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$YbIn_{1-x}Ag_xCu_4$: Crossover from first-order valence transition to heavy Fermion behavior

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Abstract

The results of an on-going study of $YbIn_{1-x}Ag_xCu_4$ are presented. $YbInCu_4$ undergoes a first-order valence transition at 40 K, while $YbAgCu_4$ is an isostructural heavy Fermion compound. We have succeeded in growing single crystals of these compounds, as well as intermediate alloys, using flux-growth techniques. A smooth evolution from $YbInCu_4$ to $YbAgCu_4$ is observed. Results on the influence of sample quality, as well as the effect of other dopants, on the valence transition in $YbInCu_4$ are also discussed.

Since being discovered by Felner and Nowik [1], $YbInCu_4$ has continued to attract attention [2]. $YbInCu_4$ is the only stoichiometric compound yet-discovered that undergoes a first-order isostructural valence transition at ambient pressure. At high temperature ($T > 100$ K) Yb is trivalent, displaying Curie–Weiss susceptibility with a paramagnetic moment near the free-ion value of $4.5\mu_B$. At the first-order transition the Yb valence is reduced to approximately 2.9 (as estimated by X-ray absorption and lattice constant measurements [1]), with a consequent increase in lattice volume of 0.5% and a loss of magnetic susceptibility and spin scattering. On the other hand, isostructural $YbAgCu_4$ [3, 4] is a moderately heavy ($\gamma = 250$ mJ/mol K^2) mixed-valence compound whose susceptibility and specific heat are consistent with a $J = \frac{7}{2}$ Kondo impurity, as described by the Coqblin–Schrieffer model [5, 6]. Both $YbInCu_4$ and $YbAgCu_4$ crystallize in the FCC C15b structure with lattice constants of 7.158 Å and 7.083 Å, respectively.

Despite such study, many details, both theoretical and experimental, are unresolved. Theoretically, there exist several competing models of such valence transitions, the γ–α transition in Ce being the prototype [7]. Experimentally, controversy exists as to the precise value of the transition temperature, T_v – values ranging from 40 to 80 K have been reported – and to the evolution of the transition upon doping away from the stoichiometric compound [1, 2, 8]. In an attempt to resolve the materials issues as well as to understand the evolution from first-order valence change to mixed valence as Ag is substituted for In, we have synthesized single crystals of and performed various physical measurements on $YbIn_{1-x}Ag_xCu_4$.

Single crystals of $YbInCu_4$ were grown by combining stoichiometric ratios of the constituent elements in a 1 : 1

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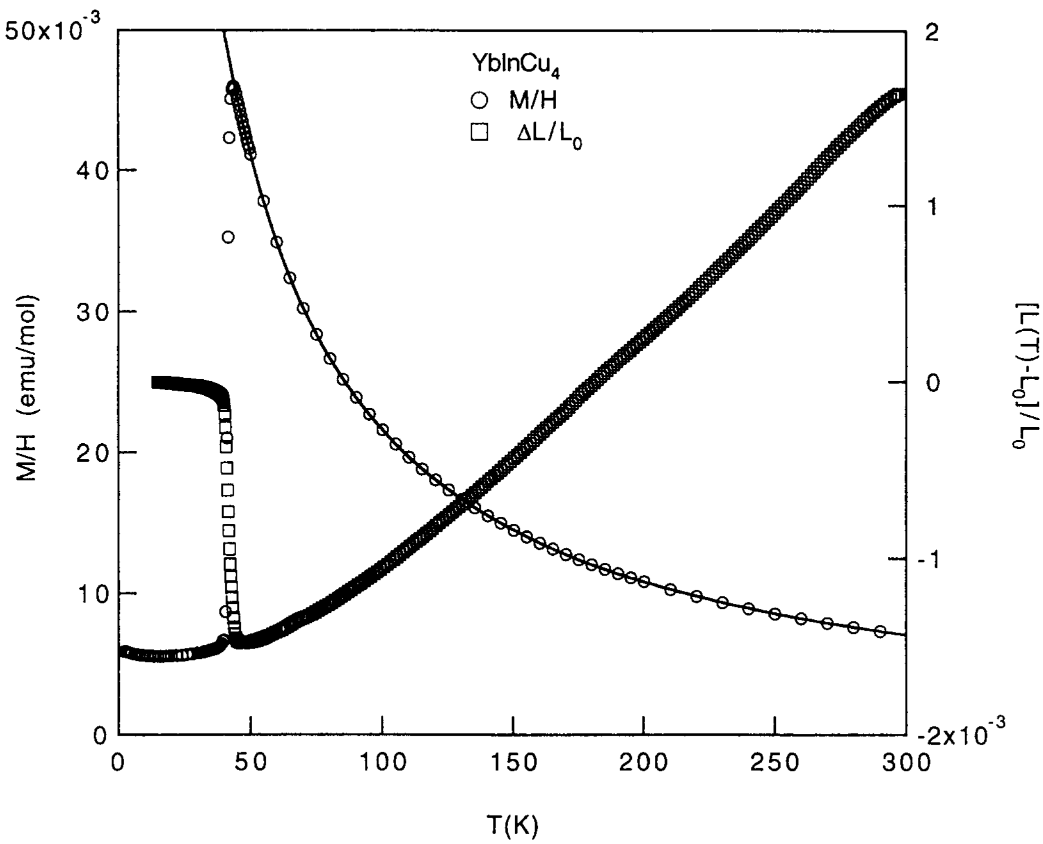

Fig. 1. Magnetic susceptibility and relative length change as a function of temperature for a single crystal of $YbInCu_4$. A Curie–Weiss fit (shown as the solid line) to the high-temperature data gives $\mu_{eff} = 4.37\,\mu_B$ and $\Theta = -7.2$ K.

ratio with InCu flux. The high purity materials (minimum 99.99% purity) were placed in an alumina crucible and sealed in an evacuated quartz tube. The sample was then heated to 1100°C and cooled slowly (20°C/h) to 800°C, at which point the excess flux was spun off, leaving tetrahedrally-shaped crystals with a typical dimension of several millimeters.

The magnetic susceptibility, measured with a SQUID magnetometer, and the relative length change, measured with a capacitance dilatometer, as a function of temperature for such a crystal are shown in Fig. 1. The midpoint of the transition occurs at 42 K with a 10–90% width of less than 2 K. All of our crystals produced in this manner have transition temperatures between 40 and 45 K with maximal widths of 5 K and show no evidence for transitions in the 50–80 K range as reported by others and as observed by us for samples made on stoichiometry in sealed Ta tubes. Presumably, the difference in both sharpness and position of the valence transition is due to the lower temperature at which the crystals are produced and the consequent ordered nature of our crystals, as evidenced by their highly-faceted morphology. Preliminary structural refinements based on neutron diffraction data [9] suggest that polycrystalline samples with higher T_v and broader transitions possess 10% disorder on the Yb and In sites, while our flux-grown single crystals have only 2–3% disorder.

We have also synthesized single crystals of $YbIn_{1-x}Ag_xCu_4$ for the full range of x values ($0 \leqslant x \leqslant 1$) in a similar manner. The room-temperature lattice parameter as a function of Ag concentration is shown in Fig. 2. Vegard's law is not obeyed over the full range of concentrations. Apparently, as the smaller Ag substitutes for the larger In, the size (and hence average valence) of Yb adjusts (Yb^{2+} is larger than Yb^{3+}) so as to keep the overall lattice parameter constant. For Ag concentrations greater than 0.5, the maximal valence compensation has occurred, the Yb-valence remains constant, and

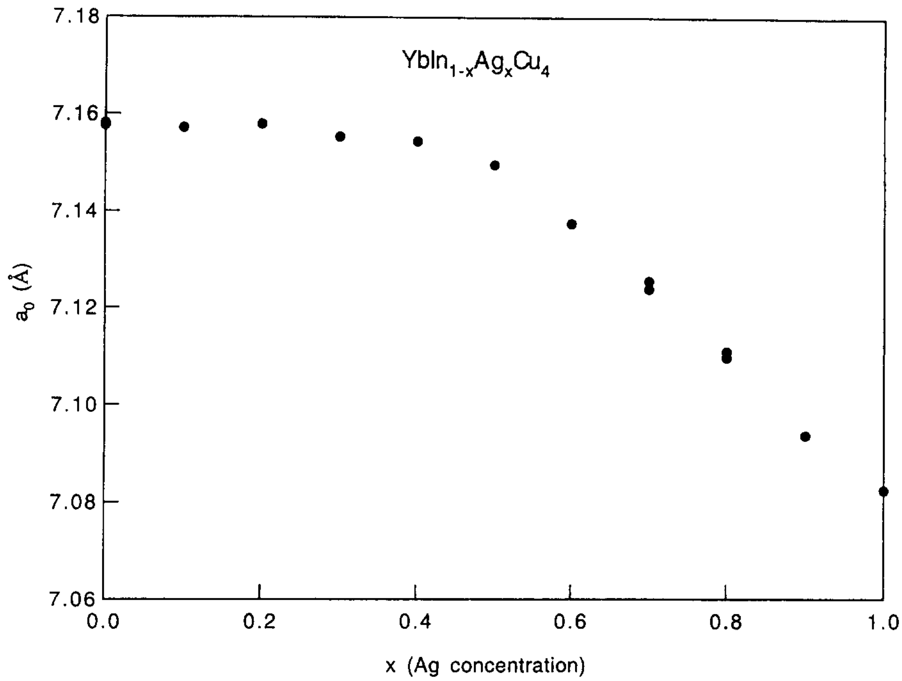

Fig. 2. Cubic lattice constant at room temperature as a function of x for $YbIn_{1-x}Ag_xCu_4$.

Vegard's law is obeyed for larger x. A similar but less dramatic effect has been observed in the mixed-valence system $Ce(In_{1-x}Sn_x)_3$ [10]. The non-linear nature of the substitution is also apparent from measurements of the low-temperature linear coefficient of specific heat. Pillmayr et al. have measured γ as a function of x for a limited range of Ag concentrations [11]. They observe that $\gamma = 50\,\text{mJ/mol}\,\text{K}^2$ and is approximately independent of x for $x < 0.3$ while γ for $YbAgCu_4$ is $250\,\text{mJ/mol}\,\text{K}^2$.

The magnetic susceptibility, χ, as a function of temperature for a series of Ag concentrations is shown in Fig. 3. Initially, T_v increases with Ag concentration, reaching an estimated critical concentration of $x = 0.15$, with $T_v = 65$ K. With further doping the low-temperature drop in susceptibility is broadened and reduced in magnitude, until, near full Ag substitution, a peak characteristic of a $J = \frac{7}{2}$ Kondo impurity develops. The high-temperature magnetic susceptibility can be fit with a $J = \frac{7}{2}$ Kondo impurity model for all x. Extracting the Kondo temperature from these fits confirms our hypothesis as to the evolution of the room temperature lattice constant: the characteristic temperature increases with x for $0 \leqslant x \leqslant 0.5$, indicating increasing mixed-valency.

Effects similar to those in the magnetic susceptibility are observed in the temperature dependence of the electrical resistivity as a function of x. Initially ($x = 0$), a sharp and hysteretic drop in resistance at T_v is observed. At intermediate x, the resistance as a function of temperature is relatively flat, due presumably to Ag–In site disorder. Finally, for $x = 1$ a coherence-induced drop in the resistance near 50 K is observed. The magnitude of the room-temperature electrical resistivity of $YbAgCu_4$ is approximately ten times less than that of $YbInCu_4$, consistent with earlier reports [11].

In addition to our work with $YbIn_{1-x}Ag_xCu_4$, we have also synthesized crystals for many other dopants. Although a detailed analysis cannot be made here due to space considerations, the following general trends have been observed. Substituting for Yb (with Sc, Y, and many of the rare earths) tends to reduce T_v while a sharp transition is maintained. All divalent, trivalent and tetravalent substitutions for In initially increase the transition temperature, with maximal T_v's near 60 K for x near 0.1, and then the transition is broadened, similar to Ag-substitution, for subsequent doping. Finally, substitution for Cu tends to eliminate all evidence of the transition at rather small (of order 10%) dopant levels.

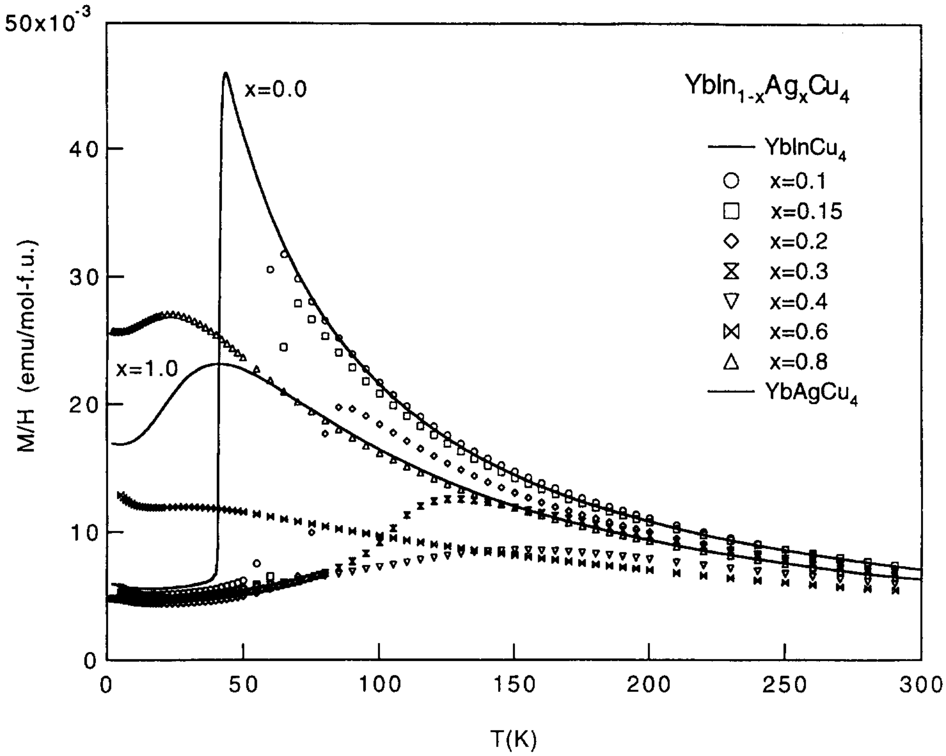

Fig. 3. Magnetic susceptibility (in units of emu/mole-formula unit) as a function of temperature for $YbIn_{1-x}Ag_xCu_4$ at various values of x.

Much work remains to be done in order to understand the distinctions between these dopants as well as the pressure and magnetic-field dependences of these effects.

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