Collapse of spin gap by Ru-site substitution in the antiferromagnetic Kondo semiconductor $CeRu_2Al_{10}$

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We investigated the Ce- and Ru-site substitution effects on the spin gap in $CeRu_2Al_{10}$ by measuring the magnetic and thermal properties of $Ce_{1-y}Ln_yRu_2Al_{10}$ (Ln = La, Pr, Y) and $Ce(Ru_{1-x}T_x)_2Al_{10}$ (T = Re, Rh) system, respectively. The magnetic susceptibility shows that the itinerant and localized nature is enhanced by Re and Rh doping, respectively. In the latter, the orientation of the magnetic moment in the antiferromagnetic ordered phase suddenly changes from the c to a axis at $x = 0.03$. The orientation of the magnetic moment to the a axis is consistent with the large anisotropy of the magnetic susceptibility in the paramagnetic region. The specific heat shows that the exponential temperature dependence, $e^{-\Delta/k_BT}$, and the electronic specific coefficient γ is not changed in the Ce-site substituted systems at least up to $y = 0.1$ but in the Ru-site substituted systems, the $e^{-\Delta/k_BT}$ dependence disappears, and the γ value increases rapidly with x. These indicate that although the spin gap is robust against the Ce-site substitution by Ln ion at least up to $y = 0.1$, the spin gap is rapidly collapsed by the Ru-site substitution and in place, the conduction electron with heavy effective mass appears at the Fermi level. The spin gap which is formed under the subtle balance between the localized and itinerant nature is easily collapsed by a small amount of Re or Rh doping.

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I. INTRODUCTION

The Kondo insulator has continued to be one of the topics in the strongly correlated electron systems [1]. This system is characterized by the hybridization gap originating from the many-body effect between the conduction and f electrons. The ground state of the Kondo insulators known up to now is the spin singlet and the magnetic order does not take place, due to the stronger c-f hybridization than the magnetic interaction. The Kondo semimetal with nonmagnetic ground state, CeNiSn, has been studied extensively as a typical compound which belongs to such a category and the experimental results have been discussed based on the existence of the V-shaped gap [2–5]. One of the big unresolved issues in this hybridization gap is the rapid collapse by doping, which should be associated with the strong correlation between the 4f and conduction electron and also the coherence effect. Although several models have been proposed for the mechanism of the gap collapse by doping, it has not yet been clarified [1,6]. When the different kinds of interaction constructing the hybridization gap and magnetic order compete with each other, a new type of ground state and also an unusual doping effect are expected.

Recently discovered $CeRu_2Al_{10}$ with the antiferromagnetic (AFM) ordering temperature $T_0 = 27$ K is the very such a compound [7,8]. The anisotropic deviation of the lattice constants from the lanthanide contraction indicates the importance of the anisotropic c-f hybridization in the AFM ordered phase [9]. There exist the following unusual properties in this compound [7–22]. (i) The AFM transition temperature is very high regardless of a large Ce-Ce distance [7,8]. (ii) The magnetic anisotropy in the AFM ordered phase is quite strange, where $m_{AF} \parallel c$ is realized in spite of a large magnetic anisotropy, $\chi_a \gg \chi_c \gg \chi_b$ in the paramagnetic region [10–12]. Here, m_{AF} is the AFM moment and χ_a is the magnetic susceptibility along the a axis, etc. Furthermore, the orientation of m_{AF} is easily changed from the c to b axis in the bc plane but is never oriented to the a axis by a small magnetic field or pressure and also by a small amount of La doping. When the magnetic field is applied to the c axis, a spin-flop transition from the c to b axis takes place at a relatively small magnetic field, H_{sf} in spite of $\chi_a \gg \chi_c \gg \chi_b$ [17–19]. A small amount of La doping makes $m_{AF} \parallel b$ more stable than $m_{AF} \parallel c$ and the orientation of m_{AF} is quite easily changed from the b to c axis by a small pressure [21]. Thus, the magnetization easy axis below T_0 is located in the bc plane in spite of $\chi_a \gg \chi_c \gg \chi_b$ in the paramagnetic region, and the magnetic anisotropy in the bc plane is small. (iii) The pressure effect on T_0 is very large and anisotropic, indicating the importance of the anisotropic c-f hybridization in the AFM ordered phase [23]. (iv) A large spin and charge gap appear in the AFM ordered phase, whose origin has not yet been clarified, although it is inevitable to understand the unusual AFM order in $CeRu_2Al_{10}$ [24–29].

Recently, in $Ce(Ru_{1-x}Rh_x)_2Al_{10}$, the drastic change of the magnetic property was reported in a small x region [30–32]. More recently, the similar doping effects were reported also in $Ce(Os_{1-x}Ir_x)_2Al_{10}$ [33–35]. This drastic change is the rotation of m_{AF} from the c to a axis at $x_c = 0.03$, which is consistent with $\chi_a \gg \chi_c \gg \chi_b$ above T_0 but could never be achieved except by Rh doping. Its origin was ascribed to the suppression of the strong c-f hybridization along the a axis by Rh doping [30]. Hoshino and Kuramoto discussed the possibility of the localized and itinerant transition in the Kondo AF magnet [36]. Thus, in the AFM Knodo semiconductor, $CeRu_2Al_{10}$, there exists a new type of doping effect, which has not been reported in the AFM heavy electron metallic compounds.

To understand the unusual AFM order in $CeRu_2Al_{10}$, we should clarify the origin of the unusual magnetic anisotropy and also spin gap in the AFM ordered phase. In the present paper, we performed the detailed investigation of the doping effects on magnetic and thermal properties in $CeRu_2Al_{10}$ to clarify the origin of the drastic change induced by doping.

II. EXPERIMENTAL

Single crystals of $Ce(Ru_{1-x}T_x)_2Al_{10}$ (T = Rh: $x = 0.02$, 0.03, 0.04, 0.05, and T = Re: $x = 0.05$) and $Ce_{1-y}Ln_yRu_2Al_{10}$ (Ln = La: $y = 0.05$ and 1, Ln = Pr: $y = 0.1$, Ln = Y: $y = 0.1$) were prepared by the Al self-flux method. The magnetic susceptibility and specific heat were measured by using MPMS and PPMS (Quantum Design), respectively. Some of the results of the magnetic susceptibility and specific heat of $Ce_{1-y}La_yRu_2Al_{10}$ were already reported in Ref. [13].

Figure 1(a) shows the temperature (T) dependence of the magnetic susceptibility(χ) of $Ce(Ru_{1-x}T_x)_2Al_{10}$ (T = Rh, Re) and $Ce_{0.9}La_{0.1}Ru_2Al_{10}$. Figures 1(b) and 1(c) show χ_a and χ_c at low temperatures, respectively. χ_b is not shown because of a small doping effect in all the cases. The inset of Fig. 1(a) shows the x dependence of the transition temperatures of $Ce(Ru_{1-x}Rh_x)_2Al_{10}$, which shows a smooth variation up to $x = 0.05$ without showing an anomaly at $x = 0.03$. In $Ce_{0.9}La_{0.1}Ru_2Al_{10}$, a doping effect on χ_a is small, while a decrease of χ_c below T_0 disappears as a result of the reorientation of m_{AF} from the c to b axis [21]. On the other hand, in Rh doping, a big change appears in χ_a. The downward deviation of χ_a from the high temperature Curie-Weiss behavior below $\sim$100 K is suppressed and a normal Curie-Weiss behavior is observed. In the low temperature region, for $x = 0.02$, χ along three crystal axes exhibit the similar T dependencies to those in $CeRu_2Al_{10}$. Especially, a decrease of χ_c below T_0 is clear, indicating that the AFM order with $m_{AF} \parallel c$ as in $CeRu_2Al_{10}$. A drastic change appears at $x = 0.03$. χ_a shows a sharp peak at T_N and a rapid decrease below T_N. On the other hand, a sharp decrease of χ_c below T_N disappears and is replaced by a weak T dependence. This indicates that the orientation of m_{AF} is changed from the c to a axis in this sample. Also for $x = 0.05$, the similar behaviors are seen in χ_a and χ_c. We note that for $x = 0.03$, there exist two transitions at $T_N = 23.5$ K and $T_0 = 25.5$ K. They are more clearly seen in specific heat, which will be shown later. This indicates that a drastic change takes place just at $x_c = 0.03$ as is clearly seen in the inset of Fig. 1(a). We note that $m_{AF} \parallel a$ is realized below T_N and $m_{AF} \parallel c$ is realized between T_N and T_0. On the other hand, in Re doping, χ_a is suppressed largely in a wide temperature range and a broad maximum is seen at $\sim$27 K.

Here, we comment the upturn of χ seen below $\sim$10 K in the present results. In La doping, it is rather isotropic and could be ascribed to a free Ce ion which does not take part in the AFM order. In Rh doping with $x = 0.02$, the upturn in χ_a is significant, although the effect on χ_c is small. This might be because the c-f hybridization along the a axis is suppressed, a singlet nature is suppressed, and a free magnetic ion character is dominant. For $x > 0.03$, the increase of χ_a below $\sim$10 K which is seen for $x = 0.02$ is rapidly suppressed and disappears completely for $x = 0.05$. This indicates that a very stable AFM order with $m_{AF} \parallel a$ is realized for $x = 0.05$.

Figures 2(a) and 2(b) show the T dependencies of the specific heat, C of $Ce_{1-y}Ln_yRu_2Al_{10}$(Ln = La,Pr,Y) and those in the form of C_{4f}/T, respectively. Here, we note that the crystalline electric field ground state of $PrRu_2Al_{10}$ is a singlet. C_{4f} is a magnetic part of C obtained by subtracting that of $LaRu_2Al_{10}$ as a phonon contribution. In $CeRu_2Al_{10}$, C_{4f} shows a mean-field-like T dependence, i.e., the $e^{-\Delta/k_BT}$ dependence with $\Delta \sim 100$ K at low temperatures and a sharp peak at T_0,

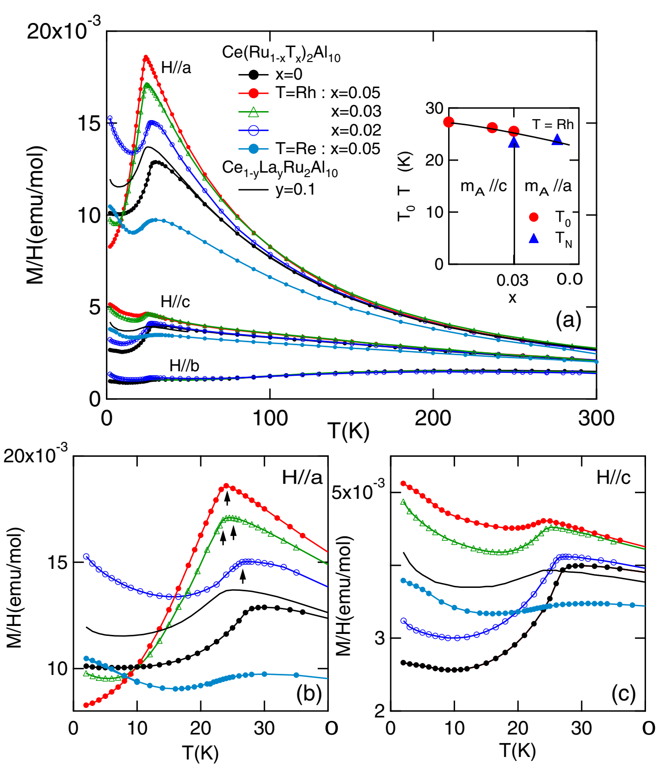

FIG. 1. (Color online) (a) Temperature dependence of χ along the three crystal axes of $Ce(Ru_{1-x}T_x)_2Al_{10}$ (T = Rh, Re) and $Ce_{0.9}La_{0.1}Ru_2Al_{10}$ measured at $H = 1$ T; (b) χ_a and (c) χ_c in an expanded scale at low temperatures. The arrows in Fig. 1(b) indicate the transition temperatures for T = Rh. The inset in Fig. 1(a) is the x dependence of the transition temperatures of $Ce(Ru_{1-x}Rh_x)_2Al_{10}$ at $H = 0$.

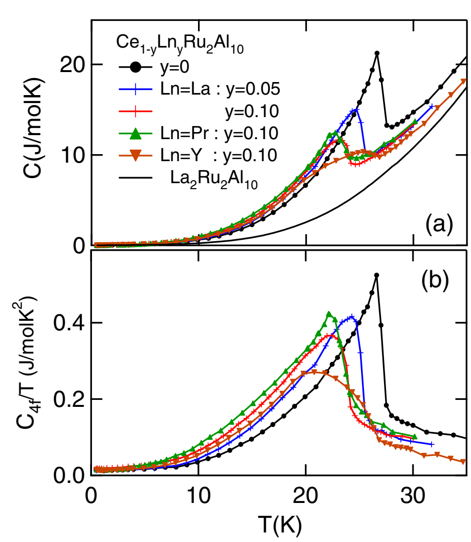

FIG. 2. (Color online) Temperature dependence of (a) C and (b) C_{4f}/T of $Ce_{1-y}Ln_yRu_2Al_{10}$ (Ln = La, Pr,Y), where the result of $Ce_{0.9}La_{0.1}Ru_2Al_{10}$ is cited from Ref. [13].

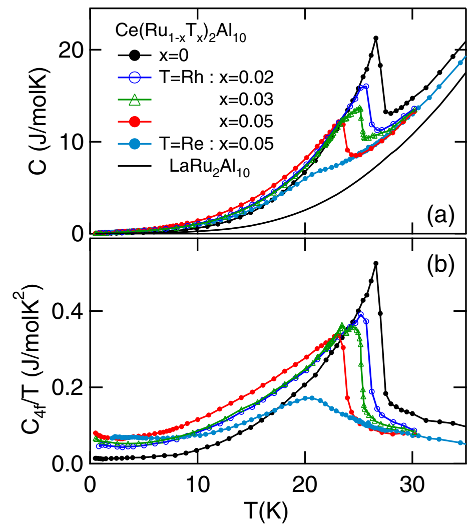

FIG. 3. (Color online) Temperature dependence of (a) C and (b) C_{4f}/T of $Ce(Ru_{1-x}T_x)_2Al_{10}$ (T = Rh : $x = 0.02$, 0.03, 0.05, T = Re: $x = 0.05$).

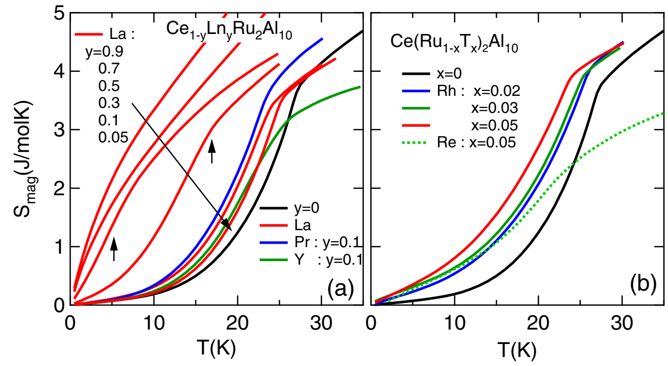

FIG. 4. (Color online) Temperature dependence of the magnetic entropy, S_{mag} of (a) $Ce_{1-y}Ln_yRu_2Al_{10}$ (Ln = La, Pr, Y) and (b) $Ce(Ru_{1-x}T_x)_2Al_{10}$ (T = Rh: $x = 0.02$, 0.03, 0.05, T = Re: $x = 0.05$). In Fig. 4(a), the results of La ($y = 0.1 \sim 0.9$) are obtained from the specific heat data in Ref. [13] and the arrows for $y = 0.5$ and 0.7 indicate the transition temperature T_0 [13].

which indicates the existence of a large spin gap in magnetic excitation spectrum. A sharp peak at T_0 is broadened by Ln doping, which is most pronounced in Y doping due to the smallest ionic radius of Y^{3+} ion. The doping effect at low temperatures below ∼5 K is small in all the doping cases at least up to $y = 0.1$. Namely, the $e^{-\Delta/k_BT}$ dependence and the electronic specific heat coefficient, γ is not affected by nonmagnetic Ln doping up to $y = 0.1$. In La-doped samples, the specific heat was investigated in a wide range of y up to 0.9, where the $e^{-\Delta/k_BT}$ dependence is not seen for $y \geqslant 0.3$ and the γ value increases with increasing y [13].

Figures 3(a) and 3(b) show the T dependencies of C of $Ce(Ru_{1-x}T_x)_2Al_{10}$ (T = Rh, Re) and those in the form of C_{4f}/T, respectively. In Rh doping, the effect is very large at low temperatures. By only a small amount of Rh doping, the $e^{-\Delta/k_BT}$ dependence disappears and in place, the γT term appears and increases rapidly with x. For $x = 0.03$, a sharp anomaly is seen at $T_N = 23.5$ K but also a peak at $T_0 = 25.5$ K. For $x = 0.05$, there exists only one magnetic transition at T_N. Although a drastic change appears at $x_c = 0.03$ in χ_a, C does not show such a drastic change but a continuous one with x up to 0.05. In contrast to Rh doping, in Re doping, a peak of C at T_0 is rapidly suppressed and only a broad maximum could be seen at $T_0 \sim 20$ K. It is difficult to estimate T_0 exactly from the present result. At low temperatures, a large increase of the γ value is seen as in Rh doping. The similar effect was recently reported in $Ce(Os_{1-x}Re_x)_2Al_{10}$ [35].

Figures 4(a) and 4(b) show the T dependencies of the magnetic entropy, S_{mag} of $Ce_{1-y}Ln_yRu_2Al_{10}$ (Ln = La, Pr, Y) and $Ce(Ru_{1-x}T_x)_2Al_{10}$ (T = Rh, Re), respectively. In La-doped samples, those with $y = 0.1 \sim 0.9$ cited from Ref. [13] are also shown. We note that for $y = 0.7$ and 0.9, due to the difficulty of the subtraction of phonon specific heat, the value of S_{mag} at high temperatures is not reliable. In all the doping cases, the slope of S_{mag} vs T below 5 K is small and is not changed up to $y = 0.1$. In La-doped samples, the slope increases with increasing y above 0.3, which corresponds to the increase of the γ value [13] and at the same time, S_{mag} at T_0 is reduced with increasing y. In the Pr-doped case, S_{mag} at T_0 is slightly reduced but is largely reduced in the Y-doped one. A rather large suppression of S_{mag} even above T_0 in the latter might be due to a modification of a phonon specific heat coming from a large difference of the ionic radius between Y and Ce.

Figure 5 shows the x and y dependence of the γ value of $Ce(Ru_{1-x}T_x)_2Al_{10}$ (T = Re, Rh) and $Ce_{1-y}Ln_yRu_2Al_{10}$ (Ln = La, Pr, Y). S_{mag} at T_0 in $CeRu_2Al_{10}$ is $\sim 0.65 \times R \ln 2$. S_{mag} at the transition temperature (T_0 and T_N) is not affected by Rh doping, i.e., almost constant up to $x = 0.05$. This is the most important point in the present paper, which will be discussed later. We note that although a big change appears in χ_a at $x_c = 0.03$, no anomalous variation is seen in the transition temperature (T_0 or T_N), a peak shape of C_{4f} and S_{mag} at T_0 or T_N. In contrast to Rh doping, in Re doping with $x = 0.05$, S_{mag} at T_0 is very much reduced. As for the doping effect on

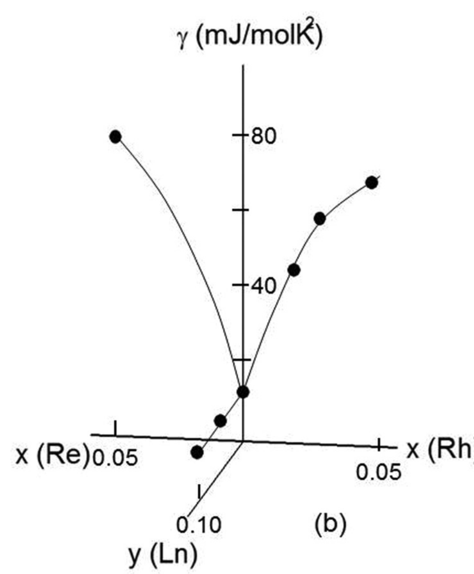

FIG. 5. x and y dependence of the γ value of $Ce(Ru_{1-x}T_x)_2Al_{10}$ (T = Rh, Re) and $Ce_{1-y}Ln_yRu_2Al_{10}$ (Ln = La, Pr, Y) obtained by subtracting that of $LaRu_2Al_{10}$.

the γ value, although it is not changed by Ln doping up to $y = 0.1$, it is rapidly enhanced with x by both Rh and Re doping. The similar doping effects were reported in Re- and Ir-doped $CeOs_2Al_{10}$ [35].

III. DISCUSSION

First, we discuss the doping effect on the ground-state properties in $CeRu_2Al_{10}$. By the nonmagnetic Ln doping, the γ value in $CeRu_2Al_{10}$ is not changed and the $e^{-\Delta/k_BT}$ dependence of C_{4f} at low temperatures exists at least up to $y = 0.1$. This indicates that the spin gap is not affected by the nonmagnetic Ln doping at least up to $y = 0.1$. In La-doped samples, with further increase of y, the anomaly at T_0 broadens due to the randomness induced by a large amount of doping, the γ value increases [13], and S_{mag} at T_0 is suppressed. The suppression of S_{mag} at T_0 by La doping is a result of the competition between the Kondo effect and magnetic interaction. The former enhances the itinerant character and forms heavy electron, and the latter enhances the localized character. With the increase of y, the latter is suppressed and the former becomes dominant, and the system continuously changes into the dilute Kondo regime [13]. The magnetic susceptibility shows the following y dependence [13]. The decrease of χ_a below T_0 is suppressed and the anomaly at T_0 is broadened. Although the decrease of χ_a below T_0 is scarcely observed for $y = 0.3$, only a Curie-like increase is seen with decreasing temperature for $y \geqslant 0.5$. We note that T_0 is recognized for $y = 0.5$ in the specific heat [13]. Considering that the existence of the spin gap was reported for $y = 0.3$ [37], a decrease of χ_a below T_0 might be a sign of the existence of a spin gap. On the other hand, the large γ value of 60 $mJ/molK^2$ for $y = 0.3$ indicates that the magnetic scattering intensity might be largely suppressed. Although the nature of the spin gap is changed in a large y region, almost the full gap is expected to exist at least up to $y = 0.1$. Thus, in Fig. 5, the γ value is plotted only below $y = 0.1$. We note that the small La-doping effect with a small doping concentration are different from the large La-doping effects on CeNiSn [3], which will be discussed later.

In contrast to the nonmagnetic Ln-doping case, Rh doping modifies the ground state largely. Apart from the drastic change in χ_a at $x_c = 0.03$, which will be discussed later, the pronounced changes are observed in χ_a above T_0 and also in the low temperature specific heat. The downward deviation of χ_a from the high temperature Curie-Weiss behavior below ~100 K disappears rapidly and χ_a starts to show a Curie-Weiss behavior by Rh doping. This indicates the enhancement of the localized nature of the $4f$ electron by Rh doping. The γ value also shows a rapid increase with x. On the other hand, in Re doping, the itinerant nature is found to be enhanced from the results of χ and C_{4f}.

The $e^{-\Delta/k_BT}$ dependence of C_{4f} means the existence of the spin gap in the magnetic excitation spectrum as mentioned above. Kondo *et al.* discussed that the AFM ordered phase in $CeRu_2Al_{10}$ has a singlet nature from the pronounced concave H dependence of the magnetization curve along the a axis and this originates from the strong c-f hybridization along the a axis [16,30]. The present results show that by Rh doping, although the $e^{-\Delta/k_BT}$ dependence disappears, and in place, the γT dependence appears. The γT term means the existence of the density of states at the Fermi level. The most important result in the present study is that *the magnitude of S_{mag} at T_0 or T_N is almost constant up to $x = 0.05$.* This clearly demonstrates that the origin of the γT term is fully magnetic. Namely, the spin degrees of freedom at the excited magnetic state induced by the spin gap formation is transferred to the low energy region by Rh doping and the γ value increases with x. This γT term is considered as a Kondo resonance state at the Fermi level. This important conclusion could be obtained precisely because $CeRu_2Al_{10}$ is the AFM compound and S_{mag} below T_0 could be estimated exactly. In CeNiSn with a nonmagnetic ground state, it is difficult to discuss the origin of the γT term induced by doping because the estimation of S_{mag} originating from the V-shape gap is difficult due to a lack of the magnetic transition temperature. We comment about the almost constant S_{mag} at T_0 or T_N with an Rh-doping concentration. In $CeRu_2Al_{10}$, S_{mag} is ~$0.65R\ln 2$ whose reduction from $R\ln 2$ is ascribed to the Kondo effect. When Rh is doped, there exist, at least, three kinds of effects. One is the enhancement of conduction electron mass as a result of the heavy electron formation, leading to the enhancement of S_{mag}. The second is the enhancement of localized character of the magnetic moment along the a axis, leading to the enhancement of S_{mag}. The third is the Kondo screening effect, reducing S_{mag}. S_{mag} at T_0 or T_N is determined by the coexistence and competition among these three effects. Although it is difficult to estimate which effect is dominant in S_{mag} at T_0 or T_N in Rh-doped $CeRu_2Al_{10}$, we consider that the rapid increase of the γ value by Rh doping originates from the collapse of the spin gap.

Here, we discuss the increase of the γ value by Re doping. Although the γ value increases rapidly as in the Rh-doping case, its origin should be different. The large suppression of χ_a is seen in a wide range of temperature below 300 K in spite of a small Re-doping concentration of $x = 0.05$ as is shown in Fig. 1. This indicates that the itinerant nature is largely enhanced in a wide range of temperatures, different from the Rh-doping case. Then, it is considered that the localized nature is suppressed and the spin gap is smeared out by Re doping. The existence of the spin gap is indicated by the suppression of χ_a below T_0, which is also seen in $Ce(Os_{1-x}Re_x)_2Al_{10}$ up to $x = 0.05$ [35]. These are indicated by the recently reported results of the inelastic neutron scattering in $Ce(Os_{1-x}Re_x)_2Al_{10}$ [38] and also in $Ce(Ru_{0.97}Re_{0.03})_2Al_{10}$ [39], where the magnitude of the spin gap is not changed but the magnetic scattering intensity is reduced. The similar doping effect on the spin gap was observed also in $Ce(Ru_{1-x}Fe_x)_2Al_{10}$ [29]. The Re and Fe dopings seem to have the common feature that the itinerant nature is enhanced. Its origin should be investigated from the standpoint that the meaning of the Re doping is simply a hole doping or not as will be discussed later. Here, we note that very high T_0 could be never explained by a small ordered moment of the order of $0.1\mu_B$/Ce as in the Re- or Fe-doping case but the large c-f hybridization should be associated with high T_0, which is suggested by the large enhancement of T_0 by a small pressure [8,23]. Then, the AFM exchange interaction seems to play a role as merely a trigger to induce the AFM transition.

We comment about the Re-doping effect on the orientation of m_{AF} below T_0 in $CeRu_2Al_{10}$ and $CeOs_2Al_{10}$. The AFM order of $m_{AF} \parallel c$ with a reduced moment of $0.18\mu_B$/Ce is reported in $Ce(Os_{0.97}Re_{0.03})_2Al_{10}$ [34]. On the other hand, very recent neutron diffraction experiment showed that $m_{AF} \parallel b$ is realized in $Ce(Ru_{0.97}Re_{0.03})_2Al_{10}$ [39]. This indicates that at least in $Ce(Ru_{1-x}Re_x)_2Al_{10}$, there exists a critical concentration where the orientation of m_{AF} is changed from the c to b axis between $x = 0$ and 0.03. This also suggests that the magnetic anisotropy in the bc plane is small, as was discussed in Ref. [21]. As mentioned in the Introduction, the magnetic anisotropy below T_0 is quite strange. Although the change of the anisotropic c-f hybridization is considered to be associated with the reorientation of m_{AF}, the mechanism is not known at present. Further investigations are necessary.

Next, we discuss the drastic change in χ_a in $Ce(Ru_{1-x}Rh_x)_2Al_{10}$ at $x_c = 0.03$ above which the AFM order with $m_{AF} \parallel a$ of $\sim 1\mu_B$/Ce consistent with $\chi_a \gg \chi_c \gg \chi_b$ in the paramagnetic region is realized, which is ascribed to the suppression of the c-f hybridization along the a axis by Rh doping. Although a drastic change is observed in χ_a at $x_c = 0.03$, an anomaly is not seen in the x dependence of the transition temperatures (T_0 or T_N), S_{mag} at T_N or T_0, and also the γ value show a smooth variation with x up to $x = 0.05$. Since S_{mag} at the transition temperature is not changed with x, the Kondo effect still should play an important role even above $x_c = 0.03$. The results indicate that a drastic change induced by Rh doping is the anisotropic phenomenon and there exists a critical Rh-doping concentration above which the localized nature along the a axis is dominant. The drastic change of the anisotropic c-f hybridization gives rise to the destruction of the spin gap as mentioned above and looks like the anisotropic itinerant-localized transition at first glance, which should be investigated more in detail in the future. This could be a new phenomenon which appears in the Kondo semiconductor with the AFM order, which is unexpected in the AFM heavy electron compounds. We note that the smooth variation of T_0 or T_N and the γ value with the Rh doping suggests that the full spin gap is not necessarily indispensable to produce the very high transition temperature in the present system.

Finally, we discuss the different doping effects between $CeRu_2Al_{10}$ and CeNiSn. In CeNiSn, a small amount of doping could destroy the gap easily because of the V-shaped gap [2–5]. In $CeRu_2Al_{10}$, since a full gap is opened, it might be difficult to destroy the gap by such a small amount of doping. However, this contradicts the experimental results. The most important effect by Rh and Re doping in $CeRu_2Al_{10}$ is the destruction of spin gap and the appearance of the Kondo resonance state as discussed above. Another big difference is the La-doping effect. Although the La-doping effect in $CeRu_2Al_{10}$ is very small, it is large in CeNiSn [2–5], which was discussed from the standpoint of the disturbance of the coherence effect, the Kondo hole, and the impurity band, etc. [1,6]. The gap in $CeRu_2Al_{10}$ is robust against the Ce-site substitution by nonmagnetic Ln ion. This could be due to the Kondo semiconductor accompanied by the AFM order. On the other hand, the Re- and Rh-doping effects in $CeRu_2Al_{10}$ are large as in the Co- and Cu-doping cases in CeNiSn. These could be considered as a hole and electron doping, respectively, if we take the deviation of the d electron number of the doped transition metal element from the mother one. Experimental results indicate that the itinerant nature is enhanced by hole doping and the localized one by electron doping and could be understood as a result of the shift of the Fermi level against the $4f$ level as was discussed in the doped $CeOs_2Al_{10}$ by Kawabata *et al.* [35]. However, the meaning of a hole and electron doping is not clear. There exists no difference in the hole- or electron-doping effect on the collapse of the V-shaped gap or Hall effect in CeNiSn, etc. [2–5]. Since all of s, p, d, and f electrons in Ce, Ru, Al contribute to the electronic states at the Fermi level, it is difficult to consider the d electron of the doped transition metal element, specifically. Experimentally, the electron- or hole-doping effect is pronounced inside the gap in both systems of CeNiSn anf CeT_2Al_{10} [2–5,31]. The d electron of the transition metal element should play an important role in the formation or destruction of the hybridization gap in $CeRu_2Al_{10}$, although the microscopic mechanism is not known at present. We do not know the reason why the different d electron number of the doped transition metal element so sensitively affects the ground-state properties in the Kondo semiconductor. However, both itinerant and localized natures of the $4f$ electron are necessary to construct the spin gap and its existence or nonexistence stands under the subtle balance between the above two contradictory natures. The spin gap is easily collapsed by a small deviation from the subtle balance induced by Rh and Re doping.

IV. CONCLUSION

To conclude, the Ce- and Ru-site substitution effects on the spin gap in $CeRu_2Al_{10}$ were investigated by measuring the magnetic and thermal properties of $Ce_{1-y}Ln_yRu_2Al_{10}$ (Ln = La, Pr, Y) and $Ce(Ru_{1-x}T_x)_2Al_{10}$ (T = Re, Rh) system, respectively. The magnetic susceptibility measurement shows that the itinerant and localized nature is enhanced by Re and Rh doping, respectively. In the latter, although no anomaly is seen in the x dependence of T_0 or T_N, the orientation of the magnetic moment in the AFM ordered phase suddenly changes from the c to a axis at $x_c = 0.03$. The magnetic moment parallel to the a axis is consistent with $\chi_a \gg \chi_c \gg \chi_b$ in the paramagnetic region. The specific heat measurement shows that the $e^{-\Delta/k_BT}$ dependence and the γ value are not changed in the Ce-site substituted systems up to $y = 0.1$ but in the Ru-site substituted systems, the $e^{-\Delta/k_BT}$ dependence disappears and the γ value increases rapidly with x. These indicate that the spin gap is robust against the Ce-site substitution by Ln ion at least up to $y = 0.1$, different from the nonmagnetic Kondo semimetal CeNiSn where the spin gap is rapidly collapsed by La doping. On the other hand, the spin gap is rapidly collapsed by the Ru-site substitution and in place, the conduction electron with heavy effective mass appears at the Fermi level. The spin gap which is formed under the subtle balance between the localized and itinerant nature is easily collapsed by a small amount of Re or Rh doping. The smooth variation of T_0 or T_N and the γ value with x through $x_c = 0.03$ in the Rh doping suggests that the full spin gap is not necessarily indispensable for producing the very high transition temperature in the present system.

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