Anisotropic Chemical Pressure Effect on the Antiferromagnetic Kondo Semiconductor
$\text{Ce}(\text{Ru}_{1-x}\text{Fe}_x)\text{Al}_{10}$

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Abstract
We have studied the Fe substitution effect on the anomalous antiferromagnetic (AFM) order in $\text{CeRu}_2\text{Al}_{10}$ by using both single- and poly-crystalline samples. Electron probe microanalysis revealed that the single crystals of $\text{Ce}(\text{Ru}_{1-x}\text{Fe}_x)\text{Al}_{10}$ with $0.5 \leq x \leq 0.8$, grown by an Al self flux method, separate into Ru-rich central part and Fe-rich surface part. On the other hand, the composition in the polycrystalline samples is homogeneous. The magnetic susceptibility, electrical resistivity and specific heat measurements on the polycrystals indicate that $T_N$ gradually decreases and disappears at $x = 0.7$. This is contrasting to the pressure induced peaking of $T_N$ at 2.5 GPa. We should remind that application of hydrostatic pressure and Fe substitution result in different lattice contractions. The rate of contraction by the hydrostatic pressure is almost isotropic up to $P_c = 4$ GPa, while that by Fe substitution is strongly anisotropic; $\Delta a/a \approx \Delta c/c \approx 2\Delta b/b$. Therefore, the contrasting changes of $T_N$ by Fe substitution and by hydrostatic pressure suggest that the degree of $c$-$f$ hybridization along the $b$-axis controls the anomalous AFM order in $\text{CeRu}_2\text{Al}_{10}$.

Keywords: Kondo semiconductor, $\text{CeRu}_2\text{Al}_{10}$, substitution, chemical pressure effect

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1 Introduction

Since the first report on the anomalous magnetic and transport properties of the ternary Ce compound CeRu₂Al₁₀ [1], much experimental and theoretical efforts have been made to clarify the enigmatic antiferromagnetic (AFM) transition occurring at $T_N = 27$ K [2-5]. This compound, crystallizing in the orthorhombic YbFe₂Al₁₀ type structure [6], is a rare example of Kondo semiconductors showing the AFM order. The questions for CeRu₂Al₁₀ are not only the unusually high $T_N$ which exceeds that of Gd counterpart ($T_N = 15.5$ K [7]), but also the maximum in $T_N$ induced by pressure and substitution of Fe for Ru [2,8-10]. To explain these facts, an itinerant AFM state on the Kondo-Heisenberg model was proposed [11], which was used to understand the resonant x-ray emission data on Ce(Ru₁₋ₓFeₓ)₂Al₁₀ [12]. In the μSR and neutron diffraction study using polycrystalline Ce(Ru₁₋ₓFeₓ)₂Al₁₀, however, the $x$ dependence of $T_N$ deviates from the result on the single crystal study at $x \geq 0.5$ [13]. This discrepancy motivated us to reinvestigate the alloy system Ce(Ru₁₋ₓFeₓ)₂Al₁₀ including careful characterization of samples. In this study, we analyzed the atomic composition of single-crystalline Ce(Ru₁₋ₓFeₓ)₂Al₁₀ samples used for the previous study [10]. In addition, we measured the magnetic susceptibility, electrical resistivity and specific heat of polycrystalline Ce(Ru₁₋ₓFeₓ)₂Al₁₀ for $0.5 \leq x \leq 0.8$, then compared the obtained $x$ dependence of $T_N$ to the reported pressure dependence of $T_N$ in CeRu₂Al₁₀ [2,8].

2 Experimental

Polycrystalline samples of Ce(Ru₁₋ₓFeₓ)₂Al₁₀ were synthesized by arc-melting the constituent amount of pure elements under an argon atmosphere. The obtained samples were annealed at 800 °C one week. Single crystals were grown from pre-melted Ce(Ru₁₋ₓFeₓ)₂ alloys and excess Al flux, details of which are described in the previous report [10]. The chemical composition of each sample was determined by the wave dispersion x-ray spectroscopy coupled to JEOL JXA-8100 electron-probe microanalyzer (EPMA) for single crystals and energy dispersion spectrometer (EDS) equipped on HITACHI S-3000N scanning electron microscope for polycrystals.

The magnetic susceptibility, $\chi$, was measured by using a commercial SQUID magnetometer (Quantum Design MPMS) in $B = 1$ T. Measurements of electrical resistivity, $\rho$, were performed by using a dc four-probe method in the temperature range $0.5 \, K < T < 300 \, K$. The specific heat, $C$, was measured by the relaxation method in a Quantum Design PPMS.

Figure 1: (a) Secondary electron and (b) backscattered electron images for single-crystalline Ce(Ru₀.5Fe₀.5)₂Al₁₀. (c) Backscattered image for Ce(Ru₀.4Fe₀.6)₂Al₁₀. A circle represents the area where $x \sim 0.4$. 
3 Results and Discussion

3.1 Sample characterization of single crystals

Figure 1 shows (a) secondary-electron (SE) and (b) back-scattered electron (BSE) images of single-crystalline Ce(Ru$_{1-x}$Fe$_x$)$_2$Al$_{10}$ with nominal $x = 0.5$. A dark gray area in the SE image is a polished (010) facet. In spite of a flat surface, the BSE image shows a clear contrast between light and shade within the facet. Because the BSE image becomes more blight where the average atomic number of composed elements is higher, the contrast in Fig. 1(b) indicates the occurrence of phase segregation in a single crystal although we used pre-melted Ce(Ru$_{1-x}$Fe$_x$)$_2$ alloys for the flux growth. The quantitative analyses revealed that the Fe concentration $x$ is ~ 0.6 for the light area in Fig. 1(b) while $x \sim 0.8$ for the shaded one. We also confirmed the homogeneity of Ce and Al over the all analyzed points of each crystal. Therefore, our EPMA on single crystals indicates that the Fe atoms in Ce(Ru$_{1-x}$Fe$_x$)$_2$Al$_{10}$ segregate to the surface of a crystal. The value of $x$ in the light area exceeds the nominal value, which should be due to the existence of Ru rich part at the center of the crystal. Indeed, at the light area on the BSE image for a crystal with nominal $x = 0.6$ shown in Fig. 1(c), we obtained the value $x \sim 0.4$. The phase segregation was observed in all measured crystals in the range $0.5 \leq x \leq 0.8$. Thus, in order to proceed the measurements with single-crystalline Ce(Ru$_{1-x}$Fe$_x$)$_2$Al$_{10}$, we need to improve the technique of single crystal growth of Ce(Ru$_{1-x}$Fe$_x$)$_2$Al$_{10}$ to prevent the phase segregation.

3.2 Physical property of polycrystals

We confirmed the agreement between the nominal and analyzed compositions as well as the homogeneous mixture of Ru and Fe for the polycrystals, on which we carried out the measurements of $\chi$, $\rho$ and $C$. Figure 2(a) shows the inverse magnetic susceptibility, $1/\chi$, of polycrystalline Ce(Ru$_{1-x}$Fe$_x$)$_2$Al$_{10}$. All samples obey the Curie-Weiss law between 300 K and 100 K and show a broad peak in $\chi$ due to Kondo effect at low temperatures. The slope of $1/\chi$ should depend on the preferred orientation of polycrystalline samples because of the strong magnetic anisotropy $\chi_a > \chi_c > \chi_b$ observed in CeRu$_2$Al$_{10}$. With increasing $x$, the gradual increases of the temperature at the maximum in $\chi(T)$ indicates the enhancement of Kondo coupling that is also reported in the previous single-crystal studies [9,10].

Figure 2(b) displays the results of $\rho(T)$ normalized by $\rho(300 \text{ K})$, $\rho/\rho_{100}$, for $x = 0, 0.5, 0.6, 0.7$ and 1. For $x = 0.5$, the disappearance of the maximum and continuous increase in $\rho$ on cooling below 40 K to 5 K is similar to those observed in single-crystalline Ce(Ru$_{1-x}$Fe$_x$)$_2$Al$_{10}$ with $x = 0.625$ and CeRu$_2$Al$_{10}$ under $P = 3$ GPa [2,9]. At $x \geq 0.6$, the semiconducting behavior observed between 70 K and 30 K for $x = 0$ disappears then a maximum due to Kondo coherence appears at $x = 0.7$. No anomalies indicating the phase transitions were observed for $x = 0.7$ down to 0.5 K.

The results of $C$ for Ce(Ru$_{1-x}$Fe$_x$)$_2$Al$_{10}$ at $T < 40$ K are shown in Fig. 2(c). In $x = 0.5$ and 0.6, a broadened $C/T$ jump due to an AFM transition is observed at 22 K and 17 K, respectively. Above 30 K, the $C/T$ values agree among $x = 0, 0.5$ and 0.6, in which the AFM transition occurs. The decrease in $C/T$ for $x = 0.7$ means that the system changes to the mixed-valence regime.

Figure 2(d) shows the $x$ dependence of $T_N$ for polycrystalline Ce(Ru$_{1-x}$Fe$_x$)$_2$Al$_{10}$ in addition to the $P$-$T$ phase diagram of CeRu$_2$Al$_{10}$ [2,8]. The values of $T_N$ were determined by the midpoint of $C/T$ and $d\chi/dT$ jumps. The $T_N(x)$ agrees well with that obtained by the $\mu$SR study [13], and gradually decreases with $x$. This dependence is in contrast to the pressure dependence of $T_N$ with a maximum before the sudden disappearance. This difference should not be explained solely by the effect of disorder because the $x$ dependence of $\rho(T)$ agrees with the pressure dependence of $\rho(T)$ for CeRu$_2$Al$_{10}$ [2]. Using the detailed pressure dependence of lattice parameters reported recently [14], we have compared the rate of lattice contraction by Fe substitution with that by application of hydrostatic pressure in Fig. 2(e). The room-temperature lattice parameters of Ce(Ru$_{1-x}$Fe$_x$)$_2$Al$_{10}$ were taken from the results obtained
Figure 2: Temperature dependence of (a) inverse magnetic susceptibility, (b) electrical resistivity and (c) specific heat for polycrystalline Ce(Ru$_{1-x}$Fe$_x$)$_2$Al$_{10}$. (d) Magnetic phase diagram of Ce(Ru$_{1-x}$Fe$_x$)$_2$Al$_{10}$ together with the pressure dependence of $T_N$ for CeRu$_2$Al$_{10}$ [2,8]. (e) Fe concentration dependence of normalized lattice parameters for Ce(Ru$_{1-x}$Fe$_x$)$_2$Al$_{10}$ taken from [13]. Those for CeRu$_2$Al$_{10}$ under pressure are taken from [14].
by the neutron diffraction [13]. For the comparison, the lattice parameters are normalized by those at $x = 0$ and ambient pressure, respectively. The range of pressure is scaled so that the slopes of $a/a_0$ coincide each other. Obviously, the contraction rate of $b$-axis, $\Delta b/b$, for Fe substitution is nearly a half of those of $\Delta a/a$ and $\Delta c/c$, while the contraction by hydrostatic pressure is almost isotropic. Therefore, in addition to the effect of disorder, the anisotropic lattice contraction, $\Delta a/a \approx \Delta c/c \approx 2\Delta b/b$, induced by Fe substitution should weaken the unusual antiferromagnetic order of CeRu$_2$Al$_{10}$. Indeed, the importance of two dimensional character within the $ac$ plane has been pointed out by the transport and optical studies [15,16]. Moreover, the importance of anisotropic $c$-$f$ hybridization for the unusual AFM in CeRu$_2$Al$_{10}$ was argued by many experiments such as the neutron scattering and detailed magnetic-field dependence of $\chi$ and $\rho$ [5,17]. Therefore, the instability of AFM order by Fe substitution should originate from the change in $c$-$f$ hybridization anisotropy due to the anisotropic lattice contraction. As another explanation, owing to the anisotropic contraction and disorder, the Fe substitution may prevent the formation of charge-density-wave instability proposed by the optical study [16], which should be experimentally examined further. In order to clarify the role of anisotropic lattice contraction for the unusual AFM order, we plan to study the uniaxial pressure effect on CeRu$_2$Al$_{10}$.

4 Summary

We have reinvestigated the Fe substitution effect on the unusual AFM order in CeRu$_2$Al$_{10}$ by using both single- and polycrystalline samples. Scanning electron images and quantitative analyses of atomic composition indicate that a phase segregation occurs in single-crystalline Ce(Ru$_{1-x}$Fe$_x$)$_2$Al$_{10}$ grown by the Al self-flux method. On the other hand, polycrystalline samples are homogeneous mixture of Ru and Fe whose nominal compositions agree with quantitative analyses. The magnetic susceptibility and electrical resistivity of polycrystalline Ce(Ru$_{1-x}$Fe$_x$)$_2$Al$_{10}$ confirm the enhancement of $c$-$f$ hybridization and suppression of semiconducting behavior above $T_N$ with increasing $x$, which are consistent with the data for single crystals. On the contrary to the peaking in $T_N$ as a function of $x$ in single-crystalline Ce(Ru$_{1-x}$Fe$_x$)$_2$Al$_{10}$ and as a function of hydrostatic pressure on CeRu$_2$Al$_{10}$, $T_N$ shows a gradual decrease with increasing $x$ up to $x_C = 0.7$. This contrasting behaviors in $T_N$ should result from the anisotropic lattice contraction observed in Ce(Ru$_{1-x}$Fe$_x$)$_2$Al$_{10}$, which emphasizes the importance of the hybridization along the $b$ axis for the unusually high $T_N$ in CeRu$_2$Al$_{10}$.

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References