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EVIDENCE FOR 4f-INSTABILITY OF DILUTE TERBIUM IN THORIUM*

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We have measured the specific heat of dilute Th_{1-x}Tb_x alloys (0.44 < x < 2.15 a/o), which rises linearly between 0.4 and 0.9 K with a slope of $\Delta C/T \approx 450 \text{ mJ/K}^2 \text{ mol Tb}$ followed by a Schottky anomaly with a maximum near 3.8 K. The high temperature $\Delta\chi T$ product was found to be 4% lower than that of Tb³⁺. The resistivity shows no minimum at low temperatures. Discussion is made in terms of non-integral valence of Tb.

1. Introduction

The superconducting transition temperature T_c of Th with Tb impurities was reported to be a linear function of the Tb concentration x down to $T_c(x)/T_{c0} = 0.1$ ($T_{c0} = 1.37 \text{ K}$ is the T_c of pure Th) [1]. This linear dependence as well as $C(T)$ measurements on some of these alloys around $T \approx T_c$ [2] show that the ThTb dilute alloy system fits into the so-called moderate coupling regime [3]. This moderate coupling regime indicates a significant metallic instability of the 4f shell of the Tb impurities.

Although they have been searched for, so far 4f shell instabilities have not been found for Tb in metals. Therefore in order to better characterize this unexpected behavior of Tb in Th, we have measured the low temperature specific heat $C(T)$ at $0.4 \text{ K} < T < 6 \text{ K}$ of some ThTb alloys with $x = 0.44, 0.82, 1.02, 1.5 \text{ a/o}$ and the temperature dependence of the susceptibility at $0.05 \text{ K} < T < 1200 \text{ K}$ of the $x = 1.02$ and 2.15 a/o samples. The resistivity was measured for an alloy with $x = 1.02 \text{ a/o}$ at $0.05 \text{ K} < T < 300 \text{ K}$.

2. Experimental and results

The alloys were obtained by arc melting the proper amount of components (Th-99.99% and Tb-99.9% pure) under an argon atmosphere. The C vs T measurements were performed in a semi-adiabatic calorimeter using the heat pulse technique with a germanium resistor as thermometer. The magnetic susceptibility data were obtained by a Faraday magnetometer using a ⁴He-bath-cryostat in the temperature range from 1.6 to 300 K, a dilution refrigerator with SQUID equipment between 0.050 and 4.2 K and a molybdenum wire furnace for temperatures above 300 K.

In fig. 1 we show the $C(T)$ measurements after subtracting the matrix contribution and after normalizing to the mole of Tb, i.e. $\Delta C = (C_{\text{alloy}} - C_{\text{Th}})/x$. The near independence of this contribution from the Tb concentration is evidence for a single impurity effect. In particular the weak concentration dependence of the temperature of the maximum (a shift from 3.3 K to only 3.8 K between $x = 0.44$ and 1.5 a/o) excludes the possibility of a simple spin-glass ordering effect as e.g. observed in ThGd alloys [4].

There are two characteristic features of the Tb contribution to the specific heat: A clear maximum between 3.5 and 3.8 K and an approximately linear term below 0.9 K. The

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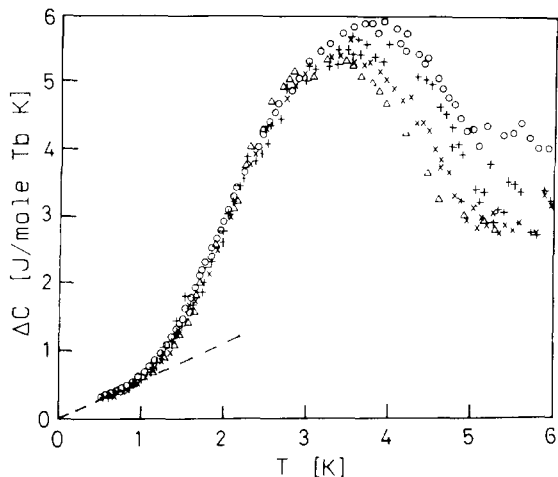


Fig 1 Temperature dependence of the specific heat increment $\Delta C = (C_{\text{alloy}} - C_{\text{Th}})/x$ of ThTb alloys (Δ) 0.44, (\times) 0.82, (+) 1.02, (\circ) 1.5 a/o

coefficient of this linear term is $\gamma = \Delta C/T = 450 \text{ mJ/K}^2\text{molTb} \pm 5\%$. Such a large value is characteristic of a heavy fermion system. The entropy of the Tb impurities is shown in fig 2, it is obtained by assuming that the linear specific heat coefficient observed between 0.4 and 0.9 K holds down to $T = 0$. At the highest temperature of our specific heat measurement ($T = 6 \text{ K}$) the entropy is near $S = R \ln 2$, only two states per Tb atom are thermally excited at 6 K.

In fig 3 we show the inverse susceptibility increment of the Tb impurities for $x = 1.02$ and 2.15 a/o between 0.05 and 20 K. The increment is defined as $(\chi_{\text{alloy}} - \chi_{\text{Th}})/x$. The first thing to

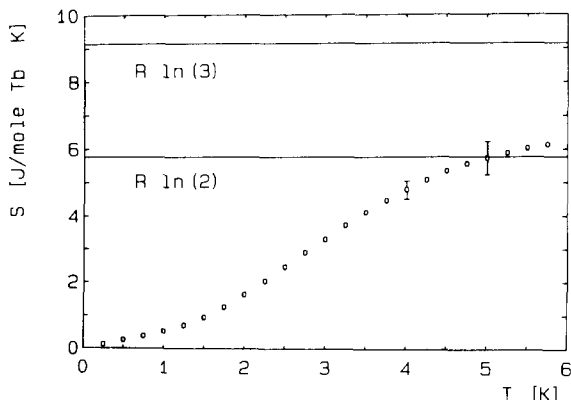


Fig 2 The entropy per mole Tb as function of temperature

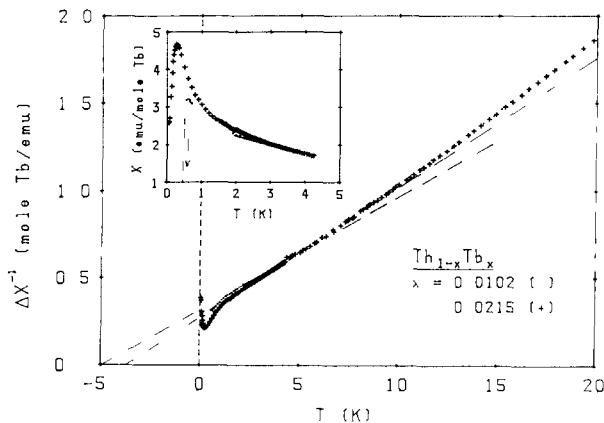


Fig 3 Inverse susceptibility as function of temperature of $\text{Th}_{1-x}\text{Tb}_x$ with $x = 0.0102$ and 0.0215 respectively. Dashed lines are guides to the eyes for Curie-Weiss behavior

note is the near independence of concentration of this quantity. Concentration dependence is only visible at the lowest temperatures where the susceptibility of the 1% alloy shows the superconducting transition at 0.48 K, while the 2% alloy is beyond the critical concentration. Secondly between 1 and 5 K the increment gives a Curie-Weiss temperature between -3.5 and -5 K , which indicates a nonmagnetic groundstate of the alloy with a condensation energy of about 4 K. Thirdly the effective moment in this temperature region is $10.4 \mu_B$ whereas between 10 and 20 K it is $9.6 \mu_B$. Both moments are close to the full effective moment of trivalent Tb ($9.72 \mu_B$). The fourth feature to note is the maximum of $\chi(T)$ seen in the 2% alloy at 0.26 K.

Fig 4 shows $(\Delta\chi T)(T)$ between 4 and 1200 K for the two alloys with $x = 1.02$ and 2.15 . Also shown are these quantities for the stable 3 and 4 valent Tb ions assuming no CEF effects and no magnetic order. While χT of $\text{Tb}^{4+}(4f^7)$ is a constant, χT for $\text{Tb}^{3+}(4f^8)$ decreases slightly with increasing temperature due to the $J = 5$ multiplet at 2932 K above the $J = 6$ Hund's rule groundstate. The measured curve approaches the ideal Tb^{3+} value above room-temperature but does not quite reach it. The average deficiency is 4% in the 1% alloy. The absolute error of this measurement due to the error of the impurity concentration is 0.3% of x , the sys-

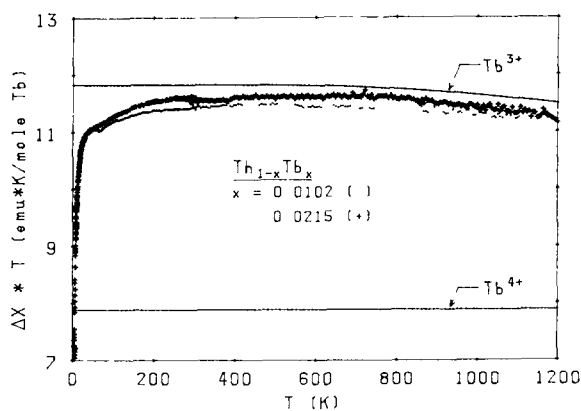


Fig 4 $[(\chi_{\text{alloy}} - \chi_{\text{Tb}})/x]T$ as function of temperature for the $\text{Th}_{1-x}\text{Tb}_x$ alloys with $x = 0.0102$ and 0.0215 . Solid lines χT calculated for $\text{Tb}^{3+}(4f^8)$ and $\text{Tb}^{4+}(4f^7)$, respectively

tematic error of the magnetic measurement is $\pm 3\%$ at 1200 K and $\pm 1.5\%$ at 300 K

3. Discussion

The near concentration independence of the low temperature susceptibility with the characteristic temperature of about -4 K is clear evidence for a nonmagnetic groundstate of the Tb impurities in Th. On the other hand the increase of the $\Delta\chi T$ product from near zero to values comparable to the Curie constant of trivalent Tb above 30 K indicates that the normal effective moment of Tb^{3+} develops very quickly, i.e. that CEF splittings are small. Finally the persistent deficiency of the measured Curie constant above 300 K compared with that of the trivalent Tb may be taken as evidence for slightly fractional valence of about 3.09.

The nonmagnetic groundstate may be due to simple CEF splitting (singlet Γ_1 or Γ_2 CEF groundstate in trivalent Tb) or it may be due to demagnetization of a magnetic groundstate (like Γ_5) caused by a 4f instability. The low temperature specific heat makes a clear decision here. The existence of a very large linear specific heat coefficient observed between 0.4 and 0.9 K is inconsistent with a trivalent Tb atom in a nonmagnetic singlet groundstate, with a singlet CEF groundstate and other magnetic

CEF states a few kelvin above, the specific heat would have to decrease exponentially with temperature below the Schottky like maximum. The low temperature specific heat and the high temperature susceptibility therefore both speak clearly for a 4f instability.

The next question is whether the maximum of the specific heat anomaly can be assigned to a quasi Schottky anomaly due to CEF splittings in the configurationally unstable Tb impurity. The low lying CEF levels responsible for this anomaly should carry nearly the full moment of Tb^{3+} because of the large effective moment at He temperature. This can only be achieved by involving a triplet Γ_5 state near or at the groundstate. It is possible to obtain a maximum of the specific heat anomaly a la Schottky at about 3.8 K with a singlet groundstate and with a triplet Γ_5 state about 10 K above. However the calculated specific heat maximum turns out to be far too large, at 6 K the entropy would then be nearly $R \ln 3$. Since the demagnetization is due to 4f instability one may also consider a triplet Γ_5 CEF groundstate with an excited singlet about 10 K above. The Γ_5 groundstate would then be demagnetized in the usual way by the instability, at a characteristic temperature of order 3–5 K as indicated by the paramagnetic Curie–Weiss temperature. However this possibility is also excluded by the specific heat data, because in that case the entropy at the specific heat maximum would have to be larger than $R \ln 3$. In other words the measured specific heat anomaly is far too low for a triplet magnetic state in, or sufficiently close to the groundstate to explain the susceptibility simultaneously in a temperature independent CEF scheme. Calculations with temperature dependent CEF splittings and temperature dependent characteristic temperatures are in progress.

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