3.1	1.0	
$\theta_{\rm D}(0)$ (K)	306	-	316	368	
$A \times 10^{5}$	0.14	0.14	0.25	0.25	
θ <sub>D</sub> (300) (K)	500	500	400	400	
S <sub>mag</sub> (J/mol K)	6.3	-	5.1	-	

law; for Ising models, to:

$$C_{\rm mag} = \frac{2qJ^2}{T} \left( \exp \frac{-2qJ}{T} + \dots \right), \tag{2}$$

J: exchange constant, q: coordination number.

Computer fits of (1) to these expressions give a good agreement with the Ising term (2) only, with 2qJ = 140 K (and  $C = 2 \times 10^{-3}$  J/mol K as expected from table 5). The fitting involves an iterative process for qJ and C and results in a standard deviation of 0.017 over the temperature range 2-40 K.

## 3.2. High temperature analysis

At high temperature, a striking feature of figs. 2 and 3 is the large difference between  $C_p$  for the Th and U corresponding compounds. This difference at 298.15 K is  $C_p = 8.98$  and 9.44 J/mol K for the sulfides and selenides, respectively.

We remind the general high temperature expression for the heat capacity at constant pressure:

$$C_p = C_{\rm dil} + C_{\rm latt} + C_{\rm lin} + C_{\rm mag} + C_{\rm Schot}, \qquad (3)$$

where:  $C_{dil}$ : dilation term accounting for the thermal lattice expansion;  $C_{latt}$ : lattice contribution;  $C_{lin} = \gamma T$ : linear contribution (usually due to conduction electrons);  $C_{mag}$ : magnetic contribution coming from the cooperative transition;  $C_{Schot}$ : Schottky term coming from the contribution of the excited electronic states.

Let us compare these terms for a uranium compound and the non-magnetic thorium isomorphous:

 $(C_{dil} + C_{latt})$  are likely very similar;

 $C_{\text{lin}}$  should be very small or 0 as seen in section 3.1;

 $C_{\text{mag}}$  only present in the uranium compounds expands as  $1/T^2$  and must be negligible far above  $T_{\text{ord}}$ .

The only unmatched contribution must thus be a Schottky term originating from the excited crystal field levels of the uranium ion. A theoretical calculation of  $C_{\text{Schot}}$  will be presented in section 4, based on a point charge model for the tetragonal  $C_{4v}$  symmetry. The theoretical predictions of this model will be compared to the experimental data and discussed in section 5. Let us now come to an estimate of the different contributions to the specific heat in eq. (3).

For the thorium oxychalcogenides, the last two terms in (3) disappear. We then make the reasonable assumptions [11]:

 $C_{\rm dil} = A C_p^2 T (A : a \text{ constant});$ 

 $C_{\text{latt}} = \text{Debye function.}$ 

A computer fitting to the experimental values leads to the constants A(300) and  $\theta_D(300)$  given in table 5. The agreement with the  $\gamma(0)$  and  $\theta_D(0)$  values is satisfactory for ThOSe.

For the uranium oxychalcogenides, the same process may be applied using calculated values for  $C_{\text{Schot}}$  ( $C_{\text{mag}}$  is negligible at high T). The fitting is repeated to get self-consistency and the agreement obtained for  $\gamma(300)$  with the  $\gamma(0)$  derived in section 3.1 is still good. The  $\theta_D(300)$  values are very different from the  $\theta_D(0)$  as predicted in section 3.1 but there is an excellent accord of the  $\theta_D(300)$ within each couple UOY/ThOY as expected from the similarity of the lattices. Similarly, one verifies in table 5 that the A values are identical for each couple UOY/ThOY.

## 3.3. Complete analysis

Let us denote:

$$C_v = C_p - C_{\rm dil} - C_{\rm lin} \tag{4}$$

As the last two terms in (4) are now known, we can calculate  $C_v$  starting from the measured  $C_p$  for all four compounds.

Eq. (3) can be rewritten for two isomorphous compounds in the full range of temperature:

$$C_v^{\text{UOY}} - C_v^{\text{ThOY}} = C_{\text{latt}}^{\text{UOY}} - C_{\text{latt}}^{\text{ThOY}} + C_{\text{mag}}^{\text{UOY}} + C_{\text{Schot}}^{\text{UOY}}$$
(5)

The commonly used "corresponding states" approximation assumes that:

$$C_{\text{latt}}^{\text{UOY}}(T) = C_{\text{latt}}^{\text{ThOY}}(KT)$$
(6)

with K a constant.

The K constants determinations and the full fit of experimental results to eq. (5) will be discussed in section 5.

Table 6 The calculated crystal field parameters (cm<sup>-1</sup>) for the uranium oxychalcogenides (reference frame rotated  $\pi/4$  around c with respect to the crystallographic axes)

	<b>B</b> <sup>0</sup> <sub>2</sub>	<b>B</b> <sup>0</sup> <sub>4</sub>	B <sub>4</sub> <sup>4</sup>	<b>B</b> <sub>6</sub> <sup>0</sup>	B <sub>6</sub> <sup>4</sup>
UOS (LS)	-0.9612	0.2137	0.3548	0.3931×10 <sup>-2</sup>	$-0.5072 \times 10^{-1}$
UOSe (NN)	$0.2030 \times 10^{1}$	0.2361	0.7598	$0.3186 \times 10^{-2}$	$-0.3953 \times 10^{-1}$
UOTe (NN)	$0.2999 \times 10^{1}$	0.2364	$0.1071 \times 10^{1}$	$0.3161 \times 10^{-2}$	$-0.3547 \times 10^{-1}$

#### 4. Crystal field model

Due to the ionic character of these compounds, we can tentatively calculate the parameters of the crystal field (CF) Hamiltonian by means of a point charge approach to obtain the energy levels scheme along the series of compounds (UOTe has been included for completeness).

The CF-Hamiltonian for the uranium ion in a

C4v tetragonal symmetry is given by

$$\mathscr{H}_{\rm CF} = B_2^0 \hat{O}_2^0 + B_4^0 \hat{O}_4^0 + B_4^4 \hat{O}_4^4 + B_6^0 \hat{O}_6^0 + B_6^4 \hat{O}_6^4, \ (7)$$

where the  $B_n^m$  are the CF-parameters and the  $\hat{O}_n^m$  the Stevens equivalent operators.

Assuming a 4 + valency for the uranium ions and a Russell-Saunders coupling scheme, the  $B_n^m$ coefficients have been calculated using a computer



Fig. 4. Schematic representation of the energy levels and wave functions for the uranium oxychalcogenides. The cubic limit is shown in the case of UOSe ( $|M\rangle$  is a short notation for  $|J, M\rangle$ ).

program previously developed and able to take into account either the nearest neighbours or the whole lattice (table 6). The values of  $\langle r^n \rangle$  given in ref. [12] have been used and the Sternheimer factors taken from ref. [13] have been included in the calculation. The CF-splitting of the <sup>3</sup>H<sub>4</sub> ground term of the U<sup>4+</sup> ions has been calculated using the lattice sum (LS) results for UOS (in better agreement with the specific heat Schottky anomaly) and the nearest neighbours (NN) for UOSe and UOTe. The energy levels and the composition of the CFstates are shown in fig. 4 whereas the values of the coefficients for the wave functions are given in table 7.

For the three compounds, the sequence of the levels is the same and in particular the ground state is a  $\Gamma_{15}^{(1)}$  doublet, in fair agreement with the experimental values of the ordered magnetic moments as shown in table 7. The first excited state is a  $\Gamma_{t4}$  singlet which, together with the ground doublet comes from the splitting of a cubic  $\Gamma_5$ triplet. In fact, the hamiltonian (7) can easily be written as a cubic plus an axial term. The cubic levels and states are shown in fig. 4 in the case of UOSe. It is evident that the departure from the cubic case is not very important in agreement with the arguments of Ayant et al. [5]. This is due both to structural effects [5] and to the strong reduction of the quadrupolar axial parameter  $B_2^0$  owing to the Sternheimer shielding. We remark that, without this reduction, the ground state would be the  $\Gamma_{14}$ singlet which cannot give rise to the observed ordered moments.

The total energy splitting is of the order of 1000 K. This agrees with paramagnetic susceptibility

Table 7

Coefficients of the wave functions corresponding to the CF levels of fig. 4 and comparison between the calculated and experimental values of the ordered moments for the three uranium oxychalcogenides

	UOS	UOSe	UOTe
α	0.988	0.962	0.935
β	-0.156	-0.274	-0.353
γ	0.730	0.935	1.000
E	0.484	0.250	0.000
$\mu_{\rm ord}^{\rm calc}$	2.32	2.16	2.00
$\mu_{\rm ord}^{\rm exp}$	2 [1]	2.2 [2]	2.0 [4]



Fig. 5. Comparison between the experimental  $(C_v^{\text{UOS}} - C_v^{\text{ThOS}})$ (T) curve and the calculated Schottky contribution CS(T); dotted line: nearest neighbour approximation, full curve: lattice sum calculation.

measurements [14] at high temperature where  $1/\chi(T)$  tends towards the slope characteristic of the J = 4 full multiplet ( $\mu_{eff} = 3.58\mu_B$ ). A complete discussion of the magnetic properties of these compounds, both in the ordered and in the paramagnetic phase will be given in a future paper.

As regards specific heat, the CF-contribution can be calculated in a straightforward way from the energy levels scheme. The calculated values for  $T > T_{ord}$  are shown in figs. 5 and 6 for UOS and UOSe respectively, both with the LS and NN approaches. Comparison with the experimental data is given below.



Fig. 6. Comparison between the experimental  $(C_v^{\text{UOSe}} - C_v^{\text{ThOSe}})$ (T) curve and the calculated Schottky contribution CS(T); dotted line: lattice sum, full curve: nearest neighbour.

	$S_{c/R}$	$\frac{S_{\infty}-S_c}{R}$	$S_{\infty} - S_c$	$S_{\infty} - S_c \qquad E_0$	$E_c - E_0$	$\frac{-E_c}{RT_{\rm ord}}$	$\frac{-E_c}{E_c-E_0}$
				(J/mol)	RT <sub>ord</sub>		
UOS	0.610	0.145	0.238	293.1	0.471	0.170	0.361
UOSe	0.519	0.095	0.183	281.3	0.383	0.104	0.272
Ising model:							
cc(q=6)	0.558	0.135	0.242		0.445	0.220	0.494
bcc(q=8)	0.582	0.111	0.191		0.458	0.172	0.376
fcc $(q = 12)$	0.590	0.103	0.174		0.461	0.152	0.329

 Table 8

 Critical values for UOS and UOSe (see section 5.2 for definition of the variables)

#### 5. Discussion

5.1. Magnetic and Schottky contributions to the specific heat

According to eqs. (5) and (6) in 3.3, a good criterion for the choice of the theoretical function  $C_{\text{Schot}}(T)$  is provided by plotting  $(C_v^{\text{UOY}} - C_v^{\text{ThOY}})$  (T) on the same graph. These plots are given as figs. 5 and 6. The difference between  $C_{\text{Schot}}$  measured and calculated is only the  $\lambda$ -shaped magnetic peak and the high temperature "tails" must be homothetic. The results of the comparison are obvious in the figures and were a major reason to choose the LS model for the sulfide and the NN for the selenide.

Now, for each couple of compounds: UOY/ThOY, the constant K of eq. (6) has been determined in the following way. We start from a temperature well above  $T_{ord}$  so that  $C_{mag}$  can be neglected in (5). In these conditions:

 $C_{latt}^{ThOY} = C_{v}^{ThOY},$   $C_{latt}^{UOY} = C_{v}^{UOY} - C_{Schot}^{UOY}$ (8)

and eq. (6) can be checked. This process has been applied to both chalcogenides and gives with a good precision:

K = 1.054 (average value in the temperature range 90–270 K for UOY) for the sulfides and K = 1.045 (110  $\leq T \leq 280$ ) for the selenides.

Once K is calculated, the magnetic contribution  $C_{\text{mag}}$  is easily obtained from eq. (5), applied in the full temperature range, in the hypothesis that  $C_{\text{Schot}}$  can be neglected below  $T_{\text{ord}}$ .

The ordering temperature is well below the calculated energy splitting  $\Delta_1$  between the first excited singlet and the ground doublet. Therefore we expect that the entropy associated with the magnetic transition should correspond at least to the contribution of the doublet only, that is Rln2 = 5.76 J/mol K. The integration of  $C_{mag}/T$  from low temperature up to the disparition of the short range order gives the  $S_{mag}$  values in table 5.

While the UOS value is very reasonable, allowing for the proximity of the first excited singlet, for UOSe,  $S_{mag}$  is even smaller than the doublet value.

This was not expected because the ratio  $T_{\text{ord}}/\Delta_1$ is greater for UOSe than for UOS. In our opinion, this low  $S_{\text{mag}}$  value for UOSe must be attributed to the experimental errors in  $C_p$  and to the uncertainties in the determination of A and K. The errors due to both sources can amount up to  $\pm 0.8$  J/mol K.

For UOTe, Stalinski et al. [6] quoted the value  $S_{mag} = 4.48 \text{ J/mol K}$  which seems really too small if we consider that the singlet is probably involved in the magnetic transition ( $T_{ord} = 162 \text{ K}$ ). That the authors got such a low  $S_{mag}$  is not surprising as they had no realistic estimate for  $C_{latt}^{UOTe}$  and used Debye functions.

## 5.2. Magnetic phase transition and critical phenomena

Given  $C_{mag}(T)$ , it is interesting to compare its behaviour to the theoretical predictions concerning the phase transition for some simple models. Experimental errors as well as computational approximations used in our analysis of the data make hopeless a study of the critical coefficients close to  $T_{ord}$ . Instead, we shall concentrate on an estimate of the exchange constant J and on the behaviour of magnetic entropies and energies below and above  $T_{ord}$ .

In section 3.1, we found that the low temperature variation of the magnetic heat capacity followed the theoretical law for a three-dimensional Ising model. Such an assumption seemed justified as many ferromagnetic ternary tetragonal actinide compounds display a huge magnetic anisotropy. This character is generally explained by a strong f-p coupling forcing the moments to align along the orbital axis of symmetry, the *c*-direction.

It is interesting to make a further check of the 3d-Ising type interaction hypothesis. If we consider the quantities:

$$\frac{S_{\rm c}}{R} = \int_0^1 \frac{C_{\rm mag}}{\tau} \,\mathrm{d}\tau \quad \text{and} \quad \frac{S_{\infty} - S_{\rm c}}{R} = \int_1^\infty \frac{C_{\rm mag}}{\tau} \,\mathrm{d}\tau,$$
(9)

with  $\tau = T/T_{ord}$ , these quantities have been calculated for a series of simple crystallographic models for Heisenberg and Ising interactions [15]. Similarly, it is useful to tabulate:

$$\frac{(E_{\rm c} - E_0)}{RT_{\rm ord}} = \frac{1}{R} \int_0^1 C_{\rm mag} dr,$$

$$\frac{-E_{\rm c}}{RT_{\rm ord}} = \frac{1}{R} \int_1^\infty C_{\rm mag} d\tau$$
(10)

which represent directly the areas under the specific curve below and above  $T_{ord}$ . Relations (9) and (10) do not depend on the magnitude of J. They are reported in table 7 for UOS and UOSe together with the theoretical values for some simple cubic Ising lattices (no data are available for tetragonal lattices). The theoretical values for Heisenberg lattices are not given as they are well off-range of the experimental data. The Ising data have been taken for an ordered doublet. On the whole, table 7 shows a good agreement with the theoretical predictions with  $q \leq 8$  for UOS and  $q \geq 8$  for UOSe.

Still referring to section 3.1, an estimate of the constants occurring in the temperature law gave,

for UOSe, qJ = 70 K. With q = 8, this leads to an exchange constant: J = 8.8 K.

Although the actual system is not isotropic and can be defined not by one but by 4 exchange constants [1], just for the purpose of self-consistency, we can try to estimate an "average crystallographic exchange constant" [1] and to make use of the theoretical relationship (bcc lattice, Ising, spin 1/2):

$$T_{\rm ord}/qJ = 0.794.$$
 (11)

The corresponding J values are 8.6 K for UOS and 11 K for UOSe.

Within the same model, [15] shows the magnetic energy to be given by:

$$E_{\rm mag}/R \approx \frac{1}{2}qJ. \tag{12}$$

As  $E_{\text{mag}} = E_0$  from table 7, we get J = 8.8 K for UOS and 8.5 K for UOSe.

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