

# Dilution effects on the antiferromagnetic Kondo semiconductor $\text{CeOs}_2\text{Al}_{10}$

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**Abstract.** We have studied the effects of dilution of Ce sublattice on the unusual antiferromagnetic (AFM) order in the Kondo semiconductor  $\text{CeOs}_2\text{Al}_{10}$  at 28.5 K by the magnetic, transport and specific-heat measurements of single crystals of  $\text{Ce}_{1-z}\text{La}_z\text{Os}_2\text{Al}_{10}$ . The effective magnetic moment and paramagnetic Curie temperature hardly change with  $z$  up to 0.5, indicating that the  $4f$  state remains unchanged at high temperatures. The suppression of the Néel temperature  $T_N$  is much weaker than that in  $5d$  hole doped system,  $\text{Ce}(\text{Os}_{1-y}\text{Re}_y)_2\text{Al}_{10}$ . Therefore, the AFM interaction is robust against the violation of the coherent Ce sublattice. The activation energy in the resistivity decreases in parallel with  $T_N$ , confirming the argument that the presence of the  $c$ - $f$  hybridization gap is a requisite for the unusual AFM order in this system.

## 1. Introduction

In the so-called Kondo semiconductors with renormalized gaps at the Fermi level, the ground states remain nonmagnetic due to the strong hybridization of the  $4f$  states and conduction bands [1]. However, recently found Kondo semiconductors  $\text{CeT}_2\text{Al}_{10}$  ( $T = \text{Ru, Os}$ ) crystallizing in the orthorhombic  $\text{YbFe}_2\text{Al}_{10}$ -type structure order antiferromagnetically (AFM) at rather high temperature  $T_N = 28$  K [2-4]. In order to elucidate the mechanism for the unusual AFM order, we have studied the effects of electron- and hole-doping on the magnetic and transport properties [5,6], electron tunneling [7] and spin-gap formation [8] in  $\text{Ce}(\text{Os}_{1-y}\text{M}_y)_2\text{Al}_{10}$  ( $M = \text{Re, Ir}$ ). These studies have revealed that  $5d$  hole doping with Re substitution for Os moves  $\text{CeOs}_2\text{Al}_{10}$  to a valence fluctuation regime while  $5d$  electron doping with Ir substitution moves to a localized Kondo regime. Furthermore, the  $5d$  hole doping suppresses the  $T_N$  more drastically than the  $5d$  electron doping, whereby the suppressions of  $T_N$  are well correlated with those of the activation energy in the electrical resistivity. Because the activation energy is a measure of the hybridization gap, this correlation suggested that the hybridization gap is necessary for the unusual AFM order in this system.

The effect of dilution of the Ce  $4f$  sublattice on the physical properties of  $\text{CeRu}_2\text{Al}_{10}$  was studied by substituting La for Ce [9-11]. It was expected that the La substitution expands the lattice and therefore the  $4f$  state would be more localized. As  $z$  is increased from 0 to 1 in  $\text{Ce}_{1-z}\text{La}_z\text{Ru}_2\text{Al}_{10}$ , the lattice parameters  $a$  and  $c$  increased by 0.25% and the  $b$  parameter increased by 0.15%. However, the magnetic susceptibility along the easy  $a$  axis for  $T > 100$  K hardly changed with  $z$  up to  $z = 0.7$  where the AFM order disappeared. Therefore, little change occurred in the effective magnetic moment per Ce atom and paramagnetic Curie temperature. The rather robust AFM order against dilution is in contrast with the



strong suppression of the AFM order observed in  $\text{Ce}(\text{Os}_{1-x}\text{M}_x)_2\text{Al}_{10}$  for  $M = \text{Re}$  and  $\text{Ir}$  [7]. In order to understand the contrasting responses to the substitution in the  $T$  sublattice and that in the Ce sublattice, we have studied the dilution effect on the AFM order in  $\text{Ce}_{1-z}\text{La}_z\text{Os}_2\text{Al}_{10}$ . Another issue in  $\text{Ce}_{1-z}\text{La}_z\text{Ru}_2\text{Al}_{10}$  is the reorientation of the ordered magnetic moment  $\mu_{\text{AF}}$  from  $\parallel c$  to  $\parallel b$ , which occurs at  $z \approx 0.07$  [11]. In this work, we have examined whether such reorientation occurs in the Os system  $\text{Ce}_{1-z}\text{La}_z\text{Os}_2\text{Al}_{10}$ .

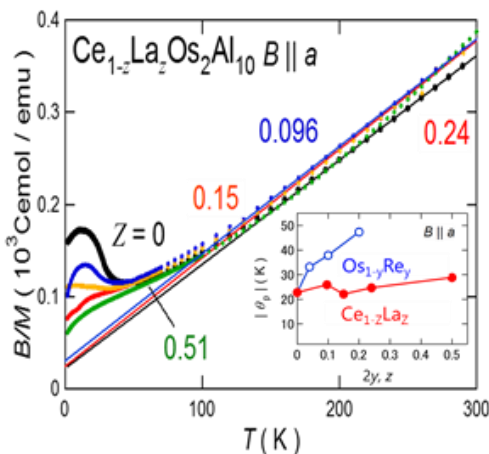
## 2. Experimental

Single crystals of  $\text{Ce}_{1-z}\text{La}_z\text{Os}_2\text{Al}_{10}$  were grown by the Al self-flux method as previously reported [4]. The chemical compositions were determined by the wave-length dispersive electron-probe microanalysis. The compositions of La ( $z$ ) in the crystals were found to slightly deviate from the initial ones ( $Z$ ). For example, starting with the compositions  $Z = 0.05, 0.10, 0.20, 0.30$  and  $0.5$ , the actual values of  $z$  were  $0.043, 0.096, 0.15, 0.24$  and  $0.51$ , respectively. A small amount of impurity  $\text{OsAl}_4$  was detected. The x-ray diffraction analysis on the powdered samples indicated that  $a$  and  $c$  parameters increase linearly by  $0.3\%$  and the  $b$  parameter increases by  $0.2\%$  as  $z$  increases from  $0$  to  $1.0$ .

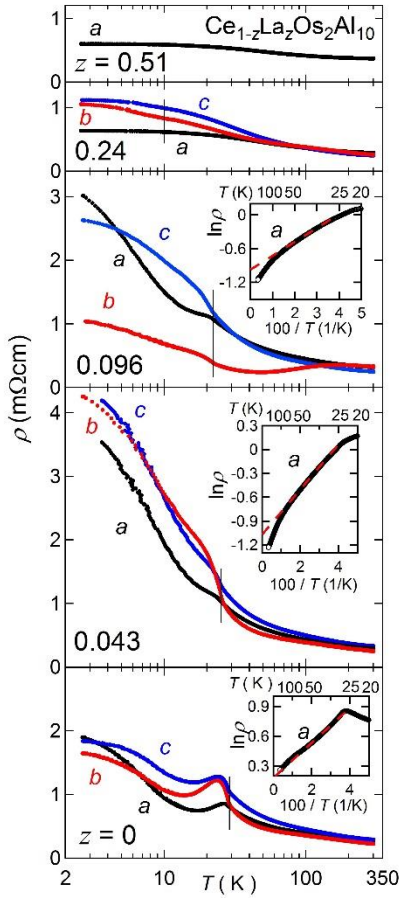
Using the samples cut along the principal axes, we measured the electrical resistivity  $\rho$ , magnetic susceptibility  $\chi$  and specific heat  $C$  in the temperature range from  $2$  to  $300$  K. The measurement of  $\rho(T)$  was performed by the ac four-terminal method. Along the three principal axes,  $\rho(T)$  was measured with bar shaped samples longer than  $0.4$  mm. A SQUID magnetometer (Quantum Design MPMS) was used for  $\chi(T)$  measurements. The magnetization up to  $14$  T was measured by the extraction method using the Quantum Design PPMS. The measurement of  $C(T)$  was performed by the thermal relaxation method on the PPMS.

## 3. Results and Discussion

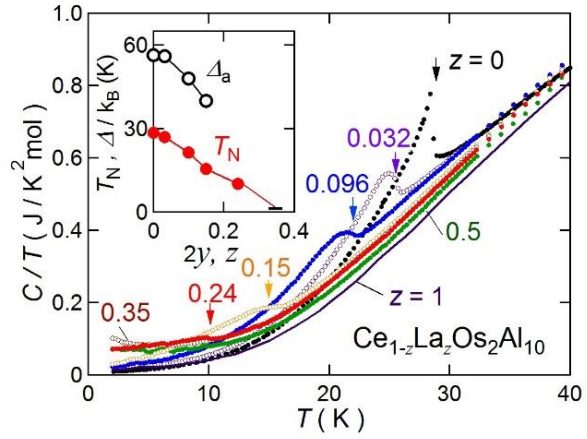
The magnetic susceptibility  $\chi$  of  $\text{Ce}_{1-z}\text{La}_z\text{Os}_2\text{Al}_{10}$  along the  $a$  axis is shown in figure 1 as  $1/\chi$  vs temperature  $T$ . The value is normalized per Ce mol. The Curie Weiss fit to the data above  $200$  K yielded the effective magnetic moment  $\mu_{\text{eff}}$  which stays at  $2.62 - 2.66 \mu_B/\text{Ce}$  for  $0 \leq z \leq 0.51$ . The absolute values of the paramagnetic Curie temperature  $\Theta_p$  stays at  $22 - 30$  K, as is shown in the inset of figure 1. Both  $\mu_{\text{eff}}$  and  $\Theta_p$  are insensitive to the La substitution, which are in common with those observed for  $\text{Ce}_{1-z}\text{La}_z\text{Ru}_2\text{Al}_{10}$  [9-11]. This result indicates that the  $4f$  hole doping does not alter the  $c$ - $f$  hybridization at high temperatures. It is in contrast with the strong effect of  $5d$  hole doping by Re substitution for Os, which shifts the system to the valence fluctuation regime as is evidenced by the large increase in  $|\Theta_p|$  (see the inset of figure 1) [5]. This opposite effect is not due to the volume effect because the unit cell volume increases by a similar ratio for both substitutions, La for Ce and Re for Os. In the latter, the  $a$



**Figure 1.** Temperature dependence of the inverse magnetic susceptibility  $1/\chi$  measured in  $B \parallel a = 1$  T for  $\text{Ce}_{1-z}\text{La}_z\text{Os}_2\text{Al}_{10}$ . The inset shows the absolute values of the paramagnetic Curie temperature  $|\Theta_p|$  for  $B \parallel a$  as a function of the doped hole concentration in  $\text{Ce}_{1-z}\text{La}_z\text{Os}_2\text{Al}_{10}$  and  $\text{Ce}(\text{Os}_{1-y}\text{Re}_y)_2\text{Al}_{10}$  [5].



**Figure 2.** Temperature dependence of the electrical resistivity  $\rho(T)$  along the principal axes for  $\text{Ce}_{1-z}\text{La}_z\text{Os}_2\text{Al}_{10}$ . The inset is the Arrhenius plot showing the thermal activation behavior of  $\rho(T)$  along the  $a$  axis.

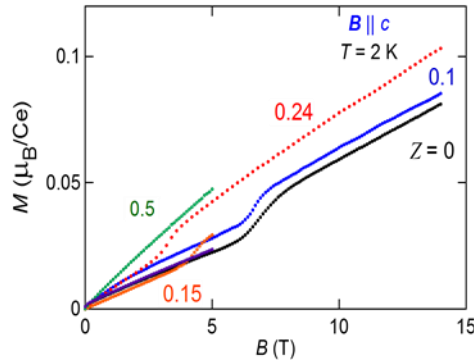


**Figure 3.** Temperature dependence of the specific heat divided by temperature  $C/T$  for  $\text{Ce}_{1-z}\text{La}_z\text{Os}_2\text{Al}_{10}$ . The inset shows the thermal activation energy in the resistivity along the  $a$  axis  $\Delta_a$  and antiferromagnetic ordering temperature  $T_N$  as a function of  $z$ .

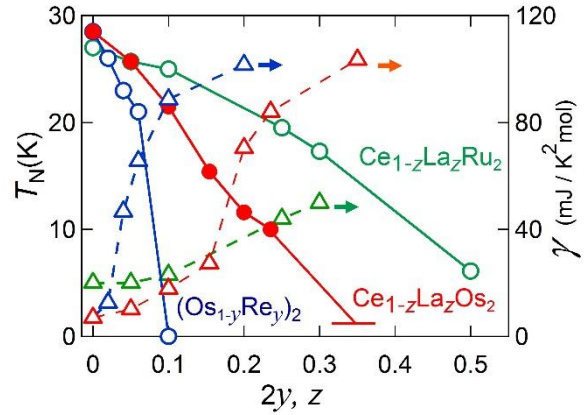
and  $c$  parameters enlarge by 0.2% and the  $b$  parameter enlarges by 0.3% as the Re content increases from 0 to 0.5 [5], whose elongations are comparable in the former as described in the previous section. We note here that the  $\chi_b$  and  $\chi_c$  at  $T > 50$  K are essentially unchanged with  $z$  but the drop in  $\chi_b$  and  $\chi_c$  at  $T < T_N$  for  $z = 0$  disappeared for  $z > 0.24$ .

The presence of the hybridization gap in  $\text{CeOs}_2\text{Al}_{10}$  manifests in the thermal activation type behaviour of resistivity,  $\rho(T) = \rho_0 \exp(\Delta/2k_B T)$  [4]. The results of  $\rho(T)$  along the three principal axes for  $\text{Ce}_{1-z}\text{La}_z\text{Os}_2\text{Al}_{10}$  are presented in figure 2 together with the Arrhenius plot of  $\rho(T // a)$  in the inset. The vertical lines denote  $T_N$ 's determined by the specific heat measurement as will be described below. For  $z = 0$ , the thermal activation behaviour is observed in two regions,  $5 < T < 16$  K and  $30 < T < 80$  K. The increase in  $\rho(T)$  at  $T < T_N$  becomes stronger for  $z = 0.043$  but is weakened as  $z$  is further increased to 0.096. However, the thermal activation behaviour above  $T_N$  remains in  $\rho(T)$  along the  $a$  axis as shown in the inset. For  $z = 0.24$ ,  $\rho(T)$ 's no longer follow the activation type form. We note here that the magnitudes of  $\rho(T=2.5$  K) for  $z = 0.043$  and 0.096 are several times larger than those of the corresponding sample  $\text{Ce}_{1-z}\text{La}_z\text{Ru}_2\text{Al}_{10}$  [10]. The larger enhancement in the Os system than in the Ru system is consistent with the smaller value of the Sommerfeld coefficient in the former, as shown below.

Figure 3 shows the temperature dependence of  $C/T$  for  $\text{Ce}_{1-z}\text{La}_z\text{Os}_2\text{Al}_{10}$ . The midpoint of the jump in  $C/T$  was taken as  $T_N$ , which is 28.5 K for  $z = 0$ . With increasing  $z$ , the jump at the AFM order shifts to low temperatures and becomes broader. A weak anomaly is noticeable at 10 K for  $z = 0.24$  but no jump is observed down to 2 K for  $z = 0.35$ . The Sommerfeld coefficient  $\gamma$  was estimated by extrapolating



**Figure 4.** Magnetization curves  $M(B)$  for the field  $B \parallel c$  at 2 K for  $\text{Ce}_{1-z}\text{La}_z\text{Os}_2\text{Al}_{10}$ .



**Figure 5.** Néel temperature  $T_N$  and Sommerfeld coefficient of the electronic specific heat  $\gamma$  as a function of  $z$  and  $2y$  in  $\text{Ce}_{1-z}\text{La}_z\text{Os}_2\text{Al}_{10}$ ,  $\text{Ce}_{1-z}\text{La}_z\text{Ru}_2\text{Al}_{10}$  [9] and  $\text{Ce}(\text{Os}_{1-y}\text{Re}_y)_2\text{Al}_{10}$  [5].

the  $C/T$  vs  $T^2$  plot to  $T = 0$ . We discuss later the dependence of  $\gamma$  on  $z$  in comparison with other doped systems. The dependences of  $T_N$  and the thermal activation energy  $\Delta_a$  in the resistivity along the  $a$  axis are plotted in the inset of figure 3. It is noteworthy that the decrease in  $T_N$  follows that of  $\Delta_a$ . This relation supports our argument that the hybridization gap is a requisite for the unusual AFM order, which has been derived from our systematic investigation of  $\text{Ce}(\text{Os}_{1-x}\text{M}_x)_2\text{Al}_{10}$  for  $M = \text{Re}$  and  $\text{Ir}$  [5,6].

As mentioned in the introduction, the direction of AFM ordered moments  $\mu_{\text{AF}}$  in  $\text{Ce}_{1-z}\text{La}_z\text{Ru}_2\text{Al}_{10}$  changes from  $\parallel c$  to  $\parallel b$  as  $z$  is increased to 0.07 [10]. In order to examine whether such reorientation occurs in  $\text{Ce}_{1-z}\text{La}_z\text{Os}_2\text{Al}_{10}$ , we have measured the magnetization curves  $M(B)$  up to 14 T at 2 K. The results of  $M(B)$  for  $B \parallel c$  are shown in figure 4. The metamagnetic anomaly at 6.5 T for  $z = 0$  is the manifestation of the spin flop transition from  $\mu_{\text{AF}} \parallel c$  to  $\mu_{\text{AF}} \perp c$  [4,5]. When  $z$  increases to 0.24, the metamagnetic anomaly still exists at  $B \parallel c = 2.5$  T, indicating the direction of  $\mu_{\text{AF}}$  to be kept along the  $c$  axis. This result is consistent with the AFM structure for  $z = 0.1$  with  $\mu_{\text{AF}} \parallel c = 0.23\mu_B$  which was determined by neutron diffraction experiments [12]. We note that the  $M(B)$  curves for  $B \parallel a$  and  $B \parallel b$  did not show any anomaly up to 14 T (not shown).

Figure 5 shows the variations of  $T_N$  and the  $\gamma$  value as a function of doping amount for the three systems:  $4f$  hole doped systems  $\text{Ce}_{1-z}\text{La}_z\text{Os}_2\text{Al}_{10}$  and  $\text{Ce}_{1-z}\text{La}_z\text{Ru}_2\text{Al}_{10}$  [9-11] and  $5d$  hole doped system  $\text{Ce}(\text{Os}_{1-y}\text{Re}_y)_2\text{Al}_{10}$  [5]. Between the two La substituted systems, the degree of suppression of  $T_N$  for the Os compound is stronger than that for the Ru compound. However, it is much milder when compared with that of Re substituted system. This is well correlated with the gradual increases in the  $\gamma$  value as a function of  $z$  in  $\text{Ce}_{1-z}\text{La}_z\text{Os}_2\text{Al}_{10}$  and  $\text{Ce}_{1-z}\text{La}_z\text{Ru}_2\text{Al}_{10}$  which are slower than that as a function of  $2y$  in  $\text{Ce}(\text{Os}_{1-y}\text{Re}_y)_2\text{Al}_{10}$ . Therefore, we conclude that the gapped electronic state in  $\text{CeOs}_2\text{Al}_{10}$  below  $T_N$  is much weakly affected by  $4f$  hole doping compared with the  $5d$  hole doping.

#### 4. Summary

We have studied the effect of dilution of the  $4f$  sublattice on the unusual AFM order in the Kondo semiconductor  $\text{CeOs}_2\text{Al}_{10}$  by measuring the magnetic, thermal and transport properties of  $\text{Ce}_{1-z}\text{La}_z\text{Os}_2\text{Al}_{10}$ . The measurements indicate that the  $4f$  hole doping hardly change both the Ce valence state and the  $c$ - $f$  hybridization strength. The AFM order is mildly suppressed by the doping of  $4f$  holes,

in contrast with the strong suppression caused by the  $5d$  hole doping. The contrasting effects provide a strong constraint for the theory to explain the mechanism of the unusual AFM order in the presence of the hybridization gap in the Kondo semiconductor.

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### References

- [1] Takabatake T, Teshima F, Fujii H, Nishigori S, Suzuki T, Fujita T, Yamaguchi Y, Sakurai J and Jaccard D 1990 *Phys. Rev. B* **41**, 9607
- [2] Strydom A M 2009 *Physica B* **404** 2981
- [3] Nishioka T, Kawamura Y, Takesaka T, Kobayashi R, Kato H, Matsumura M, Kodama K, Matsubayashi K and Uwatoko Y 2009 *J. Phys. Soc. Jpn.* **78** 123705
- [4] Muro Y, Kajino J, Umeo K, Nishimoto K, Tamura R and Takabatake T 2010 *Phys. Rev. B* **81** 214401
- [5] Kawabata J, Takabatake T, Umeo K and Muro Y 2014 *Phys. Rev. B* **89** 094404
- [6] Yamada Y, Kawabata J, Onimaru T and Takabatake T 2015 *J. Phys. Soc. Jpn.* **84** 084705
- [7] Kawabata J, Ekino T, Yamada Y, Sakai Y, Sugimoto A, Muro Y and Takabatake T 2015 *Phys. Rev. B* **92** 201113(R)
- [8] Bhattacharyya A, Adroja D T, Strydom A M, Kawabata J, Takabatake T, Hillier A D, Sakai V G, Taylor J W and Smith R I 2014 *Phys. Rev. B* **90** 174422
- [9] Tanida H, Tanaka D, Sera M, Moriyoshi C, Kuroiwa Y, Takesaka T, Nishioka T, Kato H and Matsumura M 2010 *J. Phys. Soc. Jpn.* **79** 043708
- [10] Oogane Y, Kawamura Y, Nishioka T, Kato H, Matsumura M, Yamamoto Y, Kodama K, Tanida H and Sera M 2012 *J. Phys.: Conf. Ser.* **400** 032073
- [11] Yoshida K, Okubo R, Tanida H, Matsumura T, Sera M, Nishioka T, Matsumura M, Moriyoshi C and Kuroiwa Y 2015 *Phys. Rev. B* **91** 235124
- [12] Adroja D T *et al.* 2015 *Phys. Rev. B* **92** 094425