The chemical substitution influence on thermopower in Yb$_{1-x}$Ce$_x$InCu$_4$

T. Voloshok$^{1, *}$, V. Pryadun$^1$, N. Mushnikov$^2$, A. Vasiliev$^1$

$^1$Low Temperature Physics Department, Moscow State University, Moscow 119991, Russia,

$^2$Institute of Metal Physics, RAS, Kovalevskaya str., 18, Ekaterinburg 620041, Russia

*tatyanavoloshok@yahoo.com

Abstract. The thermopower measurements of Yb$_{1-x}$Ce$_x$InCu$_4$ alloys ($x \leq 0.2$) were performed in a temperature range 4 – 170 K by the longitudinal steady-state four probe method. At $T_V \sim 40$ K, the intermetallic ternary compound YbInCu$_4$ experiences an isostructural phase transition associated with the partial change in the valence state of the Yb ions. The thermopower $S$ of YbInCu$_4$ is negative. The valence transition is clearly seen in $S$ vs. $T$ dependence as a step-like anomaly at $T_V$. The character of thermopower dramatically changes with Ce substitution. The thermopower of Ce-substituted compounds is positive and almost linearly increases at low temperatures, reaching maximum at $T < T_V$. Then it decreases revealing minimum and rises again. Upon Ce substitution it became possible to observe the deep minimum in $S(T)$ typical for Yb compounds.

1. Introduction

Yb-based intermetallic compounds as well as Ce- or U- based compounds show anomalous physical properties associated with hybridization between localized 4f (5f) electrons and conduction electrons and are called Kondo systems. Thermoelectric power $S$ of Kondo systems has larger value than usual metals, reflecting huge electronic density of states near the Fermi level and showing complicated temperature dependence with multi-peak structure and sign reversal [1]. The appearance of several extrema in $S(T)$ has various physical reasons. These are the Kondo scattering on the groundstate multiplet at Kondo temperature $T_K$ or scattering on thermally populated crystal electric field levels. As a rule the sign of $S(T)$ for Ce- and Yb- based compounds is opposite due to the electron-hole “mirror” symmetry of energy spectrum.

At $T_V \sim 40$ K, the intermetallic ternary compound YbInCu$_4$ experiences an isostructural phase transition associated with the partial change of the valence state of the Yb ions [2]. $\text{L}_{\text{III}}$-edge X-ray absorption and thermal expansion studies confirm that the valence state of the ytterbium ions, at $T_V$, changes from Yb$^{2.9}$ to Yb$^{2.8}$ upon cooling. This change is indicated by sharp anomalies in the thermodynamic and kinetic properties of YbInCu$_4$. Lattice volume expands on 0.5% at $T_V$. The magnetization drops by an order of magnitude upon cooling. Above $T_V$ the magnetic susceptibility obeys the Curie-Weiss law with small Curie-Weiss constant $\Theta \approx -5$ K and with an effective magnetic
moment $\mu_{\text{eff}} = 4.54\mu_B/$Yb that is 90% of the magnetic moment associated with Yb$^{3+}$ ions ($g = 8/7$, $J = 7/2$). These values of $\mu_{\text{eff}}$ and $\Theta$ could be ascribed to Kondo interaction with characteristic temperature of high temperature phase $T_{K^+} \sim 25$ K [3]. At $T < T_V$ the magnetic susceptibility is characterized by enhanced Pauli susceptibility, which could be interpreted as Kondo-behavior with characteristic temperature of low temperature phase $T_{K^-} \sim 400$ K [4]. In Refs. [3, 4] it was suggested that the phase transition in YbInCu$_4$ is due to the alteration in the Kondo scales, i.e. in the matrix element of the interaction between the 4f-electrons and the conduction electrons.

Partial substitution of ytterbium by other lanthanides yields changes of the characteristic feature at $T_V$ and of Kondo temperatures $T_{K^-}$ and $T_{K^+}$. The substitution of Yb by Ce results in an increase of $T_V$ in accordance with the variation of the crystal lattice parameter [5]. At increasing Ce content, the anomalies in thermal expansion and magnetic susceptibility at the transition diminish and broaden significantly [4, 5]. The low temperature phase $T_{K^-}$ decreases while the high temperature phase $T_{K^+}$ increases with Ce content. The result of the opposite trends in $T_{K^-}$ and $T_{K^+}$ concentration dependencies is the appearance of a unique energy scale at about $x \sim 0.25 \div 0.30$ and the evolution from a first order phase transition to a behavior pertinent for Kondo systems [6].

In present work, resistivity and thermoelectric power in stoichiometric YbInCu$_4$ and partially Ce-substituted Yb$_{1-x}$Ce$_x$InCu$_4$ were studied in wide temperature range. Since the sign of thermopower is different for Ce- and Yb-based compounds it was of interest to determine it in these “mixed” systems.

2. Experimental

Polycrystalline samples of Yb$_{1-x}$Ce$_x$InCu$_4$ ($x = 0, 0.04, 0.08, 0.12, 0.16, 0.20$) were prepared by inductive melting from pure metals with subsequent annealing for 1 month at $870$ °C. These samples were confirmed to be single phase by an X-ray diffraction measurements. The resistivity was measured by standard four probe method in the absence of temperature gradient in the sample. The measurements of thermoelectric power were performed in self-made setup by the longitudinal steadystate four probe technique with a temperature gradient equal to 2% of the current temperature. The sample holder, surrounded by a special shell to suppress the thermal radiation, was placed into the vacuum chamber evacuated better than $10^{-6}$ bar. The sample temperature and the temperature gradient were stabilized better than 0.01% by an Oxford intelligent temperature controller with calibrated “Allen-Bradley” carbon resistors.

3. Results and discussion

The temperature dependences of resistivity $\rho$ in YbInCu$_4$ and thermoelectric power $S$ are shown in Fig. 1.

![Fig. 1. The temperature dependences of thermopower (left axis) and resistivity (right axis) in YbInCu$_4$.](image1)

![Fig. 2. The temperature dependences of thermopower (left axis) and resistivity (right axis) in Yb$_{0.88}$Ce$_{0.12}$InCu$_4$.](image2)
At heating, the \( c \) vs. \( T \) curve in \( \text{YbInCu}_4 \) presents a sharp jump at \( T_v \). The absolute values of \( c \) in high temperature phase increases after the repeated thermal cycling that is usual for this system [2]. The \( S(T) \) is negative in all temperature range measured, revealing a step-like anomaly at \( T_v \). These results are similar to that presented in Ref. [7], but the absolute values of \( S \) at about \( T_v \) are significantly higher than in Ref. [7]. Since the values of thermopower are very sensitive to deviations from stoichiometry this fact can reflect difference in chemical compositions of the samples studied.

The temperature dependences of \( c \) and \( S \) in \( \text{Yb}_{0.88}\text{Ce}_{0.12}\text{InCu}_4 \) are shown in Fig. 2. The \( c(T) \) curve seems similar to that of parent compound but exhibits broad anomaly at higher temperature. The \( S(T) \) dependence dramatically changes with \( \text{Ce} \) substitution. The thermopower becomes positive and almost linearly increases at low temperatures, reaching maximum at \( T < T_v \). Then it decreases revealing minimum and rises finally. The \( S \) vs. \( T \) curves for the \( \text{Yb}_{1-x}\text{Ce}_x\text{InCu}_4 \) series are shown in Fig. 3. All curves exhibit a maximum at low temperatures. The positions of the maxima \( T_{\text{max}} \) and their magnitudes increase with \( \text{Ce} \) content with the only exclusion that the thermopower magnitude of \( x = 0.20 \) sample is somewhat smaller than expected. The positions of high temperature minima \( T_{\text{min}} \) increase with \( \text{Ce} \) content also but the magnitudes of the maxima remain constant for all samples except the sample with \( x=0.04 \).

The temperature dependence of \( S \) in parent compound \( \text{YbInCu}_4 \) could be qualitatively understood using the approach developed in Ref. [8]. In this work, the thermoelectric properties of \( \text{Yb} \)-compounds are explained by the single-impurity Anderson model in the presence of the crystal electric field splitting of the 4f ground-state multiplet. The low temperature part of \( S(T) \) curve is the fragment of the curve with the single wide minimum typical for the \( \text{Yb} \)-systems in a valence fluctuation state. The phase transition at \( T_v = 40 \text{ K} \) switches on the \( S \) vs. \( T \) dependence to the curve which corresponds to the bigger pressure, e.g. to the state with smaller crystal lattice unit volume.

It was shown in Ref. [8] that the sign of \( S(T) \) is positive if the Fermi window shows more states above the chemical potential than below it, the sign of \( S(T) \) is negative in the opposite case. It is known that density of states’ peak in \( \text{YbInCu}_4 \) is situated in the valence band just below the Fermi level [9]. Therefore, it causes the negative sign of thermopower \( S \). Upon increasing \( \text{Ce} \) content the electronic contribution to the specific heat, i.e. the density of states at the Fermi level increases [6]. Alloying with \( \text{Ce} \) leads likely to the appearance of an additional density of states feature with Fermi level within the rising branch of it. This leads to the positive sign of \( S \) in \( \text{Ce} \)-substituted samples at low temperatures. At heating the Yb ions contribution become dominant.
The S(T) dependence as well as the temperature dependence of specific heat C in Yb$_{0.8}$Ce$_{0.2}$InCu$_4$ (from [6]) are shown in Fig. 4. The positions of high temperature minimum $T_{\text{min}}$ as well as the phase transition temperature $T_V$ taken from the specific heat measurements are shown in the inset to Fig. 4. It is seen, that for $x \leq 0.12$ $T_{\text{min}}$ coincides with $T_V$, e.g. there are no “real” minima of S(T) at these temperatures in these samples. They are minima caused by the phase transition. In samples with $x \geq 0.16$ $T_{\text{min}}$ becomes larger than $T_V$ and the typical minima appear on S vs.T curves.

In summary, in present work new data on thermopower in Yb$_{1-x}$Ce$_x$InCu$_4$ are obtained. The evolution from a first order phase transition to a behavior pertinent for Kondo systems in Yb$_{1-x}$Ce$_x$InCu$_4$ is evident. Upon Ce substitution it became possible to observe the deep minimum typical for Yb compounds. More detailed and quantitative analysis of the data presented will be given elsewhere.

References

[1] Bauer E 1991 Adv. Phys. 40 417
[2] Felner I and Nowik I 1986 Phys. Rev. B 33 617
   Felner I, Nowik I, Vaknin D, Potzel U, Kalvius G M, Wortmann G, Schmiester G, Hilscher G, Gratz E, Schmitzer C, Pillmayr N, Prasad K G, de Waard H and H. Pinto 1987 Phys. Rev. B 35 6956
   Sarrao J L 1999 Physica B 259-261 128
   Cornelius A L, Lawrence J M, Sarrao J L, Fisk Z, Hundley M F, Kwei G H, Thompson J D, Booth C H and Bridges F 1997 Phys. Rev. B. 56 7993
[3] Sarrao J L, Ramirez A P, Darling T W, Freibert F, Migliori A, Immer C D, Fisk Z and Uwatoko Y 1998 Phys. Rev. B 58 409.
[4] Mushnikov N V, Goto T, Kolomiets A V, Yoshimura K, Zhang W and Kageyama H 2004 J. Phys.: Condens. Matter 16 2395
[5] Mushnikov N V, Goto T, Ishikawa F, Zhang W, Yoshimura K and Gaviko V S 2002 J. Alloys and Compounds 345 20
[6] Voloshok T , Mushnikov N, Tristan N, Klingeler R, Buchner B, Vasiliev A 2007 Phys. Rev. B 76 172408
[7] Ocko M, Sarrao J L, Aviani I, Drobac D, Živkovic I and Prester M 2003 Phys. Rev. B 68 075102
[8] Zlatic V and Monnier R 2005 Phys. Rev. B 71 165109
[9] Takegahara K, Kasuya T 1990 J. Phys. Soc. Jap. 59 3299