Alloying and pressure effect on the mixed-valence state of Yb in YbInCu$_4$

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Abstract

The susceptibility and thermal expansion of Yb$_{1-x}$R$_x$InCu$_4$ ($x \leqslant 0.25$; R = Y, La and Ce) have been measured at ambient and high pressures. These compounds undergo a first-order valence transition from an intermediate-valence state to a nearly trivalent state with increasing temperature. The valence change at the transition is $\delta v \sim 0.1$ for YbInCu$_4$. It decreases on both alloying and applying pressure for all the compositions studied. From the pressure effect on the susceptibility of YbInCu$_4$, the Grüneisen parameter for the Kondo energy Ω_K is determined to be -34.5 and -20 for the low-temperature and the high-temperature state, respectively. The Γ coefficient characterizing the hybridization strength between the 4f and conduction electrons for the intermediate-valence state is nearly five times larger than that for the high-temperature local-moment state. The obtained results suggest that the change of the 4f–conduction band electron hybridization rather than the volume dependence of the Kondo interaction is responsible for a large modification of the physical properties of the YbInCu$_4$-based compounds at the valence transition.

1. Introduction

The YbInCu$_4$ compound undergoes a first-order temperature-induced isostructural valence phase transition at ambient pressure [1, 2]. Above the critical temperature $T_v \sim 40$ K the

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compound exhibits a Curie–Weiss susceptibility with an effective paramagnetic moment close to the free Yb^{3+} ion value of 4.54 μ_B. The valence of the Yb ion decreases suddenly by ~ 0.1 at T_v [3, 4]. In spite of the small change in the valence, both the susceptibility and the electrical resistivity greatly decrease and a Pauli paramagnetic state is realized below T_v.

Because of such unusual behaviour, the valence transition in $YbInCu_4$ has extensively been studied with different experimental techniques. Neutron and x-ray diffraction studies show that $YbInCu_4$ has a cubic $AuBe_5$-type structure, in which the Yb ions are completely ordered at the 4c site [5, 6]. On cooling the compound a sharp lattice expansion ($\Delta a/a = 0.15\%$) takes place at T_v without change in the crystal symmetry [3–5]. A study of the Cu nuclear quadrupole resonance shows that a stable localized 4f-electron state for $T > T_v$ changes to a Fermi-liquid state with strong hybridization between the 4f and conduction electrons for $T < T_v$ [7]. Electrical resistivity and Hall effect measurements reveal that the carrier concentration increases by a factor of ten on decreasing the temperature below T_v [2, 4].

The valence transition of $YbInCu_4$ is easily affected by either applying high pressure or alloying. The pressure effect on the critical temperature T_v was studied by means of resistivity, magnetic susceptibility and thermal expansion measurements [2, 8–10]. The value of T_v is found to decrease by applying pressure; $dT_v/dP \sim -20$ K GPa^{-1}. This result is consistent with the stabilization of the high-temperature trivalent state of Yb having smaller size. The size effect is usually also observed by chemical alloying. The substitution of ion with larger radius (La or Eu^{2+} for Yb, and Sn or Ag for In) increases the valence transition temperature, while the alloying of ions with smaller radius decreases T_v [3]. In $Yb_{1-x}R_xInCu_4$ with R = Y, Lu, however, the observed transition temperature decreases rapidly with increasing x, which cannot be explained by the volume effect [11]. It should be noted that the change of the electron count has a large impact on Yb valence in the $YbXCu_4$ materials with different X metals [2].

The valence of Yb in some of $YbXCu_4$ compounds including X = In was determined by measurements of x-ray absorption at the Yb L_{III} edge [3, 4]. On the other hand, thermal expansion measurements also give direct information on the change in the 4f electron occupancy at the valence transition since the volume change at T_v is proportional to the valence change [3, 4]. An important advantage of this technique is that the valence change at T_v can be determined accurately as a function of pressure [10]. In the present study we have measured the thermal expansion of $Yb_{1-x}R_xInCu_4$ with R = Y, La or Ce for $x \leqslant 0.25$ at ambient and high pressures to examine the effects of alloying and pressure on the valence state of Yb in $YbInCu_4$-type compounds.

2. Experimental details

Polycrystalline samples of $Yb_{1-x}R_xInCu_4$ with R = La or Ce were prepared by induction melting of the high-purity constituents in alumina crucibles. Due to the volatile nature of Yb, a small excess of this constituent was used in the initial melt. The ingots were crushed and remelted using a semi-levitation technique to achieve better mixing of the components and smaller grain size. They were wrapped with Ta foils, sealed in quartz tubes filled with purified argon gas and annealed for one month at 870 °C. After annealing the samples, the valence phase transition for most of the compositions occurs within a temperature range of less than 2 K, which is indicative of a good homogeneity and is comparable to the best samples reported [2]. However, the Y-substituted samples, prepared and annealed by such a method for $x > 0.08$, display a broadened double-step valence transition [11]. Therefore, we used in this study single crystals of $Yb_{1-x}Y_xInCu_4$ with $x = 0$, 0.1 and 0.2 grown in an In–Cu flux, having a sharper transition. Details of the single-crystal growth are reported in [12]. Powder x-ray-diffraction study indicates that all the samples are single phase with the cubic C15b

structure. For the three systems studied, partial replacement of Yb with R = Y, La or Ce leads to an increase in the lattice parameter, as reported previously [11, 12].

The dc magnetic susceptibility of YbInCu$_4$ under pressure was measured using a Quantum Design SQUID magnetometer in the temperature range 5–200 K in a magnetic field 0.5 T. Hydrostatic pressure up to 1.4 GPa was applied to the sample using a specially designed high-pressure clamp cell of 8.8 mm in diameter made of a CuTi alloy with a very small susceptibility [13].

Thermal expansion measurements under pressure were carried out with WK-09-031CF-350 strain gauges (Micro-Measurements, USA). A gauge glued on the sample and a reference gauge glued on a quartz plate were placed inside the pressure cell and connected to a dc Wheatstone bridge. A clamp-type pressure cell of 25 mm in outer diameter was used to apply high hydrostatic pressure up to 1.6 GPa. For both magnetization and thermal expansion measurements, the samples inside the cell were placed in a Teflon capsule filled with a liquid pressure medium, Fomblin. Since the pour point of Fomblin is ∼220 K, the pressure variation inside the pressure cell is expected to be small within the temperature range 5–140 K.

The temperature dependences of both the susceptibility and the sample length measured on cooling and heating the sample show a small hysteresis around T_v. All the dependences presented in this study were measured on heating the sample.

3. Experimental results and discussion

3.1. Effect of alloying with Y, La or Ce on the valence state of Yb

Both single-crystalline and polycrystalline YbInCu$_4$ samples studied show a very sharp valence phase transition. The transition temperature T_v, defined as the temperature at which $d\chi/dT$ becomes a maximum, is slightly different: $T_v = 39$ K for the polycrystal of YbInCu$_4$ and 42 K for the single crystal. However, the values correspond well to those reported previously [2, 10]. The susceptibility measurements for the Yb$_{1-x}$Y$_x$InCu$_4$ single crystals show that T_v decreases with increasing x [2, 11, 12]. At high temperatures the molar susceptibilities of the crystals for different x coincide, indicating that both the effective magnetic moment μ_{eff} and the paramagnetic Curie temperature θ_p are unchanged (according to our measurements, $\mu_{\text{eff}} = 4.13\,\mu_B$/Yb and $\theta_p = -1.3$ K for YbInCu$_4$ single crystal). For La- and Ce-substituted materials, the valence phase transition shifts to the high-temperature region with increasing concentration [11]. The transition remains very sharp for all the La-substituted samples and at least up to $x = 0.12$ for the Ce-substituted ones. At higher Ce concentration the temperature dependence of the susceptibility shows a broad anomaly. This behaviour seems to be similar to that of the dense Kondo lattice compound YbAgCu$_4$ [14]. However, we found that the Yb$_{1-x}$Ce$_x$InCu$_4$ samples for $x = 0.16$ and 0.20 exhibit a first-order field-induced valence transition at low temperatures [15], which changes to a second-order one with increasing temperature. At high temperatures the molar susceptibility slightly decreases with increasing both the La and Ce concentrations. For Yb$_{1-x}$La$_x$InCu$_4$ the estimated value of μ_{eff} does not change, while θ_p gradually decreases with increasing x with $d\theta_p/dx = -26$ K. Alloying with Ce also causes the decrease of θ_p at small x, while for $x \geqslant 0.08$ the susceptibility in the temperature range 80–150 K does not follow the Curie–Weiss law [11].

For most of the samples, a small upturn of the susceptibility appears at low temperatures below 10 K, which is usually attributed to a small amount of impurities [12] or a partial Yb disorder. However, it was shown recently that for Yb$_{1-x}$Y$_x$InCu$_4$ single crystals the Curie-like upturn can be eliminated completely using proper sample preparation conditions [16]. For Yb$_{1-x}$Ce$_x$InCu$_4$ the upturn will be caused mainly by magnetic Ce ions. By subtracting the
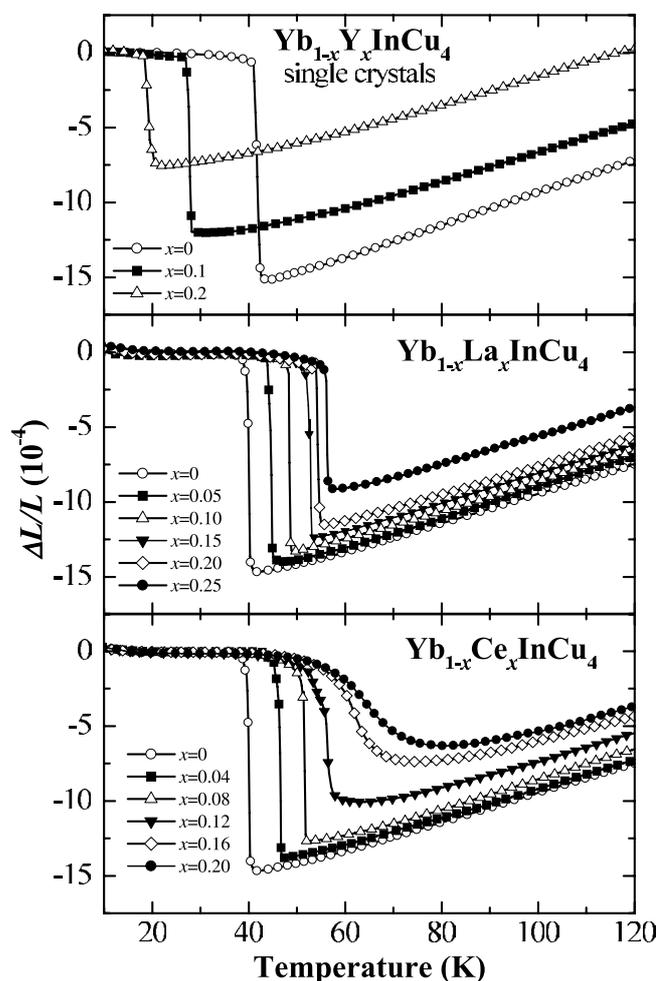
Figure 1. Linear thermal expansion curves of $Yb_{1-x}Y_xInCu_4$, $Yb_{1-x}La_xInCu_4$ and $Yb_{1-x}Ce_xInCu_4$, for different x at ambient pressure.

temperature-independent Pauli-paramagnetic term and fitting the susceptibility upturn to the Curie law we estimated the value of μ_{eff} for the substituted Ce ions, which does not exceed half of the value of the free Ce^{3+} ion $\mu_{eff} = 2.54\,\mu_B$ [11]. This suggests that the Ce ion is in the mixed valence state.

Figure 1 shows the linear thermal expansion $\Delta L/L$ of the $Yb_{1-x}R_xInCu_4$ (R = Y, La and Ce) samples as a function of temperature. The valence transition is very sharp at T_v, indicating that these samples are of high quality. For parent $YbInCu_4$ an abrupt change of $\Delta L/L$ at T_v, $\delta L/L = (\Delta L/L)_{low} - (\Delta L/L)_{high} = 0.15\%$, is consistent with the data reported previously [3, 5, 6, 10]. For all the compositions, the transition temperature corresponds well to that determined from the susceptibility measurements [11, 12]. The change of $\Delta L/L$ decreases monotonically with increasing x. Since the crystal structure of $YbInCu_4$ is unchanged by the transition [3], the volume change at T_v is equal to three times as large as the change of $\Delta L/L$.

The concentration dependence of the volume change $\delta V/V(T_v)$ is shown in figure 2(a). The valence change of Yb at T_v can be estimated from the thermal expansion data as follows [3].
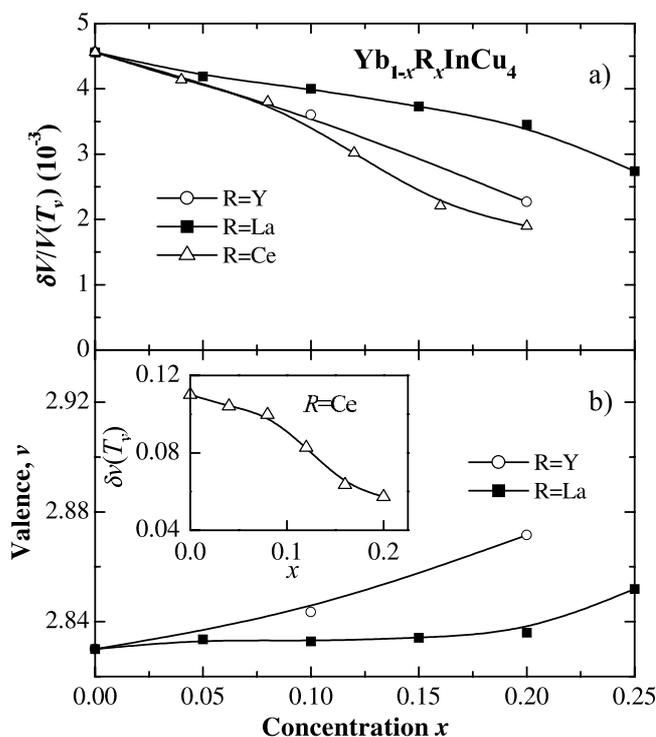
Figure 2. Concentration dependence of the volume change at the valence transition in Yb$_{1-x}$R$_x$InCu$_4$ for R = Y, La, Ce (a), low-temperature valence for R = Y, La (b) and valence change at the transition for R = Ce (inset).

The cubic Laves phase compound YbAl$_2$ has a lattice parameter larger by 1.5% than that expected for Yb^{3+}Al$_2$ because Yb is in a mixed valence state with a valence $v = 2.5$. Considering the Vegard rule and taking into account that the Yb content in YbInCu$_4$ is only half of that in YbAl$_2$, the valence change at T_v is estimated to be $\Delta v = 0.1$. In order to obtain the absolute value of the valence in YbInCu$_4$, the valence state in the high temperature phase was assumed to be +3 [10] since the effective paramagnetic moment μ_{eff} is close to that expected from the free Yb^{3+} ion. However, careful measurements of the susceptibility always show that the value of μ_{eff} is slightly lower than the free ion value 4.54 μ_B [17–19]. The crystal-field effect cannot give an appreciable decrease of μ_{eff} since the splitting of the $J = 7/2$ multiplet of the Yb^{3+} ion in the cubic crystal electric field does not exceed 44 K in YbInCu$_4$ [20]. According to the Anderson single-impurity model, the deviation of the valence from 3+ is expected in the high-temperature phase by the Kondo effect ($T_K = 25$ K), which reduces the effective 4f hole occupation [4]. Measurements of x-ray absorption at the Yb L$_{III}$ edge show that the valence of Yb in the high-temperature phase of YbInCu$_4$ is slightly lower than 3: $v = 2.9$ [3] or 2.93–2.96 [4, 21, 22]. In the present study we adopt the value $v = 2.94$ for the valence of Yb in the high-temperature phase of YbInCu$_4$. The valence is decreased to 2.83 in the intermediate-valence state [4]. Our susceptibility data for the Y- and La-substituted compounds indicate that the value of μ_{eff} remains almost unchanged [11, 12]. Therefore the valence of Yb at high temperatures is considered to be nearly constant. Considering the amount of Yb in Yb$_{1-x}$R$_x$InCu$_4$ (R = Y and La), we calculated the low-temperature valence of Yb in the alloys from the volume change at T_v. As seen from figure 2(b), the valence

for $Yb_{1-x}La_xInCu_4$ remains unchanged at least up to $x = 0.2$, while Y alloying leads to an increase of the valence. Probably the interaction of the 4f electrons of Yb with the 4d-band electrons of Y is weaker than that with the 5d-band electrons of La, which reduces the Kondo effect and increases the valence in the mixed-valence state.

On the other hand, Ce ions are usually unstable and have an intermediate valence between Ce^{3+} and Ce^{4+}. Therefore one can expect that the Ce substitution for Yb in YbInCu$_4$ will increase the concentration of the valence electrons and reduce the valence of Yb. We observed that the volume change of $Yb_{1-x}Ce_xInCu_4$ at T_v is smaller than those of the Y- and La-substituted compounds with the same concentration. In order to explain these results we consider that the Yb valence in the high-temperature phase of $Yb_{1-x}Ce_xInCu_4$ is not constant and decreases with increasing x. This consideration is supported indirectly by the measurement of the concentration dependence of the lattice parameters. The ionic radius of Ce^{3+} is smaller than that of La^{3+}, while the lattice expansion due to the Ce alloying is considerably larger [11]. Taking into account the ionic radii of the corresponding elements and intermediate valence of Ce, we can expect that the lattice expansion of $Yb_{1-x}Ce_xInCu_4$ for a fixed Yb valence should be somewhat intermediate between those of the systems with La ($da/dx = 9.4$ pm) and Y ($da/dx = 4.6$ pm) [11]. The observed large lattice expansion $da/dx = 15.2$ pm for $Yb_{1-x}Ce_xInCu_4$ [11] can be explained by the decrease of the Yb valence $dv/dx = -0.75 \pm 0.23$ at room temperature. Since the estimation is very rough, L_{III}-edge absorption measurements are strongly needed to clarify the Yb valence state in $Yb_{1-x}Ce_xInCu_4$. We cannot determine the absolute value of the Yb valence in the mixed valence state, so we show the valence change at the transition in the inset of figure 2, which decreases with increasing x.

3.2. Pressure effect on the susceptibility and thermal expansion

Although the effect of hydrostatic pressure on the valence phase transition in YbInCu$_4$ was studied in several papers, these data are mainly restricted to the pressure variation of T_v [2, 8, 23]. We carefully measured the magnetization of single-crystal YbInCu$_4$ under pressure using a SQUID magnetometer to establish the pressure effect on the susceptibility in both the low-temperature and high-temperature phases. Figure 3 shows the magnetic susceptibility of YbInCu$_4$ as a function of temperature for several fixed pressures up to 1.4 GPa. The valence phase transition remains very sharp under pressure and T_v gradually decreases. As seen from the inset in figure 3, the pressure dependence of T_v is slightly non-linear. The value of dT_v/dP amounts to -20 K GPa^{-1} up to pressure $\sim$0.7 GPa and decreases with further increasing pressure. The non-linearity of dT_v/dP was evidenced previously by measuring the resistivity under high pressure up to 3.3 GPa [24].

The temperature-independent susceptibility in the low-temperature state increases with increasing pressure. According to the exact Bethe ansatz solution of the Coqblin–Schrieffer impurity model [25], the thermodynamic properties in the Fermi-liquid state at low temperatures, in which the f and conduction-band states are strongly hybridized, are determined by the Kondo energy scale T_0. The zero-temperature susceptibility $\chi(0)$ is proportional to $1/T_0$ [25]:

$$\chi(0) = \frac{N_A \nu(\nu^2 - 1)g_J^2 \mu_B^2}{24\pi k_B T_0}, \tag{1}$$

where N_A is the Avogadro number, $\nu = 2J + 1$ is the degeneracy of the ground state and g_J is the Lande factor. The Kondo scale T_0 determined using equation (1) is shown as a function of pressure in the inset in figure 3. The value of T_0 decreases nearly linearly; $dT_0/dP = -184$ K GPa^{-1}. Sarrao *et al* [26] measured the susceptibility under high pressure. Their data give a slightly lower value $dT_0/dP = -158$ K GPa^{-1}. The decrease of T_0
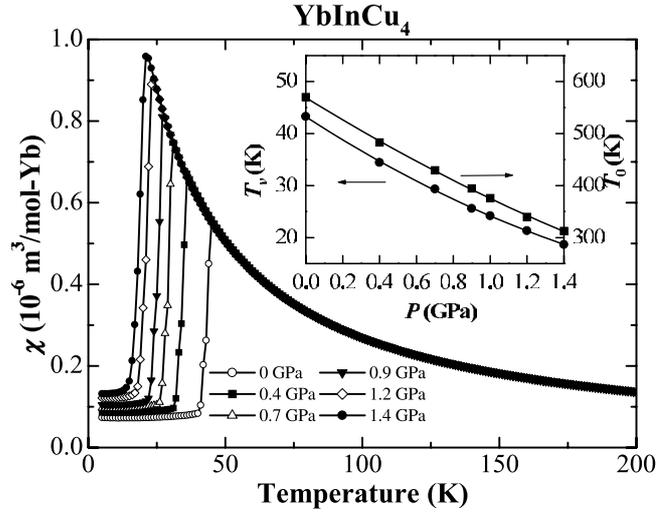
Figure 3. Temperature dependence of the molar susceptibility of single-crystal YbInCu₄ for different pressures. Inset: pressure dependence of the valence transition temperature T_v (circles) and the low-temperature Kondo scale T_0 (squares) for YbInCu₄.

implies that the low-temperature coherent Kondo state is destabilized by the external pressure. According to our data, a good linear relation holds between T_0 and T_v, similar to that reported for the $Yb_{1-x}Y_x InCu_4$ and $Yb_{1-x}Lu_x InCu_4$ systems [11, 12].

In materials where the physical properties are dominated by the Kondo effect, the magnitude of the volume dependence of the Kondo interaction is characterized by the Grüneisen parameter for the Kondo temperature T_K,

$$\Omega_K = -\frac{d \ln T_K}{d \ln V} = \frac{B}{T_K}\frac{d T_K}{d P} = \frac{B}{T_0}\frac{d T_0}{d P}, \tag{2}$$

where B is the bulk modulus. The Kondo temperature is defined as $T_K = C/\chi(0)$ (where $C = N_A \mu_B^2 J(J+1)/3k_B$ is the $J = 7/2$ Curie constant for Yb) and it is proportional to the low-temperature scale T_0: $T_K = [2\pi/(2J+1)]T_0$ [17]. Using the value of $B = 83$ GPa (at $T = 20$ K) [10] we obtain $\Omega_K^{LT} = -34.5$ for the low-temperature mixed-valence state of YbInCu₄. This value practically coincides with that determined from specific heat measurements [26] and is consistent with $\Omega_K^{LT} = -40$ estimated from the magnetostriction data [27].

Since the effect of pressure on the susceptibility is very small for $T > T_v$ as shown in figure 3, we could not determine the pressure dependences of the values of μ_{eff} and θ_p obtained by direct fitting of the susceptibility to the Curie–Weiss law. In order to obtain these dependences we carefully measured the temperature dependences of the susceptibility under pressure up to 0.7 GPa along the three main crystallographic directions of the single crystal and then averaged the data at fixed pressures. The observed anisotropy of the magnetic properties of YbInCu₄ is small, which was discussed thoroughly in a previous paper [19]. As representative data, we show in figure 4(a) the pressure variation of the susceptibility $\chi(P)/\chi(0)$ at 150 K. The susceptibility increases linearly with pressure with a rate $d \ln \chi/d P = 0.043$ GPa^{-1}. Svechkarev *et al* [27] obtained a similar value from susceptibility measurements at fixed temperatures under pressure up to 0.15 GPa (closed circles in figure 4(a)). However, the authors of [27] reported a large negative value of $\theta_p = -13$ K, positive pressure derivative $d\theta_p/d P = 6.4$ K GPa^{-1} and pressure-independent effective moment. According to our data
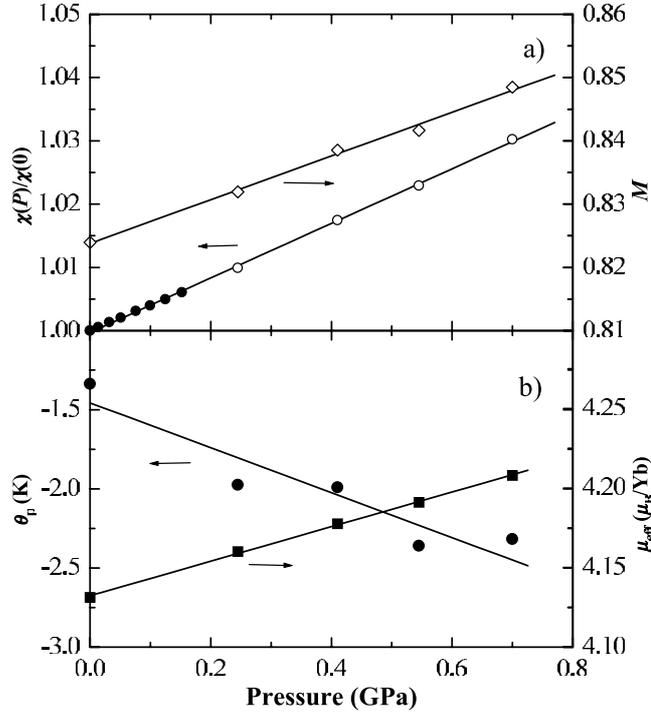
Figure 4. Pressure dependence of the reduced magnetic susceptibility $\chi(P)/\chi(0)$ and the reduced effective magnetic moment $M = \chi T/C$ at 150 K (a) and the parameters θ_P and μ_{eff} obtained from the Curie–Weiss fit (b) for single-crystal YbInCu$_4$. The lines represent the linear fits to the experimental data.

presented in figure 4(b), θ_p is of the order of -1 K and decreases with increasing pressure with a rate $d\theta_p/dP = -1.4$ K GPa^{-1}. The value of μ_{eff} increases slightly with pressure, $d\mu_{eff}/dP = 0.11$ μ_B GPa^{-1}. Similar changes of the Curie–Weiss parameters under pressure were reported by Matsumoto *et al* [9].

In the Kondo regime, the deviation of the effective moment from its free-ion value is considered to be a monotonic function of T_K. For YbInCu$_4$ the deviation is small, and the value of $T_K \approx 25$ K is determined from inelastic neutron scattering [28] and from fitting the reduced effective moment $\chi T/C$ to the prediction of the $J = 7/2$ Kondo model [2, 4]. In figure 4(a) we show representative data of the values $M \equiv \chi T/C$ for $T = 150$ K as a function of pressure. (Actually, $\chi T/C$ means the ratio of the square of the effective moment of Yb and that of the free Yb^{3+} ion.) The value of M is found to be practically temperature independent and increases linearly with pressure. This is indicative of the decrease of the Kondo effect by applying pressure. The average value of dM/dP determined at different temperatures is $\langle dM/dP \rangle = 0.035$ GPa^{-1}. The increase of M with pressure is caused by the increase of the 4f hole occupation n_f, which is related to the valence v of the Yb ion by $n_f = v - 2$. On the other hand, in the Kondo impurity limit the Kondo temperature is connected with the value of n_f as follows [4, 29]:

$$T_K = \frac{2J + 1}{\pi} \Gamma \left(\frac{1 - n_f}{n_f} \right). \tag{3}$$

Here the coefficient $\Gamma = V_{kf}^2 \rho(\varepsilon_f)$ is the hybridization strength between the 4f and the conduction electrons. V_{kf} is the hybridization matrix of the 4f and conduction electrons and
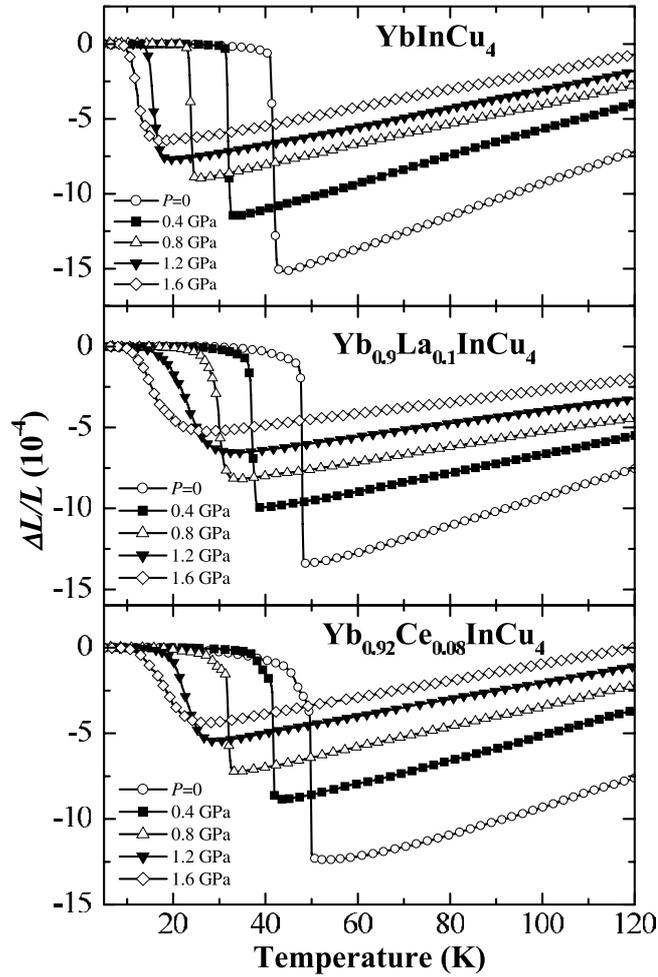
Figure 5. Linear thermal expansion curves of YbInCu$_4$, Yb$_{0.9}$La$_{0.1}$InCu$_4$ and Yb$_{0.92}$Ce$_{0.08}$InCu$_4$ for different pressures.

$\rho(\varepsilon_f)$ is the conduction electron density of states at the Fermi level. Therefore, for small change of n_f produced by applying pressure, an approximate linear relation can be expected between M and T_K. Then we obtain $\mathrm{d}T_K/\mathrm{d}P = -5$ K GPa^{-1} and the Gruneisen parameter for the high-temperature Kondo state $\Omega_K^{HT} = -20$. The absolute value of Ω_K^{HT} is lower than the previous estimate $\Omega_K^{HT} = -32$ [27]. Yb-based compounds have negative values of Ω_K, but Ce-based compounds have positive values [27], which reflects the general tendency of f-state depopulation in Ce- and Yb-based compounds on applying pressure. The observed small difference in the values of the Gruneisen parameters for the low- and high-temperature phases implies that the Kondo volume collapse model [30] cannot explain the valence phase transition in YbInCu$_4$ because this model considers a strong volume dependence of the Kondo temperature.

From the comparison of the Gruneisen parameters for the low- and high-temperature states of YbInCu$_4$ one can see that the change of the Kondo temperature at the transition will decrease with increasing pressure. Therefore, the change of the 4f hole occupancy will also
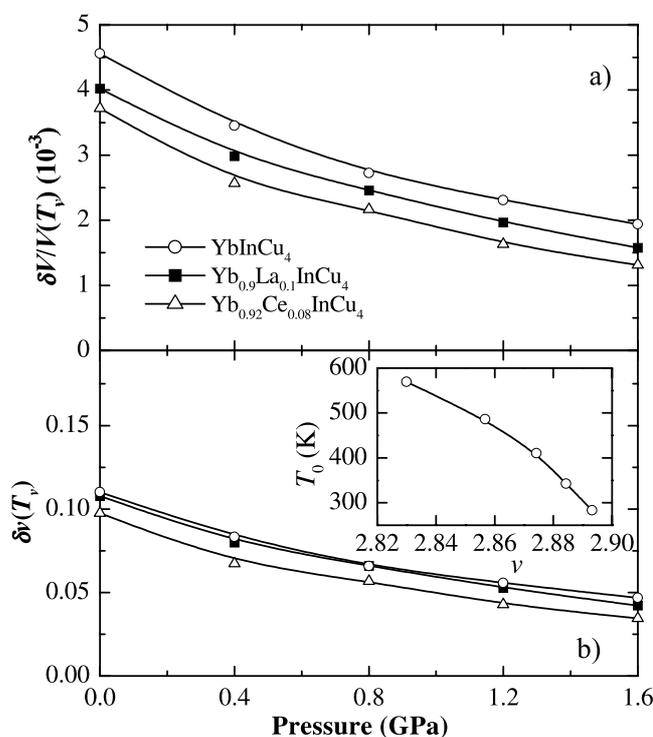
Figure 6. Pressure dependence of the volume (a) and valence (b) change at the valence phase transition in $YbInCu_4$, $Yb_{0.9}La_{0.1}InCu_4$ and $Yb_{0.92}Ce_{0.08}InCu_4$. Inset: T_0 as a function of Yb valence v for $YbInCu_4$.

decrease. Figure 5 shows thermal expansion curves under pressure for three representative samples: single-crystal $YbInCu_4$ and polycrystalline $Yb_{0.9}La_{0.1}InCu_4$ and $Yb_{0.92}Ce_{0.08}InCu_4$. For all the samples, the abrupt change of $\delta L/L$ at $T = T_v$ decreases with increasing pressure. This is consistent with the above consideration based on the susceptibility data under pressure. The volume change at the transition $\delta V/V(T_v)$ is a nonlinear function of pressure (figure 6(a)). These dependences are very similar for the three studied samples. The values of the valence change at T_v (figure 6(b)) for pure $YbInCu_4$ and the La-substituted sample almost coincide. In the pressure range 0–0.8 GPa the valence increases with the rate $dv/dP = 0.055$ GPa^{-1}, which is consistent with a value of $dv/dP = 0.045$ GPa^{-1} reported previously [10]. Above 0.8 GPa, the valence increases more gradually. The origin of this behaviour is not clear. However, it correlates with the nonlinear dependence of $T_v(P)$ [24] and may be associated with an additional interaction in $YbInCu_4$ under high pressure. It was found recently that single crystals of $Yb_{1-x}Y_xInCu_4$ exhibit a weak ferromagnetic ordering under pressure [19, 31]. Taking into account a negative value of $d\theta_P/dP$ found in the present study, the appearance of ferromagnetic interaction is difficult to explain. Weak ferromagnetism found in [31] may originate from a canted antiferromagnetic structure. Additional low-temperature high-pressure experiments are necessary to understand this behaviour in further detail.

From the comparison of the susceptibility and thermal expansion data it became clear that the low-temperature susceptibility for both pure and doped $YbInCu_4$ is determined by the valence of Yb in the mixed valence state. In the inset of figure 6 we plotted the values of the low-temperature scale T_0 as a function of the Yb valence v for $YbInCu_4$. It is seen that the coherent
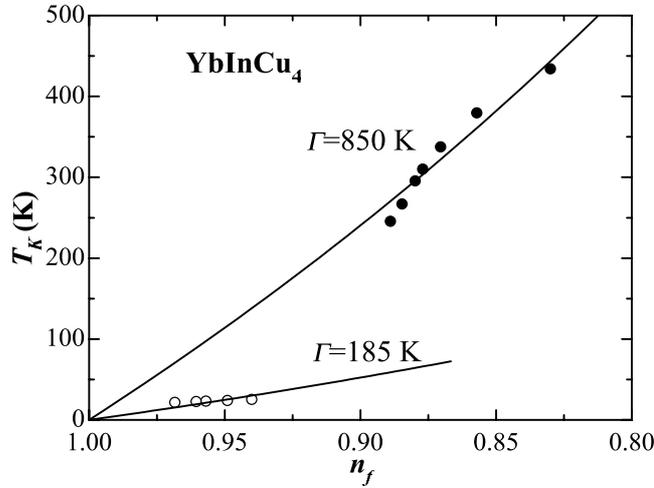
Figure 7. Kondo temperature T_K as a function of the 4f hole occupation n_f for YbInCu₄. Closed and open circles show the data for the low- and high-temperature states, respectively. The lines represent the fits to equation (3).

Kondo interaction gradually decreases with increasing valence of Yb. On the other hand, in the case of $Yb_{1-x}Ce_xInCu_4$, we observed that both T_v and $\chi(0)$ increase simultaneously with increasing x [11]. This suggests that the valence does not directly affect the stability (i.e. the temperature range of existence) of this state. In figure 7 we plotted the Kondo temperature T_K determined from susceptibility measurements of YbInCu₄ under pressure versus the 4f hole occupation n_f obtained from thermal expansion measurements. The experimental data are shown for the low- and high-temperature states by solid and open circles, respectively. Fitting the data to equation (3) gives $\Gamma = 850$ K for the low-temperature state. Cornelius *et al* [4] reported a similar value of $\Gamma = 900$ K for $YbIn_{1-x}Ag_xCu_4$ compounds with different x. For the high-temperature state with a weak Kondo interaction we obtain $\Gamma = 185$ K. Perhaps, a large change of nearly fivefold in the hybridization strength Γ of the 4f and conduction band electrons is the driving force for the drastic change of the physical properties observed at the valence phase transition in YbInCu₄.

4. Conclusions

In summary, we have measured under pressure the magnetic susceptibility of YbInCu₄ and thermal expansion of $Yb_{1-x}R_xInCu_4$ compounds with R = Y, La and Ce exhibiting the isostructural valence transition. We determined the alloying and pressure effect on the effective magnetic moment, the paramagnetic Curie temperature and the valence of Yb ion. The Grüneisen parameter for the Kondo temperature and the hybridization strength between the 4f and the conduction electrons were estimated for both low-temperature and high-temperature phases. The observed results can be interpreted in terms of the Kondo single-impurity model. However, the volume dependence of the Kondo interaction (i.e., the Kondo volume collapse model) cannot explain the observed strong variation of the Kondo temperature at the transition. The large change of the 4f–conduction band electron hybridization is considered to be responsible for the strong modification of the physical properties of YbInCu₄-based compounds at the valence transition.

Acknowledgments

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