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Ground state properties of the $\text{YbCu}_{5-x}\text{Au}_x$ ($0 < x \leq 1.8$) solid solution

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Abstract

Samples prepared across the $\text{YbCu}_{5-x}\text{Au}_x$ solid solution system remain cubic AuBe_5 -type up to $x = 1.8$. As the Au concentration x is increased, the Au atoms first replace the Cu atoms on the 4c sites of the $F\bar{4}3m$ space group until the sites are fully occupied, and then replace atoms on the 16e sites until the structure becomes unstable. The composition at $x = 1$ is at the crossover between two kinds of disordered sublattices and the ground state properties follow a non-monotonic behaviour through $x = 1$.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

$\text{YbCu}_{5-x}\text{M}_x$ solid solutions (where $\text{M} = \text{Ag}, \text{Au}, \text{In}$) crystallizing in the cubic AuBe_5 -type structure have recently received considerable attention due to the different evolution of ground state properties depending on the M element. The common starting point with $x = 0$, YbCu_5 , showing dense Kondo behaviour, has been synthesized in the cubic AuBe_5 -type single phase only under high pressure of 1.5 GPa at 900 °C [1], and replacement of Cu by elements such as Ag, Au and In stabilizes the cubic structure already under ambient pressures. In $\text{YbCu}_{5-x}\text{In}_x$ the Cu/In substitution drives the system through a crossover from a Kondo lattice behaviour at $x = 0$ to a valence fluctuation system for $x = 1$ [2]. The latter exhibits a temperature induced first-order valence transition at $T_v \approx 40\text{--}60$ K, depending on slight off-stoichiometries of the sample. On the other hand, $\text{YbCu}_{5-x}\text{Ag}_x$ exhibits Kondo lattice behaviour in the $0 < x \leq 1$ substitutional range with a systematic variation of characteristic quantities, such as the Kondo temperature, the coefficient of the electronic specific heat and the Pauli paramagnetic susceptibility [1, 3]. $\text{YbCu}_{5-x}\text{Au}_x$, however, shows a different evolution of ground state properties compared with the above-mentioned cases. In particular, Cu/Au

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substitution in $\text{YbCu}_{5-x}\text{Au}_x$, in the present investigated range $0 < x \leq 1$, drives the system from a high T_K to a low T_K Kondo scenario and, concomitantly, long range magnetic order occurs for $x > 0.4$ [4, 5].

The respective YbCu_4M ($\text{M} = \text{Au}, \text{In}, \text{Ag}$) compounds, crystallizing in the form of an ordered ternary derivative of AuBe_5 , were initially supposed to be stoichiometric compounds [6] and only later on was it recognized that they are points of crystallographic order in $\text{YbCu}_{5-x}\text{M}_x$ solid solutions.

Following this concept, we report a study on an extension of the work concerning $\text{YbCu}_{5-x}\text{Au}_x$, showing that the cubic AuBe_5 solid solution actually extends well beyond the ordered compound up to $x = 1.8$. This is of particular interest because the alloy with $x = 1$ is the ordered stoichiometric compound YbCu_4Au showing a mutual interplay of Kondo effect, magnetic order and crystal field splitting.

2. Experimental details

Samples were prepared using high frequency (hf) melting under argon of elemental mixtures either on a cooled copper mould or sealed in Ta containers under continuous shaking of the crucible. Subsequently, a heat treatment at $T = 600^\circ\text{C}$ for 14 days in an argon atmosphere was carried out.

X-ray diffraction (XRD) data for the evaluation of lattice parameters and for structure refinements were recorded using a Philips diffractometer (Cu $K\alpha$ radiation). Rietveld matrix full profile structure refinements were carried out using the program FULLPROF [7]. Most of the alloys were characterized by optical and electronic microscopy and by quantitative electron probe microanalysis (EPMA). The electrical resistivity and magnetoresistivity of bar shaped samples (about $1 \times 1 \times 1.5 \text{ mm}^3$) were measured using a four-probe dc method in the temperature range from 0.4 K to room temperature and fields up to 12 T.

3. Results and discussion

A series of alloys along the $\text{YbCu}_{5-x}\text{Au}_x$ compositional line at 16.67 at.% Yb have been prepared. The annealed samples remain cubic AuBe_5 -type single-phase ones up to $x = 1.8$, as determined from XRD and EPMA. Alloys prepared with Au concentration $1.8 < x < 2.5$ remain nearly single phase although, generally, phase compositions slightly richer in Yb (≈ 18 at.% Yb) are observed. Moreover, their x-ray patterns present a few satellite peaks close to the main peaks of the cubic AuBe_5 structure, this resembling the formation of superstructures derived from the cubic AuBe_5 -type structure, as in the case of the heavy fermion compound $\text{YbCu}_{4.5}$ which forms from the cubic structure via the introduction of Cu-deficient shear planes [8].

The values of the lattice parameter a for $\text{YbCu}_{5-x}\text{Au}_x$ determined in this work are reported in figure 1 together with those evaluated by Yoshimura and co-workers [5]. The a values, and consequently the unit cell volume, continue to increase linearly on increasing x through $x = 1$, with a slight change of slope. At $x = 1$ the sample crystallizes in the MgCu_4Sn -type structure, an ordered substitutional version of the cubic AuBe_5 , where Yb, Cu and Au are located in 4a, 16e and 4c Wyckoff positions of the $F\bar{4}3m$ space group, respectively.

For $0 < x \leq 1$, Cu atoms are replaced by the bigger Au atoms in the crystallographic site 4c of the AuBe_5 -type structure, where a larger space as compared with the 16e site is available (see tables 1 and 2) and a complete substitution is possible. For $1 < x \leq 1.8$ an additional amount of Au replaces Cu in the 16e site. A Rietveld refinement carried out on the

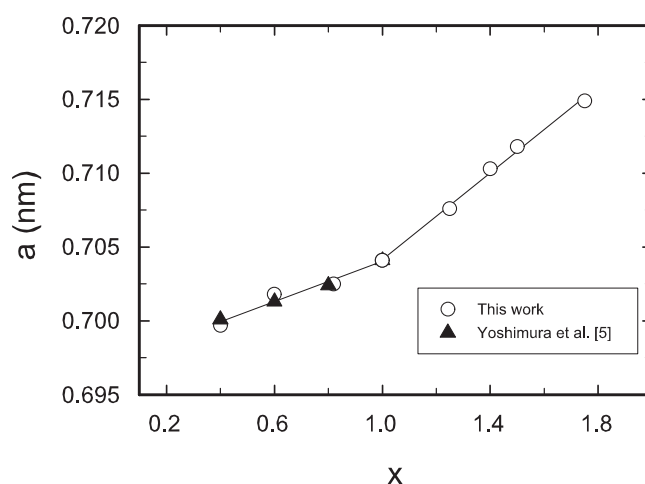


Figure 1. Lattice parameter a versus x for $\text{YbCu}_{5-x}\text{Au}_x$.

Table 1. Structural parameters of $\text{YbCu}_{3.5}\text{Au}_{1.5}$ refined from x-ray data in the space group $F\bar{4}3m$. 'Occ.' = occupation number; residual values: $R_B = 0.0288$, $R_F = 0.0348$, $R_{WP} = 0.0531$; * = fixed.

Atom	Site	x	y	z	Occ. (%)
Yb	4a	0	0	0	100.0*
Au1	4c	0.25	0.25	0.25	100.0*
Cu	16e	0.6254(4)	0.6254(4)	0.6254(4)	89.1(2)
Au2	16e	0.6254(4)	0.6254(4)	0.6254(4)	10.9(2)

Table 2. Interatomic distances (nm) in $\text{YbCu}_{3.5}\text{Au}_{1.5}$ calculated from table 1. All distances less than 0.5 nm are shown.

Au1–12(Cu/Au2)	0.295	(Cu/Au2)–3Yb	0.294
Au1–4Yb	0.308	(Cu/Au2)–12(Cu/Au2)	0.436
(Cu/Au2)–6(Cu/Au2)	0.252		

alloy prepared at $x = 1.5$ indeed shows a good agreement with the above-mentioned model (see table 1). The starting atomic position parameters were taken from the crystallographic data of the MgCu_4Sn structure type and the reliability factors obtained are $R_F = 0.0348$ and $R_B = 0.0288$. Figure 2 shows the Rietveld plot obtained for the best agreement between calculated and observed profiles.

The $\text{YbCu}_{5-x}\text{Au}_x$ solid solution extends up to $x = 1.8$, corresponding to a replacement of only 20% of Cu by Au on the 16e site, and the single-phase behaviour is probably constrained for geometrical reasons. In fact an atom located at the 16e site has six nearest neighbours with equivalent 16e positions at an interatomic distance of $d_{16e-16e} = 0.252$ nm (for the sample at $x = 1.5$, see table 2), which is smaller than both $(R_{\text{Au}} + R_{\text{Cu}})$ and $(2R_{\text{Au}})$. Assuming for Au and Cu metallic radii of 0.144 and 0.128 nm respectively, we obtain for the interatomic contacts the values $\Delta_{\text{Au-Au}} = (2R_{\text{Au}}) - d_{16e-16e} = 0.036$ nm and $\Delta_{\text{Au-Cu}} = (R_{\text{Au}} + R_{\text{Cu}}) - d_{16e-16e} = 0.020$ nm. Thus we expect that Au atoms on 16e sites favour atoms of Cu instead of Au as nearest neighbours, and that accordingly only a rather low amount of Au (20%) replaces Cu on this site.

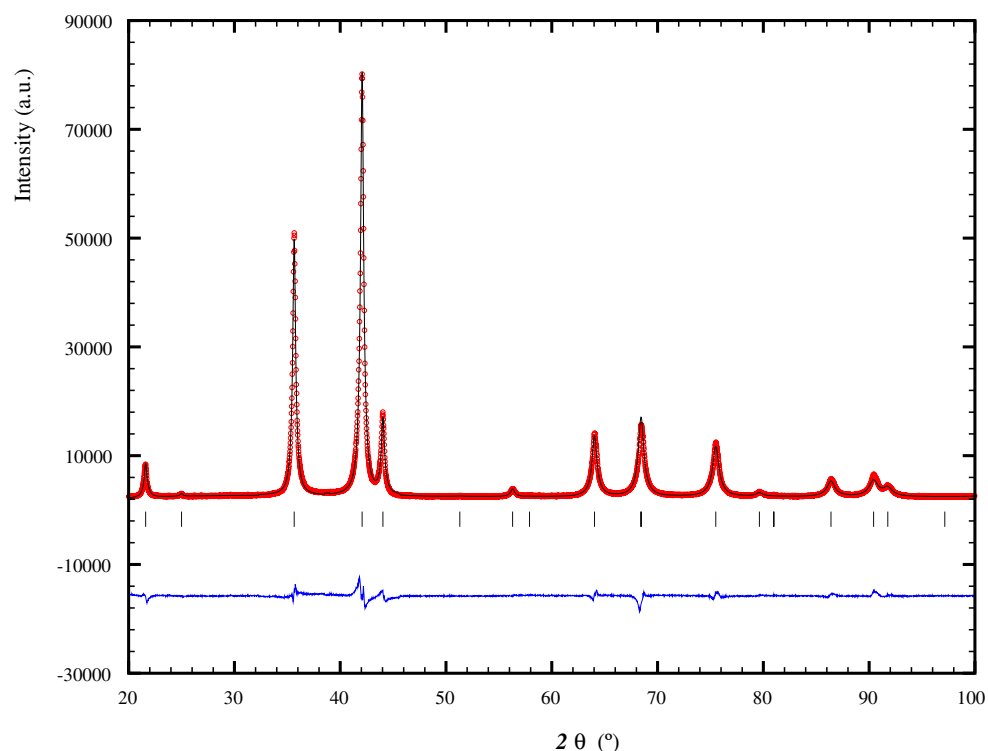


Figure 2. The experimental x-ray diffraction powder pattern of $\text{YbCu}_{3.5}\text{Au}_{1.5}$ compared with the calculated diffraction diagram. The experimental data are shown by the symbols, while the line through the data represents the results of the Rietveld refinement. The lower curve is the difference curve. The ticks indicate the 2θ values of AuBe_5 -type Bragg peaks.

As the concentration at $x = 1$ is at the crossover between two kinds of disordered sublattices, the physical properties are expected to show distinct features as x is varied through $x = 1$. The temperature dependences of the electrical resistivity ρ of cubic $\text{YbCu}_{5-x}\text{Au}_x$ for different x values in the range $0.7 \leq x \leq 1.8$ are shown in figure 3. The high temperature region of the samples investigated shows a logarithmic increase on decreasing the temperature which is attributed to incoherent Kondo scattering. A maximum or pronounced shoulder-like structure at about 10–20 K relates to crystal electric field splitting of the Yb^{3+} spin-orbit ground state with $J = 7/2$ in the presence of Kondo interaction. Distinct differences, however, are obvious for the crystallographically ordered compound $x = 1$, in comparison to alloys above or below that concentration. While at low temperatures YbCu_4Au is characterized by typical features of a Kondo lattice, the more disordered alloys ($x > 1$ and $x < 1$) exhibit a behaviour which, in general, is associated with single-impurity systems. Thus, crystallographic disorder due to the Au/Cu substitution on both the 4c and 16e sites is considered responsible for the destruction of a Kondo lattice state.

Figure 4 summarizes the isothermal magnetoresistance $\rho(B)/\rho(0)$ taken at $T = 2$ K as a function of magnetic field at various Au concentrations for $\text{YbCu}_{5-x}\text{Au}_x$. For all the samples the magnetoresistance is negative and its magnitude increases with decreasing Au content (for $1.75 \geq x \geq 1$), ranging from values of -11% at 12 T at $x = 1.75$ to -60% at 12 T for the sample at $x = 1$. With further decrease of the Au content, $\rho(B)/\rho(0)$ becomes smaller again.

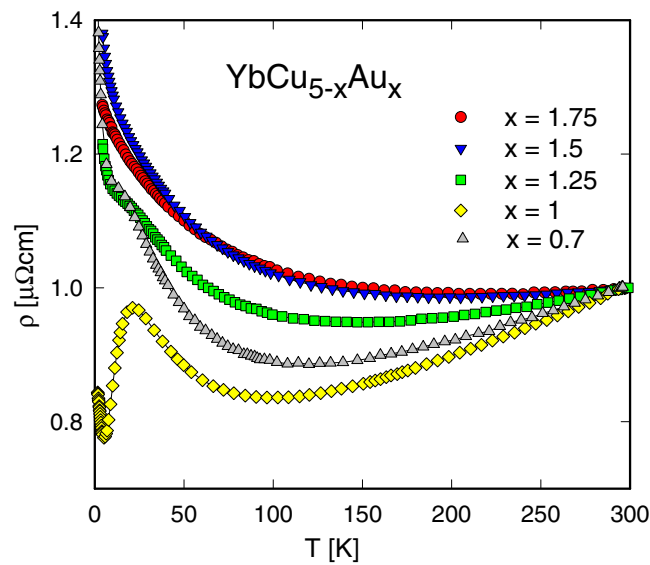


Figure 3. The temperature dependent resistivity ρ of $\text{YbCu}_{5-x}\text{Au}_x$ for various concentrations x , displayed in a normalized representation.

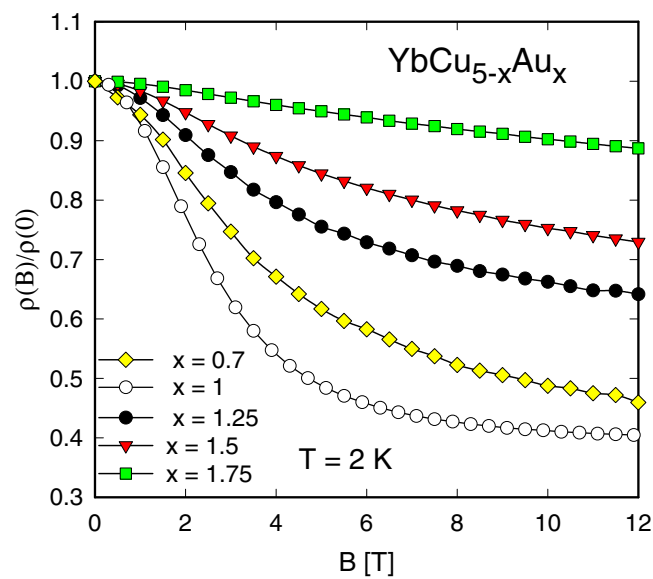


Figure 4. The isothermal magnetoresistance $\rho(B)/\rho(0)$ of $\text{YbCu}_{5-x}\text{Au}_x$ for various concentrations x at $T = 2$ K. $\rho(B)$ and $\rho(0)$ are the resistivities at a magnetic field B and at zero field, respectively.

These latter observations confirm once more the exceptional position of YbCu_4Au within the solid solution series. In fact, a detailed study concerning the magnetoresistance at $T = 2$ K for concentrations $0 < x \leq 1$ corroborates the above-stated trend [3].

Although the Cu/Au substitution is isoelectronic, it causes significant changes of electronic properties. An analysis of the magnetoresistance data in terms of the Schlottmann–Batlogg

model [9] for the concentration range $0.2 \leq x \leq 1$ reveals a monotonic decrease of the Kondo temperature T_K from ≈ 40 K for the former to $T_K < 1$ K for the latter. A similar analysis applied to the samples with $x = 1.25, 1.5$ and 1.75 reverses the above results and T_K starts to increase again, up to about 19 K for $x = 1.75$. This non-monotonic $T_K(x)$ dependence signifies that the Au substitution on the 4c site originates changes of the electronic structure which are distinctly different from those affected by such substitutions on the 16e sites.

In summary, we have shown that a solid solution forming the AuBe₅ structure exists in YbCu_{5-x}Au_x well beyond the already known boundary $0 < x \leq 1$, extending, presumably, up to $x = 1.8$. Although the Cu/Au substitution is isoelectronic, distinct ranges with different physical properties exist for $0 < x \leq 1$ and $1 < x \leq 1.8$. T_K exhibits the lowest value for the YbCu₄Au ordered compound, which marks the transition between disordered 4c sites and disordered 16e sites.

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