THE EFFECT OF THORIUM SUBSTITUTION IN CeCu$_2$Si$_2$ AND CeNi$_2$Si$_2$

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Resistivity, $\mu_\text{III}$ absorption, and X-ray diffraction have been made on several alloys of the form Ce$_{1-x}$Th$_x$Cu$_2$Si$_2$ and the related system Ce$_{1-x}$Th$_x$Ni$_2$Si$_2$. In the Cu-based compounds the transport measurements indicate that the Kondo effect is substantially quenched with increasing Th substitution. In both the Cu and Ni based alloys $\mu_\text{III}$ absorption measurements of Ce show a decrease of the Ce valence with Th substitution. These results are in accord with the action of Th substitution in other Ce intermetallic compounds, however, they stand in contrast to the action of Th in elemental Ce.

1. Introduction

The volume collapse and demagnetization that occurs in elemental Ce and many of its compounds has been the focus of a large number of experimental studies [1,2]. In many of these studies volume mismatch or charge mismatch alloying has been employed in order to stabilize or destabilize the higher valent (lower volume) $\alpha$ Ce phase. In particular the substitution of Th for Ce is perhaps the best way of increasing the conduction electron population in Ce systems.

Interestingly while Th substitution in elemental $\gamma$ Ce has been found to stabilize the higher valent $\alpha$ phase one almost invariably finds that Th substitution rapidly destabilizes the higher valent ‘$\alpha$-like’ phase in Ce intermetallic compounds (see fig. 1). For example in the ‘$\alpha$-like’ compound CePd$_4$, 40% Th substitution induces an essentially ‘$\gamma$-like’ phase [3]. Similarly in the ‘$\gamma$-like’ compounds CeAl$_2$ and CeAl$_3$ work by Buschow and van Daal and by Croft et al. indicates that Th substitution stabilizes the magnetic moments (suppresses the Kondo effect) and moves the material further away from the ‘$\gamma$-like to $\alpha$-like’ instability [4,5].

Motivated by the great interest in the heavy fermion superconducting ground state of CeCu$_2$Si$_2$, the key role that (Kondo type) spin fluctuations play in this system, and the track record of Th for Ce substitution in rapidly quenching spin fluctuations we have investigated the Ce$_{1-x}$Th$_x$Cu$_2$Si$_2$ system along with the Ce$_{1-x}$Th$_x$Ni$_2$Si$_2$ system. As we will see these 1:2:2 compounds respond to Th substitution qualitatively like binary intermetallic systems but with the response being smaller in magnitude due presumably to strong covalent bonds constraining the crystal structure response.

Transport and lattice measurements on the CeCu$_2$Si$_2$ based system will be interpreted in terms of the quenching of Kondo spin fluctuations along with the upturn of magnetic interactions, and the breakup of Kondo lattice coherency.

Fig. 1. $\mu_\text{III}$ spectra. Top: Ce$_{1-x}$Th$_x$Cu$_2$Si$_2$ (x = 0 dots x = 0.6 solid line). Middle: Ce$_{1-x}$Th$_x$Ni$_2$Si$_2$ (x = 0 dots x = 0.6 solid line). Bottom: Ce$_{1-x}$Th$_x$ (x = 0 solid line x = 0.83 dots).
2. Experimental

Mother samples of CeCu₃Si₂, ThCu₃Si₂, CeNi₃Si₂, and ThNi₃Si₂ were first prepared by mixing stoichiometric amounts of the constituent elements. The Ce₁₋ₓThₓCu₂Si₂ and Ce₁₋ₓThₓNi₂Si₂ series were then prepared by arc melting components from the mother samples. The Ce₁₋ₓThₓCu₂Si₂ series samples were then wrapped in Ta foil, sealed in a Quartz tube with a Zr getter under a partial pressure of Ar. These samples were annealed at 1100°C for 6 days. Diffraction patterns of all Cu based samples yielded the ThCr₂Si₂ structure only. Trace impurities were observed in the Ni based alloys. Total weight losses for each sample were less than 1%.

LIII absorption slides were made with powdered sample which had been passed through a 45 micron sieve. The LIII spectra were fit with a procedure similar to as in ref. [3].

3. Results and discussion

The above mentioned stabilization of an ‘α-like’ higher valence by Th substitution into γ Ce is illustrated in fig. 1 with LIII spectra of an Ce₁₋ₓThₓ alloy and a schematic of γ-Ce. By contrast Th substitution in CeCu₂Si₂ and CeNi₂Si₂ tends to decrease the Ce valence as previously observed in binary Ce intermetallics. The Ce valence is reduced from 3.08 in CeCu₂Si₂ to 3.03 with 60% Th substitution. Normalizing to the main (3+) peak height we compare the LIII spectra of CeNi₂Si₂ and Ce₁₋ₓThₓNi₂Si₂ x = 0.58 sample (fig. 1). The fact that the thorinated compound lies beneath the pure compound in the post-first peak region evidences a small decrease in Ce valence in the Th substituted compound. However, this valence decrease is so small that comparing fitted valences would not be meaningful. Thus although the tendency to stabilize a smaller Ce valence with Th substitution is common in the 1:2:2 compounds and binary intermetallics the magnitude of the effect is much smaller in the 1:2:2 compounds. Presumably the 1:2:2 compounds’ insensitivity to the rare earth lattice electron count is related to hard Si covalent bonds partially fixing atomic positions and therefore partially fixing the Ce hybridization which dominates the Ce valence change.

Our structural and transport results on the Ce₁₋ₓThₓCu₂Si₂ system suggest a crossover in the properties of this system near x ~ 0.2. Lattice parameter results show a general Vegards’ law behavior in the a, c

Fig. 2. Resistivity versus temperature for Ce₁₋ₓThₓCu₂Si₂. Resistivity normalized to 1 at 300 K.

Fig. 3. Top: Low temperature resistive peak height Pₘ versus concentration. Ce₁₋ₓThₓCu₂Si₂ system with solid line through data (circles). Ce₁₋ₓLaₓCu₂Si₂ represented by dashed line (from ref. [7]). Bottom: Temperature of resistive peak Tₘ versus concentration. Solid line through data (triangles) represents Th substituted system; the dotted line represents the La substituted system (from ref. [7]).
and cell volume but with a small c-axis expansion in the $0 < x < 0.3$ range. This c-axis expansion (relative to Vegard's law) of about 0.05 Å is centered on $x = 0.2$ and causes a cell volume expansion in the same region.

Resistivity results in the 1.5–300 K temperature range are shown in fig. 2. In the $x > 0.2$ regime two features point to the quenching of Kondo type spin fluctuations and the depression of their energy scale $T_{SF}$. The high temperature ($T = 100$ K) local maxima in the resistivity, associated with the Kondo type scattering from the excited crystalline electric field level, disappears with increasing $x$, and the resistivity in this range becomes phonon-like [6]. The height of the low temperature local maxima decreases rapidly with increasing $x$ above $x = 0.2$. In both the form of the resistivity and in the general conclusion regarding the suppression of spin fluctuations the Ce$_{1-x}$Th$_x$Cu$_2$Si$_2$ system appears quite analogous to the Ce$_{1-x}$Th$_x$Al$_2$ and the Ce$_{1-x}$Th$_x$Al$_3$ systems. In fig. 3 we plot the temperature of the low temperature maxima ($T_M$) in the resistivity and its height ($P_M$) for the Ce$_{1-x}$Th$_x$Cu$_2$Si$_2$ system along with (for comparison) similar published results for Ce$_{1-x}$La$_x$Cu$_2$Si$_2$ (system taken from ref. [7]).

In the $x > 0.2$ range for the Th alloys, as mentioned above, we interpret the rapid decrease of $P_M$ with increasing $x$ as due to the rapid depression of spin fluctuations. By contrast the steady increase of $P_M$ for the La system indicates the persistence of strong single impurity Kondo type scattering for all $x$ in this latter system.

The increase of $T_M$ in the Th alloy in the $0.3 < x < 0.5$ range presumably reflects the increasing dominance of intersite magnetic interaction effects over Kondo type scattering in this range. The opposite effect for $T_M$ in the La alloy system is consistent with spin fluctuations remaining strong (a nearly constant $T_{SF}$) in spite of interaction effects. The eventual fall off of $T_M$ in the Th system with increasing $x$ (for $x > 0.5$) should reflect the inevitable weakening of interaction effects with dilution. Presumably the rapid decrease in $T_{SF}$ with increasing $x$ is also important in the $0 < x < 0.2$ range also. At present we believe this rapid $T_{SF}$ decrease coupled with a faster breakup of intersite coherency in the Kondo lattice lead to the dramatic differences for $x < 0.2$ in the La$^{3+}$ and Th$^{4+}$ substituted systems. Further magnetic susceptibility work to elucidate the onset of magnetic order (long range or spin glass) in this range is planned.

Finally, it is interesting to note that resistivity measurements in our lab indicate that superconductivity in the Ce$_{1-x}$Th$_x$Cu$_2$Si$_2$ system decreases with $x$ to $T = 0$ at about $x = 0.2$. In the Ce$_{1-x}$La$_x$Cu$_2$Si$_2$ system, on the other hand, the suppression of superconductivity is much more rapid (with a critical concentration of about $x = 0.1$) [9]. This final observation is also consistent with the strong decrease of the spin fluctuation energy scale $T_{SF}$ in the Th system. The Kondo type resonance at the Fermi energy $E_F$ which is believed to support superconductivity in this system has a height proportional to $1/T_{SF}$ [8]. The lowering of $T_{SF}$ could therefore lead to an enhancement of the density of states at $E_F$ thereby enhancing the superconducting $T_c$. A similar effect is apparently operative in the CeCu$_2$(Si$_{1-x}$Ge$_x$)$_2$ system where superconductivity is depressed anomalously slowly at low germanium concentrations. Here Ge substitution acts to stabilize a higher volume and lower $T_{SF}$ (e.g. the L$_{III}$ value of Ce in CeCu$_2$Ge$_2$ is 3.02 as compared to 3.08 in CeCu$_2$Si$_2$).

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References