

Interplay between the valence phase transition and Kondo behavior in $\text{Yb}_{1-x}\text{La}_x\text{InCu}_4$ and $\text{Yb}_{1-x}\text{Ce}_x\text{InCu}_4$ probed by the specific heat

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At $T_V \sim 40$ K, the intermetallic compound YbInCu_4 experiences an isostructural phase transition associated with a change in the valence state of Yb ions and with the alteration in the energy scale for Kondo interaction. Our study of the specific heat C in the temperature range of 0.4–300 K at partial substitution of Yb for La and Ce reveals qualitatively different trends in the evolution of this phase transition for the both doping series. In $\text{Yb}_{1-x}\text{La}_x\text{InCu}_4$, with $0 \leq x \leq 0.25$, the anomalies in the specific heat exhibit features pertinent for the first order phase transition. In $\text{Yb}_{1-x}\text{Ce}_x\text{InCu}_4$, with $0 \leq x \leq 0.2$, doping with Ce causes an evolution from the first order phase transition in the parent compound to a behavior characteristic for concentrated Kondo systems with a unique energy scale. The entropy change at the phase transition ΔS diminishes systematically reaching 5.6 J/mol_{Yb} K in $\text{Yb}_{0.8}\text{Ce}_{0.2}\text{InCu}_4$ as compared to 12.6 J/mol_{Yb} K in YbInCu_4 . This suggests that the Ce doping influences the valence of the Yb ions.

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At $T_V \sim 40$ K, the intermetallic ternary compound YbInCu_4 experiences an isostructural phase transition which is associated with the partial change of the valence state of the Yb^{3+} ions.^{1,2} This change is indicated by sharp anomalies in the thermodynamic and kinetic properties of YbInCu_4 . For example, at T_V the electric resistance and the magnetization drop by an order of magnitude upon cooling. The magnetic susceptibility obeys the Curie-Weiss law above T_V and it is temperature independent below.³ L_{III} -edge x-ray absorption² and thermal expansion⁴ studies confirm that the valence state of the ytterbium ions, at T_V , changes from $\text{Yb}^{+2.9}$ to $\text{Yb}^{+2.8}$ upon cooling.

Among the intermetallic stoichiometric compounds, the phase transition in YbInCu_4 is unique. Its closest analog is the γ - α transition under pressure in metallic Ce which is described by the model of Kondo volume collapse.⁵ In this model, the magnetoelastic component of the Kondo interaction provides the nonlinear correlation between the concentration of $4f$ electrons and the parameters of the crystal lattice which leads to a first order phase transition. While the model of the Kondo collapse describes the phase transition in metallic Ce, it is insufficient for the quantitative description of the valence transition in YbInCu_4 . In particular, it does not describe the pressure dependence of T_V .⁶

In Refs. 6 and 7 it was suggested that the phase transition in YbInCu_4 is due to the change in the matrix element of the interaction between the $4f$ electrons and the conduction electrons. Usually, the strengths of hybridization of localized and delocalized electrons are characterized by the Kondo temperature T_K . It is hence important to study the isostructural YbXCu_4 compounds since the chemical substitutions can influence significantly the coupling of the electron subsystems. The chemical substitutions lead to different ground states, e.g., at $X=\text{Au}$ and Pd the magnetically ordered state is formed at low temperatures, whereas for $X=\text{Ag}$, Cd , Zn , and Cu , the compounds exhibit properties pertinent for heavy fermion systems. The compounds with $X=\text{Mg}$ and Tl remain Pauli paramagnets down to lowest temperatures.³ The substi-

tution of Yb for Gd, Dy, Ho, and Er leads to the disappearance of the valence phase transition and results in the formation of long-range magnetic order at low temperatures.⁸ Interestingly, the increase of the conduction electrons concentration, which is realized in GdCdCu_4 , is accompanied by the rise of the magnetic ordering temperature.⁹ Magnetic ordering is also supported by the application of high quasihydrostatic pressure in YbInCu_4 where the nonmagnetic phase transforms to a weakly ferromagnetic one at high pressure.¹⁰

Partial substitution of ytterbium by other lanthanides yields changes of the characteristic feature at T_V . The substitution of Yb by La and Ce results in an increase of T_V in accordance with the variation of the crystal lattice parameter.¹¹ The thermodynamic characteristics of the solid solutions $\text{Yb}_{1-x}\text{Ce}_x\text{InCu}_4$ and $\text{Yb}_{1-x}\text{La}_x\text{InCu}_4$ appear to be qualitatively different, however. At substitution of Yb for La, the anomalies in the magnetization and the thermal expansion decrease in magnitude but remain very sharp. In contrast, at substitution of Yb for Ce, the anomalies at the transition diminish and broaden significantly.^{7,11}

In the present work, the role of substitutions at the rare-earth position on the specific heat of solid solutions $\text{Yb}_{1-x}\text{La}_x\text{InCu}_4$ ($0 \leq x \leq 0.25$) and $\text{Yb}_{1-x}\text{Ce}_x\text{InCu}_4$ ($0 \leq x \leq 0.2$) was studied in the temperature range of 0.4–300 K. In order to separate the phonon contribution from the specific heat the nonmagnetic isostructural compound YInCu_4 was measured, too.

Polycrystalline samples of YInCu_4 , $\text{Yb}_{1-x}\text{La}_x\text{InCu}_4$ with $x=0, 0.05, 0.10, 0.15, 0.20$, and 0.25 , and $\text{Yb}_{1-x}\text{Ce}_x\text{InCu}_4$ with $x=0, 0.04, 0.08, 0.12, 0.16$, and 0.20 were prepared by inductive melting from pure metals with subsequent annealing for 1 month at 870 °C. In the temperature range of 5–300 K, the measurements of the specific heat were performed by means of a quasiadiabatic “Termis” calorimeter, while at low temperatures of 0.4–20 K, the data were taken by a “Quantum Design” Physical Properties Measurement System.

The temperature dependences of the specific heat C in YbInCu_4 and YInCu_4 are shown in Fig. 1. The specific heat

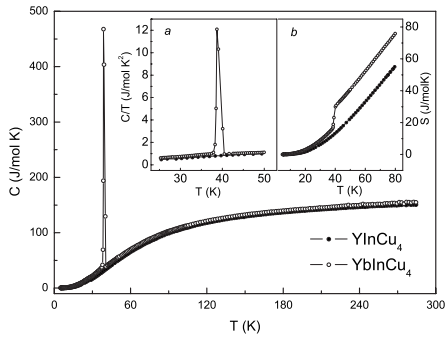


FIG. 1. The temperature dependences of specific heat in YInCu_4 and YbInCu_4 . In inset a, the dependences C/T vs T are shown in the vicinity of phase transition T_V . Inset b represents the temperature dependences of entropy in both compounds.

curve of the nonmagnetic material YInCu_4 is fitted well by the sum of the Debye function and three Einstein functions in the whole temperature range. At high temperatures, the specific heat of YInCu_4 approaches the thermodynamic limit $3Rn \approx 150 \text{ J/mol K}$, where $R=8.31 \text{ J/mol K}$ and $n=6$ is the number of atoms per formula unit. The data on YInCu_4 allow us to extract the phonon contribution in $\text{Yb}_{1-x}\text{La}_x\text{InCu}_4$ and $\text{Yb}_{1-x}\text{Ce}_x\text{InCu}_4$ by applying a scaling procedure which considers the ionic masses.¹² As shown in Fig. 1, the specific heat of YbInCu_4 exceeds that of YInCu_4 which is both due to the magnetic degrees of freedom present in the former material and the higher mass of Yb ions compared to the Y ones. At $T_V \sim 40 \text{ K}$, the $C(T)$ dependence in YbInCu_4 shows very sharp peak marking first order valence phase transition. In inset a in this figure, the C/T vs T dependences for both compounds are shown where the data for YInCu_4 are already rescaled with regards to the ionic masses. Comparing the data of both compounds yields an entropy jump of $\Delta S = 12.6 \text{ J/mol K}$ at T_V , as shown in inset b in Fig. 1. This value is in good agreement with the value of ΔS given in Ref. 6. We mention, however, that the uncertainty in ΔS for a first order transition is quite large due to the finite resolution of the measuring devices.

The temperature dependences of the specific heat in the series of solid solutions $\text{Yb}_{1-x}\text{La}_x\text{InCu}_4$ ($0.05 \leq x \leq 0.25$) are shown in Fig. 2. With increasing La content, the anomaly in $C(T)$ shifts to higher temperatures, keeping the shape characteristic for the first order phase transition. The amplitude of the peak changes from sample to sample arbitrarily which can be attributed to the fluctuation of the homogeneity of the samples and experimental limitations in the resolution of setup. The C/T vs T^2 dependences in $\text{Yb}_{1-x}\text{La}_x\text{InCu}_4$ at low temperatures are shown in the inset of Fig. 2. In this presentation, the electronic part of the specific heat is given by the cutoff of ordinate, while the slope of the curve gives the phonon part. Evidently, neither the electronic nor the phononic contributions are very sensitive to x .

Figure 3 displays the temperature dependences of specific heat in the series of solid solutions $\text{Yb}_{1-x}\text{Ce}_x\text{InCu}_4$ ($0.04 \leq x \leq 0.20$). With increasing Ce content, the anomaly at the phase transition shifts to higher temperatures. In contrast to the finding for the La-doped compounds, the anomaly at T_V changes qualitatively upon Ce doping. We observe a sharp

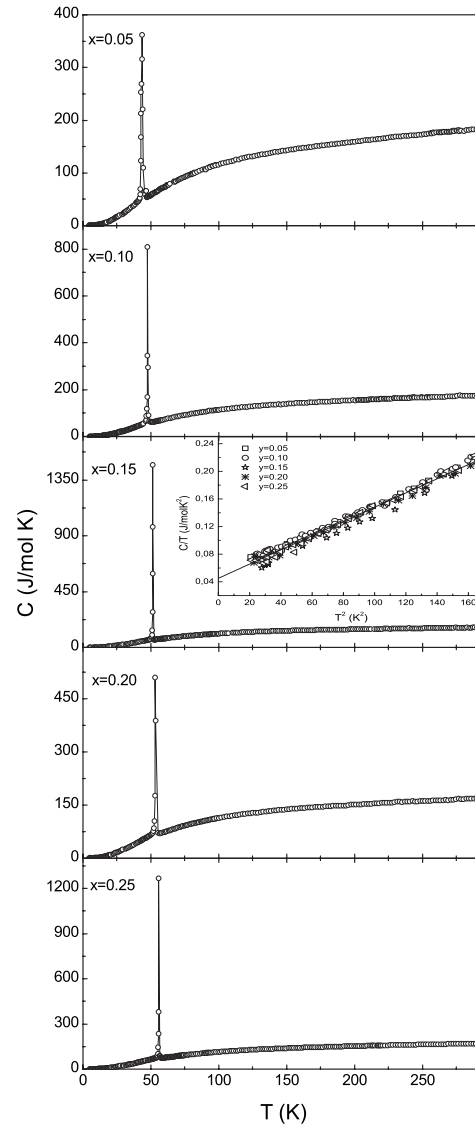


FIG. 2. The temperature dependences of specific heat in $\text{Yb}_{1-x}\text{La}_x\text{InCu}_4$ ($0.05 \leq x \leq 0.25$) series of compounds. The inset to middle panel represents C/T vs T^2 dependences at low temperatures.

peak at low x , while it is rounded and of smaller amplitude at higher doping level. We mention that, in $\text{Yb}_{0.96}\text{Ce}_{0.04}\text{InCu}_4$, the data exhibit a double anomaly which can be attributed to the liquations persisting in this alloy even after the prolonged annealing. It should be noted that as-cast alloys show extremely broad transition.¹³ A newly prepared sample of the same composition shows a single sharp anomaly, as it is shown in the inset in Fig. 3. For the subsequent analysis, we used the data obtained on the sample of the original series, however.

In order to estimate changes in the electronic and phononic specific heat in the $\text{Yb}_{1-x}\text{Ce}_x\text{InCu}_4$ series, in Fig. 4 we present the C/T vs T^2 dependences in the range of 0.4–20 K. Obviously, there appears significant change of the electronic contribution which increases systematically with increasing Ce content (inset a). Note, at low temperatures all samples exhibit additional anomalies. For $\text{Yb}_{0.92}\text{Ce}_{0.08}\text{InCu}_4$,

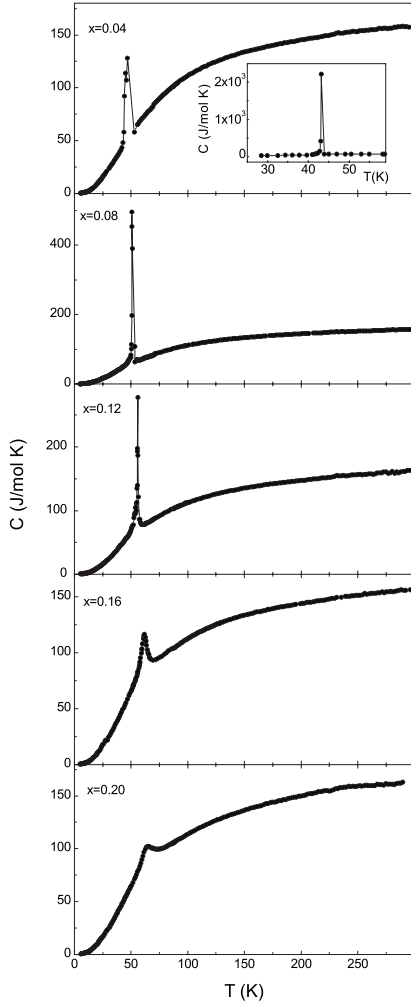


FIG. 3. The temperature dependences of specific heat in $\text{Yb}_{1-x}\text{Ce}_x\text{InCu}_4$ ($0.04 \leq x \leq 0.20$) series of compounds. The inset to upper panel represents C vs T dependence in $\text{Yb}_{0.96}\text{Ce}_{0.04}\text{InCu}_4$ sample obtained under different thermal treatments.

this anomaly is shown enlarged in inset b in Fig. 4. We attribute this low-temperature anomalies to the presence of an impurity phase of Yb_2O_3 , in which long-range magnetic order evolves below $T_N = 2.3$ K.¹⁴ From the magnitude of this anomaly, the volume content of the impurity phase was estimated as 0.2%.¹⁵ The presence of the impurity phase, however, does not affect the analysis described below.

The experimental data shown in Figs. 2 and 4 imply that, at low temperatures, the specific heat of the samples studied can be explained in terms of the electronic and phononic parts, i.e., by

$$C = \gamma T + \beta T^3. \quad (1)$$

The electronic part is characterized by the Sommerfeld coefficient γ which is proportional to the density of states $N(E_F)$ at the Fermi level,

$$\gamma = \frac{2}{3} \pi^2 k_B^2 N(E_F). \quad (2)$$

The phononic part is characterized by the slope of C/T vs T^2 curve,

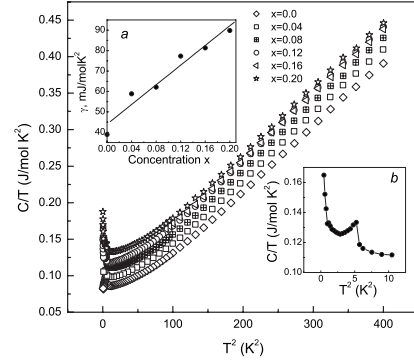


FIG. 4. The C/T vs T^2 dependences in $\text{Yb}_{1-x}\text{Ce}_x\text{InCu}_4$ at low temperatures. Inset a represents the concentration dependence of Sommerfeld coefficient γ ; the straight line is a guide for the eye. Inset b enlarges the anomaly in specific heat at low temperatures, tentatively ascribed to the impurity phase Yb_2O_3 .

$$\beta = (12/5) \pi^4 R n (T/\Theta)^3, \quad (3)$$

which allows us to estimate the Debye temperature Θ .

The data show that the partial substitution of Yb for La does not affect the electronic specific heat significantly. Besides, the Debye temperature of $\Theta \sim 230$ K remains practically unchanged. In contrast, the partial substitution of Yb for Ce induces a clear increase of the electronic contribution to the specific heat, while the phononic contribution changes insignificantly. The concentration dependence of the Sommerfeld coefficient, shown in inset b in Fig. 4, reflects the increase of the density of states at Fermi level in the Ce-substituted compounds.

The specific heat study reveals qualitative differences in behavior of $\text{Yb}_{1-x}\text{La}_x\text{InCu}_4$ and $\text{Yb}_{1-x}\text{Ce}_x\text{InCu}_4$ series of compounds. We mention that this observation is in agreement with previous magnetization and thermal expansion studies.^{7,11} To be more precise, in $\text{Yb}_{1-x}\text{La}_x\text{InCu}_4$ in the range $0 < x < 0.25$, the electronic density of states is nearly constant and the first order phase transition persists. The phase transition in La-substituted compounds, as well as in the parent compound YbInCu_4 , can be treated as a jumplike change in the interaction of the conduction electrons with the $4f$ electron states of the Yb ions. The measure of this interaction is the Kondo temperature T_K . In the high-temperature phase, the Kondo temperature is close to the temperature of the valence phase transition $T_K^+ \sim T_V \sim 40$ K.¹³ At low temperatures, its value is determined by the Sommerfeld coefficient,

$$T_K^- = 4.7 \pi^2 R / 24 \gamma. \quad (4)$$

This formula is valid for Yb ions with a magnetic moment $J = 7/2$.^{16,17} The fact that the Sommerfeld coefficient $\gamma \sim 40$ mJ/mol K^2 is virtually the same in every compound of the $\text{Yb}_{1-x}\text{La}_x\text{InCu}_4$ ($0 < x < 0.25$) series implies that the Kondo temperature of the low-temperature phase does not change upon La doping. To be specific, it amounts to $T_K^- \sim 400$ K.

A qualitatively different behavior is observed in $\text{Yb}_{1-x}\text{Ce}_x\text{InCu}_4$. For $0 < x < 0.2$, the data imply the evolution from a first order valence phase transition to a behavior

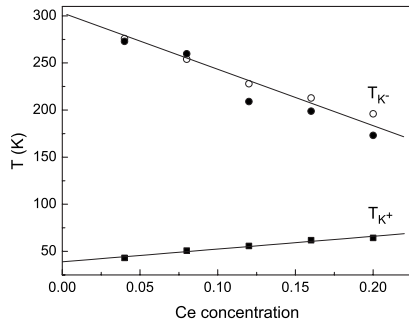


FIG. 5. The concentration dependences of the Kondo temperatures T_K^+ (squares) determined as the temperature of the valence phase transition and T_K^- calculated from specific heat (full circles) and magnetic susceptibility (open circles) data in $\text{Yb}_{1-x}\text{Ce}_x\text{InCu}_4$ series of compounds.

which is typical for a Kondo system with a unique energy scale. Concomitantly, upon increasing Ce content the electronic contribution to the specific heat, i.e., the electronic density of states at the Fermi level increases and the Kondo temperature of low-temperature phase decreases.

The obtained data on specific heat can be put in correspondence with earlier published data on low-temperature magnetic susceptibility $\chi(0)$ in the same set of Ce-substituted samples.¹¹ Following the calculations within the Bethe ansatz of the Coqblin-Schrieffer model given in Ref. 16, the T_K^- for $J=7/2$ and $g=8/7$ can be estimated from the relation

$$T_K^- = 14.5 \mu_B^2 / 24 \pi k_B \chi(0). \quad (5)$$

The concentration dependences of T_K^- calculated from Eqs. (4) and (5) for $\text{Yb}_{1-x}\text{Ce}_x\text{InCu}_4$ system are shown in Fig. 5. Except for the parent compound, very good correspondence is seen for T_K^- estimated from various thermodynamic properties.

The Kondo temperature of the high-temperature phase T_K^+ increases in a similar way as the temperature of valence phase transition.¹³ The concentration dependences of T_K^+ is also shown in Fig. 5. The result of the opposite trends in T_K^- and T_K^+ concentration dependences is the appearance of a unique energy scale and the evolution from a first order phase transition to a behavior pertinent for Kondo systems.

The reliable determination of the entropy change at the phase transition is possible when applied to $\text{Yb}_{1-x}\text{Ce}_x\text{InCu}_4$ system. Using the procedure employed for the parent compound, we calculated the entropy change at phase transition ΔS_{expt} normalized per mole Yb. These data are collected in

TABLE I. Experimental ΔS_{expt} and linearly extrapolated ΔS_{LE} entropy changes at phase transition in $\text{Yb}_{1-x}\text{Ce}_x\text{InCu}_4$ system.

Ce content x	0	0.04	0.08	0.12	0.16	0.20
ΔS_{LE} (J/mol _{Yb} K)	12.6	12.1	11.6	11.1	10.6	10.1
ΔS_{expt} (J/mol _{Yb} K)	12.6	9.7	7.7	6.4	6.9	5.6

Table I. It was found that this value diminishes systematically reaching $\Delta S=5.6$ J/(mol_{Yb} K) in $\text{Yb}_{0.8}\text{Ce}_{0.2}\text{InCu}_4$ as compared with $\Delta S=12.6$ J/(mol_{Yb} K) in the parent compound. The change in the entropy of phase transition was found to be significantly larger than the reduction in Yb content, which is represented by linear extrapolation ΔS_{LE} . It suggests that the Ce ions are not strictly trivalent diluents but they influence the valence states of Yb ions. In fact, it was established earlier in thermal expansion measurements that in Ce-substituted samples, the valence change of Yb ions at phase transition is smaller.⁷ At present, we have no clear indications that Ce ions themselves change their valence at phase transition.

We have reported a systematic study of the effect of partial substitution in the rare-earth subsystem on the specific heat of $\text{Yb}_{1-x}\text{La}_x\text{InCu}_4$ and $\text{Yb}_{1-x}\text{Ce}_x\text{InCu}_4$. The parent compound YbInCu_4 exhibits a first order phase transition at $T_V \sim 40$ K, which is associated with the change of the valence state of the rare-earth ions. The partial substitution of Yb for La does not influence the character of the phase transition (just gradually shifts it to the high-temperature range) and the electronic specific heat stays constant. In contrast, the partial substitution of Yb for Ce results in qualitative changes in the character of the phase transition. At rising Ce content, the electronic specific heat increases, while the sharp first order phase transition transforms to a behavior typical for Kondo systems. It was found that with increasing Ce content, the entropy change at phase transition diminishes systematically in $\text{Yb}_{1-x}\text{Ce}_x\text{InCu}_4$ which suggests that the Ce doping affects the valence of the Yb ions.

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