High Magnetic Transition Temperature and Semiconductor-like Transport Properties of Mn-doped $\alpha$-YbAlB$_4$

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Abstract. We succeeded in growing single crystals of $\alpha$-YbAl$_{1-x}$Mn$_x$B$_4$ by the substitution of Mn for the Al site in the intermediate-valence rare-earth heavy fermion system $\alpha$-YbAlB$_4$. We performed specific heat and resistivity measurement on single crystals of $\alpha$-YbAl$_{0.60}$Mn$_{0.40}$B$_4$ ($x = 0.40$). In the specific heat measurement on $\alpha$-YbAl$_{0.60}$Mn$_{0.40}$B$_4$, a sharp peak was observed at magnetic transition temperature $T_M = 9.7(6)$ K. The resistivity measurements on $x = 0.40$ also show a semiconductor-like behavior in the entire temperature range from 2 - 300 K. An inclination change was also observed at 10(1) K in resistivity measurement. These results indicate a magnetic order. The magnetic transition temperature is quite high compared to its temperatures observed in the other Yb-based heavy fermion compounds.

1. Introduction

The strongly correlated electron systems such as Cu- and Fe-based high-$T_c$ superconductors and heavy fermion materials show a rich variety of interesting phenomena. Particularly, the various rare earth heavy fermion (HF) compounds with large effective mass have been reported to show exotic behaviors at low temperatures [1-3]. The ground states in the typical HF systems are essentially understood within the framework of the Doniach’s phase diagram. When an energy scale characterized by Kondo effect ($T_K$) is larger than that by a RKKY interaction scale ($J_{RKKY}$), its ground state produces a non-magnetic Fermi liquid state. In contrast, when $T_K < J_{RKKY}$, the ground state becomes magnetic ordered state. As these two energy scales competes at absolute zero temperature, a second order phase transition emerges at a so-called quantum critical point (QCP). Near this QCP, a new type of metallic state not obeying Landau Fermi liquid theory and unconventional superconductivity emerge. Various characteristic energy scales (i.e., $T_K$, magnetic transition temperature $T_{M\perp}$) associated with their large effective mass in the HF rare-earth systems are relatively low compared with those in strongly correlated 3$d$-electron systems, namely the ground state is easily tuned by non-thermal control parameters. Therefore, the phenomena near the QCP in the HF systems have been investigated with applying pressure, magnetic field and chemical doping mostly in the Ce-based HF systems [1,2]. Some of these properties around a QCP are successfully described by Self-Consistent-Renormalization (SCR) theory in mostly Ce-based HF materials [4,5]. The Yb-based HF systems can be viewed as having one 4$f$-hole for Yb$^{3+}$ in contrast to one 4$f$-electron for Ce$^{3+}$. So, the Yb-based HF systems are expected to have QCP interpreted as one hole system and had been less studied about the behaviors around QCP compared with the Ce-based system. A prototypical Yb-based HF system, YbRh$_2$Si$_2$, has a weak antiferromagnetism with $T_N = 65$ mK and has been intensively studied as a unconventional
antiferromagnetic quantum criticality [6]. The 5% Ge-doped sample indeed exhibits a reduction of \( T_N \) and is found to show non-Fermi liquid behaviors [7].

\( \beta \)-YbAlB\(_4\) is the first example showing HF superconductivity (\( T_c = 80 \) mK) in the Yb-based HF family [8,9]. This material also shows non-Fermi liquid behaviors without tuning any control parameter such as composition, pressure or magnetic field [10]. The temperature dependences of the electrical resistivity, magnetization, and specific heat exhibit nontrivial temperature-power law exponents that are not able to be explained by the conventional SCR theory [8-10]. In contrast, \( \alpha \)-YbAlB\(_4\), an isomorphism phase of \( \beta \)-YbAlB\(_4\), shows the Kondo lattice and Fermi liquid behavior at low temperatures [11]. The specific heat at low temperatures becomes almost constant with Sommerfeld coefficient \( \gamma \sim 130 \) mJ/mol-K\(^2\). The magnetic susceptibility also shows saturating tendency below 8 K. The temperature dependence of the resistivity, moreover, exhibits \( T \)-square below 100 mK. Notably, these two compounds both show valence fluctuation behavior (non-integer state) with \( \text{Yb}^{2.7(0)}\) for \( \alpha \)-YbAlB\(_4\) and \( \text{Yb}^{2.9(0)}\) for \( \beta \)-YbAlB\(_4\) as revealed by the Hard X-ray Photoemission Spectroscopy measurements [12]. As usual, Kondo lattice and valence fluctuation behaviors do not coexist. An average occupation number of \( f \)-electron states is close to an integer in the typical HF system forming the Kondo lattices. The valence fluctuation behavior has never been seen in the Ce-based HF compounds.

In order to investigate the intriguing coexistence of Kondo lattice system and valence fluctuating system, the chemical doping effect of the Fe substitution on Al site in both \( \alpha \) and \( \beta \)-YbAlB\(_4\) has been studied [13]. The chemical substitution mainly serves as the combination of electron doping and the chemical pressure effect. In a previous study, \( \alpha \)-YbAl\(_{0.95}\)Fe\(_{0.05}\)B\(_4\) shows a kink at 7.5(5) K in the magnetic susceptibility measurements and a peak at 6.7(3) K in the heat capacity measurements, respectively [13]. These results suggest forming an antiferromagnetic order below \( \sim 7 \) K. The magnetism should not arise from the Fe ion because the magnetization in \( \alpha \)-LuAl\(_{0.75}\)Fe\(_{0.25}\)B\(_4\) does not detect any magnetic transition. X-ray diffraction measurement supports that the Fe doping can be regarded as a positive chemical pressure. This chemical pressure effect is reported on YbCu\(_{0.9}\)Al\(_x\) as well [14]. If the Doniach’s picture is applicable in \( \alpha \)-YbAl\(_{1-x}\)Fe\(_x\)B\(_4\), it is expected that the QCP emerges in the range \( 0 < x < 0.07 \). This \( T_N \) is high compared with that of the other Yb-based HF systems [6,14-16].

On the periodic table, since Fe is not located in the vicinity of Al, it is difficult to judge whether the electron doping effect or the chemical pressure is important to understand the mechanism of high \( T_N \) antiferromagnetism. We need to study the effect in other substitution. Here, we synthesized with using Mn as a chemical doping instead of Fe in order to compare these two effects.

2. Experimental

We have grown single crystals of \( \alpha \)-YbAl\(_{1-x}\)Mn\(_x\)B\(_4\) (\( 0 \leq x \leq 0.57 \)) by excess Al flux method. The pure elements, Yb (Ames laboratory, ingot 99.99%), Al (Kyusyu-Mitsui Aluminum Co., Ltd., piece, 99.999%), B (Ceradyne. Inc., piece, 99.9999%), and Mn (Rare Metallic Co., Ltd., piece, 99.99%), were placed into an alumina crucible. The crucible and its contents were heated under an Ar atmosphere. After the crucible was removed from the furnace, excess aluminum flux was removed by etching in 1 mol/NaOH solution. One of the single crystals we synthesized is shown in figure 1. The growth direction in 40% Mn-doped crystal is preferentially along \( ab \)-plane, which is different from the non-doped crystal grown along \( c \)-axis. Our synthesized samples \( \alpha \)-YbAl\(_{1-x}\)Mn\(_x\)B\(_4\) were confirmed to have same orthorhombic structure as \( \alpha \)-YbAlB\(_4\) from powder X-ray diffraction pattern. This measurement also detected the lattice parameters as \( a = 5.9006(2), b = 11.411(1), c = 3.4401(1) \) Å for \( \alpha \)-YbAl\(_{0.60}\)Mn\(_{0.40}\)B\(_4\). From the lattice parameters (\( a = 5.9220(2), b = 11.4730(3), c = 3.5060(5) \) Å) for \( \alpha \)-YbAlB\(_4\) [17], the volume in Mn doping affects positive chemical pressure as observed in Fe doping. The Mn concentration \( x \) was estimated by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) within 0.6% error. To evaluate the physical properties, temperature dependence of electric resistivity and specific heat were measured with a commercial physical property measurement system.
Quantum Design, PPMS) on \( \alpha\)-YbAl\(_{0.60}\)Mn\(_{0.40}\)B\(_4\) because single crystals with enough size were obtained to measure specific heat and resistivity in both along \( ab\)-plane and \( c\)-axis. The specific heat was obtained using the relaxation method. For the resistivity, standard four-probe method was used. Electrical contacts were made to the crystal by spot welding technique. The electrical current \( I \) of 0.5 mA was applied parallel to \( ab\)-plane and \( c\)-axis in the temperature range of 2-300 K.

### 3. Results and Discussion

We performed the specific heat \((C)\) and electrical resistivity \((\rho)\) measurements on \( \alpha\)-YbAl\(_{0.60}\)Mn\(_{0.40}\)B\(_4\) single crystals. Figure 2 shows the specific heat data divided by temperature for \( 2 \text{ K} \leq T \leq 40 \text{ K} \). Here, the magnetic contribution \( C_{\text{mag}}/T \) was calculated by subtracting \( C/T \) of \( \alpha\)-LuAlB\(_4\) from that of \( \alpha\)-YbAl\(_{0.60}\)Mn\(_{0.40}\)B\(_4\). \( \alpha\)-YbAlB\(_4\) data was taken from the reference [11]. As shown in Fig. 2, a peak was observed at \( T_M = 9.7(6) \text{ K} \) across a transition. The same type of the peak is also observed in the heat capacity measurements for \( \alpha\)-YbAl\(_{1-x}\)Fe\(_x\)B\(_4\) and is confirmed to be an antiferromagnetic transition temperature from its magnetization results [13]. Assuming that this peak comes from antiferromagnetic order, the \( T_N \) for Mn doping is higher than the maximum of \( T_N \) (~7 K) for \( \alpha\)-YbAl\(_{0.93}\)Fe\(_{0.07}\)B\(_4\) [13]. Additionally, the \( T_N \) value is higher than that of the typical Yb-based HF systems, i.e., YbRh\(_2\)Si\(_2\) \( (T_N = 65 \text{ mK})\) [6], YbCu\(_2\)Al\(_2\) \( (T_N = 2 \text{ K})\) [14], YbNi\(_2\)Ge\(_2\) \( (T_N = 2.1 \text{ K})\) [15], YbAuCu\(_4\) \( (T_N = 0.6 \text{ K})\) [16], and YbPbCu\(_4\) \( (T_N = 0.8 \text{ K})\) [16]. In high pressure transport study of \( \beta\)-YbAl\(_4\), it is reported that a magnetic phase transition is observed and reached 30 K under pressure of 8 GPa [18]. In the chemical substitution study of \( \beta\)-YbAl\(_{1-x}\)Fe\(_x\)B\(_4\) \((x = 0.06)\), the same type of the magnetic phase transitions are also observed at 9.5(5) K under ambient pressure and reached 20 K under pressure of 4 GPa [13,19]. The origin of such a high magnetic transition temperature with a 2-digits order in the \( \beta\)-phase may be related with that in pure \( \alpha\)-phase and its Fe or Mn doped systems.

The temperature dependences of the electrical resistivity both along \( ab\)-plane (in-plane) and along \( c\)-axis of \( \alpha\)-YbAl\(_{0.60}\)Mn\(_{0.40}\)B\(_4\) are shown in Figure 3. \( \alpha\)-YbAlB\(_4\) data were taken from the reference [11]. The resistivity value at room temperature (300 K) is over 500 \( \mu\Omega \)cm both in \( ab\)-plane and in \( c\)-axis of \( \alpha\)-YbAl\(_{0.60}\)Mn\(_{0.40}\)B\(_4\). These resistivity values are higher than those of pure \( \alpha\)-YbAlB\(_4\), where the Mn-doped resistivity values are 2 times larger than non-doped values for the \( ab\)-plane, 14 times larger in \( c\)-axis components, respectively. Moreover, the pure \( \alpha\)-YbAlB\(_4\) indicates \( \rho_{ab} > \rho \) in contrast to \( \rho_{ab} < \rho \).
in the Mn-doped $\alpha$-YbAlB$_4$. Interestingly, the resistivity value in $\alpha$-YbAl$_{0.60}$Mn$_{0.40}$B$_4$ shows semiconducting-like behavior in contrast to the metallic-like one in $\alpha$-YbAlB$_4$. As usual, applying pressure makes band touching, so this effect makes materials more metallic [20]. The inset of Figure 3 shows temperature derivative of resistivity of $\alpha$-YbAl$_{0.60}$Mn$_{0.40}$B$_4$ along $ab$-plane at zero field. Arrows at 10(1) K refer the point where inclination changes of resistivity which is defined by the temperature derivative of resistivity.

Figure 2. The zero-field specific heats divided by temperature $C_{\text{mag}}/T$ vs. $T$ are shown for $\alpha$-YbAl$_{0.60}$Mn$_{0.40}$B$_4$ (red) and $\alpha$-YbAlB$_4$ (black).

Figure 3. The temperature dependences of the resistivities of $\alpha$-YbAl$_{0.60}$Mn$_{0.40}$B$_4$ (red) and $\alpha$-YbAlB$_4$ (black) along $ab$-plane and $c$-axis at zero field. The inset shows temperature derivative of resistivity of $\alpha$-YbAl$_{0.60}$Mn$_{0.40}$B$_4$ along $ab$-plane at zero field. Arrows at 10(1) K refer the point where inclination changes of resistivity which is defined by the temperature derivative of resistivity.

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4. Summary

We have obtained single crystals that are partially substituted with Mn for Al in $\alpha$-YbAlB$_4$. The Mn doping provides a positive chemical pressure effect as in the Fe doping case. The heat capacity measurements on $\alpha$-YbAl$_{0.60}$Mn$_{0.40}$B$_4$ founds a magnetic transition at $T_M = 9.7(6)$ K. This high magnetic transition temperature is one of the characteristic properties of $\alpha, \beta$-YbAlB$_4$. The electrical resistivities under chemical pressure behave as semiconductor-like as shown in $\alpha$-YbAl$_{0.60}$Mn$_{0.40}$B$_4$, even $\alpha$-YbAlB$_4$ remains metallic under external pressure [21]. At 10(1) K, there are incremental changes in $\rho(T)$ both along $ab$-plane and along $c$-axis. It comes from forming magnetic order which suppresses electronic scattering.

Here, there is one problem about origin of semiconductor-like transport. We need to think about two effects for Mn doping, namely doping induced lattice disorder and conduction-electron contributions. Specially, in the latter case, assuming that it comes from the hybridization between conduction electrons and localized $f$-electrons, $\alpha$-YbAl$_{1-x}$Mn$_x$B$_4$ is one of Kondo insulators with orthorhombic structure. All Kondo insulators had been observed in only cubic structure, such as YbB$_{12}$.
and so on, until Kondo insulator-like behaviors were observed in CeNiSn and Ce$_7$Al$_{10}$ ($T$ = Ru, Os) with orthorhombic structure [24-26]. The nodal hybridization theory pointed out that transport behavior in $\alpha,\beta$-YbAlB$_4$ can be the results of a doped Kondo insulator [27]. Therefore, we need further experiments, especially on transport, in the series of the Mn-doped $\alpha$-YbAlB$_4$ to clarify the contribution of these two effects and to get wide knowledge for stabilizing a Kondo insulator from QCP in $\beta$-YbAlB$_4$.

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