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SPECIFIC HEAT OF THE U AND Th OXYCHALCOGENIDES AnOY (An = U, Th ; Y = S, Se)

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ABSTRACT

The U oxychalcogenides UOY (Y = S, Se, Te) all belong to the PbFCl type crystal structure and become antiferromagnetic at low temperature [1-3].

The effective moments in the high temperature range are in agreement with a 4+ valency for the U atoms. However the ordered moment values deduced from neutron diffraction (2-2.2 μ_B) and the curvatures observed in the inverse susceptibility curves are indicative of a crystal field (CF) splitting of the ground multiplet.

Specific heat measurements were performed at Harwell (UOS, UOSe, ThOSe) and Grenoble (ThOS) on powder samples prepared in Wroclaw. All Cp (T) curves show the normal sigmoid form with superimposed λ-shaped peaks for UOS and UOSe. They also display large differences between the Cp values for each U and isomorphous Th compound. Typical values are given below.

		UOS	UOSe	ThOS	ThOSe
Cp(298.15)	[J/Mol.K]	76.23	82.09	67.25	72.65
S(298.15)	[J/Mol.K]	94.15	108.04	76.34	93.5
T_N	[K]	55.35	69.8		
C_{pmax}	[J/Mol.K]	35.6	49.5		

After estimation of dilatation terms and conversion of Cp into Cv, the high temperature, $\Delta C_v = C_v(UOY) - C_v(ThOY)$ plots (Fig. 1 and 2) show the characteristic behaviour of a magnetic + Schottky term, as the residual contribution at $T > T_N$ cannot be reasonably attributed to a difference in the lattice specific heats of U and Th compounds.

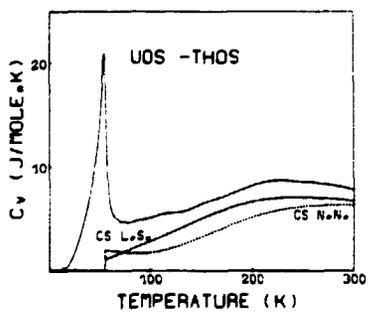
To give an estimation of the Schottky term the CF-splitting has been calculated in the PCM approximation for UOY (Y = S, Se, Te) compounds. The

Sternheimer shielding factors have been taken into account. The calculation has been carried out in two limits : either the nearest neighbours (n.n.) are taken into account or the integration extends to the whole lattice (l.s.). The model gives a ground $\Gamma_{t5}^{(1)}$ doublet and a first excited singlet Γ_{t4} with an energy separation of 226 K, 102 K and 58 K respectively for the three compounds. The remaining states are well separated from the ground pair ($\gtrsim$ 750 K, except $\Gamma_{t1}^{(1)}$ for UOS which lies at 530 K) and the total splitting is about 1000 K. The model accounts well for the ordered moments of the UOY compounds and for the trend and order of magnitude of T_N in a molecular field approach.

The available susceptibility data also agree qualitatively with a ground doublet-singlet system [4].

The Schottky contribution calculated from the model is in fair agreement with the experimental behaviour of ΔC_v if the lattice sum results are choosen for UOS and the n.n. ones for UOSe in the theoretical model (Fig. 1 and 2).

Fig. 1



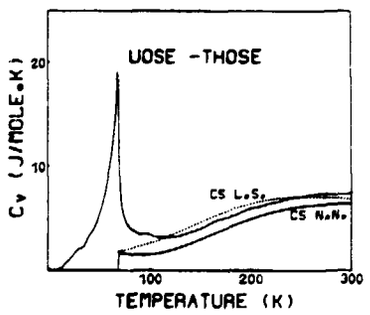


Fig. 2

Values of the magnetic entropy can be estimated from the experimental curves. The agreement with the calculated values, corresponding to a quasi-triplet ground state, is satisfactory. A low experimental value for UOSe could be indicative of a splitting of the first excited singlet greater than the calculated one.

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