LOW TEMPERATURE SPECIFIC HEAT OF ThU

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ABSTRACT

The low temperature specific heat of the weakly magnetic system ThU has been measured in both the normal and superconducting states. U impurities are found to enhance the normal state electronic specific heat coefficient γ at an unusually large rate of 4.85 ± 0.50 mj / mole $^{\circ}K^2$ at. % U. The specific heat jump at the superconducting transition for an alloy of composition 0.075 at. % U follows the BCS law of corresponding states suggesting that the system ThU is essentially nonmagnetic at superconducting temperatures.

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It has recently been shown[1] that dilute <u>Th</u> U alloys exhibit normal and superconducting state anomalies due to U 5f moments similar to those which have been observed for 3d solutes dissolved in noble and simple metal hosts. U impurities in Th, like Mn impurities in Al for example, are weakly magnetic. This was established by measurements of the normal state electrical resistivity, magnetic susceptibility, thermo-electric power, and the depression of the superconducting transition temperature. In order to gain further information concerning the magnetic character of this interesting system we have measured the low temperature specific heat of a series of <u>Th</u> U alloys in the normal and superconducting state.

Samples were prepared from 99.95% pure Alfa Inorganics-Ventron thorium and high purity Los Alamos uranium by arc melting in an argon atmosphere. In spite of the large size of the samples (∿ 11 gms), inhomogeneities in U concentration were deduced to be satisfactorily small. The T_c's, as measured by an a.c. mutual inductance technique, were somewhat broader than, but in agreement with, previous measurements[1] on much smaller samples (∿ 50 mg.).

The low temperature specific heat was measured in a He^3 calorimeter, described elsewhere.[2] Temperature were determined with a Cryocal 250 Ω germanium resistor calibrated against (1) a precalibrated Cryocal 1000 Ω germanium resistor from 10 °K to 4.2 °K, (2) the vapor pressure of He^4 from 4.2 °K to 1.5 °K, and (3) a CMN magnetic thermometer below 1.5 °K. 64 calibration points between 0.35 °K and 5.6 °K were fitted to the expression

$$\ell n\ T = \sum_{0}^{6} ai\ (\ell n\ R)^{i}$$

with a maximum relative deviation of 2×10^{-3}. The reproducibility of the resistor was found to be better than 10^{-3} °K.

For each sample, between 30 and 45 specific heat points were taken in the temperature range 1.5 °K to 5.0 °K which could be fitted to the expression

$$C_V = \gamma T + \beta T^3$$

within the experimental error. We give in Table I the resulting values of γ and β as deduced by a least-squares fit to the data for the three Th U samples measured. For pure Th, γ is in fair agreement and β in good agreement with the values previously reported by Gordon et al.[3] The disagreement in γ may be due to the different temperature ranges covered in the two experiments.

Also presented in Table I are the values for the specific heat jump ΔC at T_c of pure Th and one Th U alloy of composition 0.075 at. % U. Our ΔC_o for pure Th agrees well with that found in the aforementioned work of Gordon et al. Figure 1 shows that the variation of $\Delta\gamma$ vs γ_o with U concentration is linear in the concentration range studied with an average slope of $d\gamma/dn = 4.85 \pm 0.50$ mj/mole °K² at. % U.

That $d\gamma/dn$ is so large is perhaps the most striking feature of the low temperature specific heat of Th U . In Table II, we compare this with the values of $d\gamma/dn$ for several other dilute alloy systems previously reported in the literature. A similarly large value (3.31 mj/mole °K² at. % U) has been observed only for the related pseudo-binary system (Th U) Al_2.[4]

If one assumes that the increase in γ is due to the formation of resonant states at the impurity sites, the relationship between $d\gamma/dn$ and the local density of states at the Fermi level $N_\ell(0)$ (ℓ corresponds to d or f states) is given by

$$\frac{d\gamma}{dn} = \frac{2\pi^2}{3} k_B^2 N_\ell(0) \qquad (1)$$

where k_B is Boltzmann's constant. Values of N_ℓ (0) deduced from expression (1) are given in Table II for the various dilute alloy systems indicated therein. For the system Th U, N_ℓ (0) equals a very large 103 states / e V - atom U.

Also given in Table I are the characteristic temperatures T_o for those systems which exhibit weakly magnetic behaviour. T_o is determined from the impurity contribution to the low temperature electrical resistivity which varies with temperature as

$$\Delta\rho = \rho_o \left[1 - (T/T_o)^2 \right] \qquad (2)$$

It is interesting to note that the increase of $d\gamma / dn$ in the sequence AlMn to Au V to Th U is correlated with a corresponding decrease of T_o. This follows from models[5] which attribute the weakly magnetic nature of these systems to localized spin fluctuations. For such models, the effective resonant state level half width Δ_{eff} is narrowed by the presence of spin fluctuations. T_o and N_ℓ (0) are expected to be of the order of Δ_{eff}/k_B and Δ_{eff}^{-1}, respectively, which accounts for their sequential inversion. For Th U, the values of $d\gamma / dn$ and T_o imply that $\Delta_{eff} \sim 0.01$ eV.

If, rather than the resonant state interpretation, Th U is regarded as a Kondo system, the apparent enhancement of γ with increasing U concentration may be due to a linearly temperature dependent low temperature ($T << T_k$, where $T_k \sim T_o$ is the Kondo temperature) tail of a specific heat anomaly which presumably would show a peak at $T \sim T_k$.[5]

Additional information regarding the magnetic character of U impurities in Th comes from the specific heat jump ΔC at the superconducting transition. Were the depression of T_c due to pair weakening interaction (such as the Coulomb repulsion between the spin up and spin down electrons of a Cooper pair) the reduced specific heat jump $\Delta C / \Delta C_o$ (where ΔC_o is the specific heat jump for the Th matrix) should follow the BCS law of corresponding states (i.e., $\Delta C / \Delta C_o = T_c / T_{co}$, where T_{co} is the transition temperature of the Th matrix). On the other hand, if the depression is caused by pair breaking interactions (i.e., spin dependent exchange scattering of conduction electrons by well-defined local moments associated with magnetic impurities), $\Delta C / \Delta C_o$ vs. $T_c\ T_{co}$ is not expected to follow the law of corresponding states. We show in Fig. 2 the reduced specific heat jump of a Th U sample of composition 0.075 at. % U along with, for comparison, the reduced specific heat jumps of Th Ce,[6] Th Gd,[7] and Al Mn.[8] The data for Th U, Th Ce and Al Mn all lie near the BCS law of corresponding states curves, whereas that for Th Gd follows the curve predicted by the pair breaking theory of Abrikosov and Gorkov[9] as calculated by Skalski et al.[10]

The $\Delta C / \Delta C_o$ vs. T_c / T_{co} behavior of Th Ce has been regarded as evidence that this system in nonmagnetic at superconducting temperatures.[11] The results shown in Fig. 2 imply that Th U and Al Mn are also essentially nonmagnetic at superconducting temperatures. This conclusion was previously inferred from the detailed T_c vs. n curves of Th Ce, Th U, and Al Mn which all exhibit relatively strong depressions of T_c which fall more slowly than linearly with n.[12] It was suggested[12] that this may be a general behavior for systems where $T_o >> T_{co}$ (T_o appears to be inmeasurably large in the Th Ce system). This is in marked contrast to the Th Gd system for which T_c vs. n is in good agreement with the behavior predicted by the AG pair-breaking theory.[13]

It is noteworthy that the experimental T_c vs. n curves for Th Ce, Th U, and Al Mn are described well by a recent theory due to Kaiser[14] concerning the effect of nonmagnetic resonant states on superconductivity. This theory predicts a modified exponential relationship between T_c and n and a BCS law of corresponding states. An analysis of the superconductivity of Th Ce[11] using the Kaiser model gives a value for the local density of states N_ℓ (0) of 4.86 states / eV - atom, which agrees reasonably well with the 7.6 states / e V- atom determined from the specific heat. Kaiser's model, however, when applied to Th U, gives a negligibly small value for N_ℓ (0), completely incompatible with the large value N_ℓ (0) = 103 states /e V - atom deduced from the specific heat. Although the form of the Kaiser expression for T_c vs. n is correct when localized spin fluctuations are present and $T_o \gg T_{co}$, the parameters of the theory (e.g., N_ℓ (0) and the intra-atomic Coulomb repulsion U_{eff}) apparently require renormalization.

Finally, we should mention that Müller-Hartmann and Zittartz[15] have obtained a stisfactory fit to the experimental T_c vs. n curve of Th U within the framework of the exchange model for $T_k / T_{co} = 32$ (orbital moments are neglected and it is assumed that the impurity spin $\underset{\sim}{S}$ equals unity). The measured value of T_o/T_{co} [where T_o is obtained from expressión (2)] is ~ 70, so it is not unreasonable to associate T_o numerically with T_k. However, this is a pair breaking model with the exchange Hamiltonian $H_{int.} = - 2J\underset{\sim}{S}\cdot\underset{\sim}{s}$ (J is the exchange interaction parameter and $\underset{\sim}{s}$ is the conduction electron spin density at the impurity site) breaking time-reversal symmetry.

Thus, it would seem surprising if the BCS law of corresponding states held for any value of T_k / T_{co} (the AG curve would correspond to the limit $T_k / T_{co} \to 0$ in the model of Müller-Hartmann and Zittartz).
However, a definitive statement cannot be made until the specific heat jump at the transition is calculated as a function of T_k/T_{co}.

Measurements of the enhancement of γ in the normal state and the specific heat jump at the superconducting transition for a wider range of U concentrations are presently in progress and will be reported elsewhere.

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TABLE I

Sample	γ $\frac{mj}{mole\ °K^2}$	θ_D °K	$\Delta\gamma/n$ $\frac{mj}{mole\ °K^2\ at.\%}$	T_c °K	$\Delta C(T_c)$ $\frac{mj}{mole\ °K}$
Th (3)	4.31 ± 0.05	163.3 ± 0.07	-----	1.374	8.4
Th	4.08 ± 0.5	160.4 ± 0.5	-----	-----	8.6 ± 0.2*
0.075 at.% U	4.45 ± 0.08	161.3 ± 1.0	4.93	0.785	5.3 ± 0.3
0.134 at.% U	4.72 ± 0.04	163.7 ± 0.7	4.78	----	-----

* The specific heat jump was determined by assuming the T_c of reference (3) which lies within the temperature interval (0.04 °K) between adjacent superconducting and normal state experimental points for the Th sample measured in this work.

TABLE II

System	$d\gamma / dn$ $\frac{mj}{mole\ ^\circ K^2\ at.\ \%}$	$\gamma_o^{-1}\ (d\gamma/dn)$ $(at.\ \%)^{-1}$	$N_\ell\ (0)$ $\frac{States}{eV - atom}$	T_o $^\circ K$
Th U	4.85 ± 0.5	1.20 ± 0.10	103	100 (1)
(Th U) Al_2	3.31 (4)	2.11	70	?
Th Ce	0.36 (6)	0.087	7.6	-----
Au V	0.60 ± 0.10 (16)	0.87 ± 0.10	12.8	248 (17)
AlMn	0.44 ± 0.04 (18)	0.32 ± 0.04	9.4	530 (19)

FIGURE CAPTIONS

Figure 1 Change in γ versus U concentration in Th U

Figure 2 Reduced specific heat jump $(\Delta C/C_o)$ at T_c versus the reduced transition temperature (T_c/T_{co}) for Th U (this work), Th Ce (Dempesy[6]), Th Gd (Decker and Finnemore[7] measured from critical magnetic fields), and Al Mn (Martin[8]) alloys. The dashed curve represents the BCS law of corresponding states, whereas the solid line is the result of the Abrikosov-Gor'kov theory as calculated by Skalski et al.[10]

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