Interplay between hybridization gaps and antiferromagnetic gap in the hole-doped Kondo semiconductor Ce(Os$_{1-y}$Re$_y$)$_2$Al$_{10}$

Jo Kawabata$^1$, Toshikazu Ekino$^2$, Yoshihiro Yamada$^1$, Akira Sugimoto$^2$, Yuji Muro$^3$ and Toshiro Takabatake$^{1,4,*}$

$^1$ Department of Quantum Matter, Graduate School of Advanced Sciences of Matter, Hiroshima University, Higashi-Hiroshima 739-8530, Japan

$^2$ Graduate School of Integrated Arts and Sciences, Hiroshima University, Higashi-Hiroshima 739-8526, Japan

$^3$ Liberal Arts and Sciences, Faculty of Engineering, Toyama Prefectural University, Imizu, Toyama 939-0398, Japan

$^4$ Institute for Advanced Materials Research, Hiroshima University, Higashi-Hiroshima 739-8521, Japan

E-mail: takaba@hiroshima-u.ac.jp

Abstract. The Kondo semiconductor CeOs$_2$Al$_{10}$ undergoes an antiferromagnetic (AFM) order at an unexpectedly high temperature 28.5 K. We have performed break junction tunneling measurements for the hole-doped system Ce(Os$_{1-y}$Re$_y$)$_2$Al$_{10}$ ($y \leq 0.1$). The tunneling spectrum $dI/dV$ for $y = 0$ displays successive openings of a hybridization gap $V_1$, an AFM gap $V_{AF}$ and another hybridization gap $V_2$ in the density of states (DOS). On cooling from 36 K to $T_N$, both the gap value $V_1$ and the DOS at the Fermi level, $E_F$, decrease by 8% of the values at 36 K. This fact indicates that the development of short-range magnetic correlations reduces the c-f hybridization gap. For $y = 0.02$, a peak appears in $dI/dV$ at $V = 0$ concurrently with the disappearance of $V_2$. With increasing $y$ further, the in-gap states develop at $E_F$, in good agreement with the increase in the Sommerfeld coefficient of the heat capacity. Thereby, $T_N$, $V_1$ and $V_{AF}$ decrease and disappear at $y = 0.05$. These facts provide compelling evidence that the presence of $V_1$ is necessary for the AFM order in CeOs$_2$Al$_{10}$.

1. Introduction

A family of cerium-based compounds CeT$_2$Al$_{10}$ (T = Fe, Os and Ru) belongs to Kondo semiconductors. For example, the resistivity $\rho(T)$ in the Os compound shows a thermal activation-type temperature dependence at 30 < $T$ < 80 K. Nevertheless, this compound undergoes an antiferromagnetic (AFM) transition at rather high Néel temperature $T_N$ of 28.5 K [1,2]. It has remained a mystery that the $T_N$ with a small magnetic moment 0.3 $\mu_B$/Ce is higher than $T_N = 18$ K for the Gd counterpart with 7 $\mu_B$/Gd [3]. Below $T_N$, the slope of $\rho(T)$ increases abruptly, most likely by the formation of a superzone gap. The analysis of anisotropic magnetic susceptibility and the x-ray absorption spectra for single crystals
determined the crystal-field ground state to be a Kramer’s doublet dominated by $|J_z| = |\pm 3/2>$, where $|J_z>$ is the c-axis component of the total angular momentum $J = 5/2$ [4].

The break junction tunneling spectroscopy (BJTS) is a powerful method to detect fine changes in the density of states (DOS) caused by AFM and charge-density-wave (CDW) transitions. The BJTS uses a crack prepared in a sample as an insulating barrier for the semiconductor-insulator-semiconductor (SIS) junction. Cracking the sample in a liquid-helium atmosphere provides a clean interface without any contamination and oxidation of reactive Ce based compounds. Furthermore, the SIS junction is not affected by the Seebeck effect so that symmetric tunneling spectra are observed [5]. The BJTS for the antiferromagnet Ce(Fe$_{0.95}$Co$_{0.05}$)$_2$ showed peaks at $V = \pm 10$ mV below $T_N = 45$ K due to a superzone gap opening in the DOS at $E_F$ [6]. The CDW gap in CeTe$_2$ was found to decrease when a short-range ferromagnetic order develops at low temperatures. This observation in CeTe$_2$ revealed the interplay between the CDW and magnetic order [7].

Recently, BJTS measurements for CeT$_2$Al$_{10}$ (T = Fe, Os) have revealed openings of two gaps ($\Delta_1 = 150$ meV, $\Delta_2 = 38$ meV) in CeFe$_2$Al$_{10}$ and three gaps ($\Delta_1 = 100$ meV, $\Delta_{AF} = 50$ meV, $\Delta_2 = 25$ meV) in CeOs$_2$Al$_{10}$ [8]. In the latter, the AFM gap $\Delta_{AF}$ develops below $T_N$. We pointed out that $\Delta_1$ and $\Delta_2$ are proportional to the Kondo temperature $T_K$, and the ratio $\Delta_1/\Delta_2$ is approximately 4 for the two compounds with $T = Fe$ and Os. These relations, $\Delta \propto T_K$ and $\Delta_1/\Delta_2 = 4$, agree with those for the double c-f hybridization gaps calculated with the periodic Anderson model for a crystal-field ground state consisting of $|J_z| = |\pm 3/2>$ [9].

The 5$d$ hole and electron doping effects in Ce(Os$_{1.5}$Re$_0.5$)$_2$Al$_{10}$ and Ce(Os$_{1.4}$Ir$_{0.6}$)$_2$Al$_{10}$ systems, respectively, have been studied by the measurements of magnetic properties, optical conductivity and muon spin relaxation ($\mu$SR) as well as neutron scattering [10-12]. It is found that the 4$f$ state in CeOs$_2$Al$_{10}$ becomes more itinerant by doping of 5$d$ holes, while the 4$f$ state is localized by the doping of 5$d$ electrons. The semiconducting increase in the $\rho(T)$ below 16 K changes to a metallic behavior at a small level of $y = 0.02$. For $y = 0.1$, $\rho(T)$ exhibits a broad maximum at around 100 K which is a characteristic of valence fluctuating Ce compounds. On the other hand, $\rho(T)$ for the electron doped sample with $x = 0.04$ shows a metallic behavior at low temperatures. For $x = 0.15$, $\rho(T)$ no longer shows the thermal activation behavior above $T_N$ nor the increase below $T_N$. In both systems doped with 5$d$ holes and electrons, the suppression of $T_N$ is well correlated with that of the thermal activation energy $\Delta k_B T_N$ in $\rho(T)$. In contrast, the Sommerfeld coefficient $\gamma$ in the specific heat increases sharply as $x$ and $y$ are increased. Therefore, we concluded that the presence of the hybridization gap $V_1$ is necessary for the AFM order in CeOs$_2$Al$_{10}$. Although the activation energy in $\rho(T)$ gives a crude estimation of the gap width, it does not provide us with the information on the temperature variation of the gap structure. Note that $\rho(T)$ depends on the scattering process and the DOS only at the Fermi level. It is important to observe how the three gaps $V_1$, $V_{AF}$ and $V_2$ in CeOs$_2$Al$_{10}$ are changed by doping the 5$d$ holes and electrons.

For this purpose, we have measured the BJTS on the system Ce(Os$_{1.5}$Re$_0.5$)$_2$Al$_{10}$ ($y \leq 0.1$). We have reported that the sample with $y = 0.02$ undergoes an AFM transition at 23 K, above which $\rho(T)$ still exhibits the activation-type temperature dependence. For $y = 0.05$, however, the AFM transition and the gap $\Delta k_B$ in $\rho(T)$ disappear. Furthermore, $\rho(T)$ in $y = 0.1$ shows a characteristic temperature dependence with a broad maximum around 100 K [10].

2. Sample preparation and break-junction tunneling measurements
For BJTS measurements, polycrystalline samples of Ce(Os$_{1.4}$Re$_0.6$)$_2$Al$_{10}$ ($y = 0, 0.02, 0.05$ and $0.1$) were prepared by arc melting and subsequent annealing in an evacuated quartz ampoule at 850 °C for 7 days [2]. The atomic composition was determined by electron-probe microanalysis, thereby the real compositions of Re were found to agree with the initial ones. In addition, a small amount of impurity phase Os$_3$Al$_{13}$ has been detected. The midpoint of the jump in the specific heat has been taken as the AFM ordering temperature $T_N$ [10].
The samples were shaped into a plate of $3\times2\times0.5$ mm$^3$ for BJTS measurements. In order to crack it perpendicularly in the middle, we cut a groove into the surface. The plate was mounted on a flexible substrate, and an adjustable force was applied from its back to make a crack in a liquid-helium chamber. The spectra of $dI/dV$, where $I$ and $V$ represent the tunneling current and the bias voltage, respectively, have been recorded using a standard lock-in technique by applying $V$ along the long axis of the sample [8]. The different thermal expansions between the sample and the substrate made the junction unstable at elevated temperatures. In fact, we could observe the spectra on heating just to 65 K.

3. Experimental results
The tunneling spectra $dI/dV$ vs the bias voltage $V$ for Ce(Os$_{1-y}$Re$_y$)$_2$Al$_{10}$ ($y = 0, 0.02$ and $0.05$) at 4.4 K are shown in Fig. 1. The spectra are normalized by the values at $V = -400$ mV. The absolute value of $dI/dV$ depends on the junction resistance $R_J$, which is determined by the thickness of insulating barrier [14]. In the high-bias range at $V = -400$ mV, the values of $R_J$ are 20 – 10000 $\Omega$ at 4.4 K whose magnitude is much larger than the sample resistance 10 – 50 m$\Omega$ measured before breaking. This relation satisfies the condition to measure the voltage drop by the tunneling current in the insulating barrier. By measuring the spectra for many junctions, we confirmed that both the gap structures and the width $V_{P-P}$ hardly depend on $R_J$ [15]. Such a result is in accordance with a principle of the tunneling spectroscopy.

There are three gap structures in the spectrum for $y = 0$. The peak structures at ± 200, 100 and 50 mV are denoted as $V_1$, $V_{AF}$ and $V_2$, respectively, whose values agree with those obtained for single crystals [8]. The peak structures of $V_{AF}$ change to a shoulder in the spectrum for $y = 0.02$, where a peak appears at $V = 0$. This peak structure develops in the spectrum for $y = 0.05$, where the gaps $V_1$ and $V_{AF}$ disappear. These changes in the spectrum with $y$ indicate that the 5$d$ hole doping suppresses the hybridization gaps and induces an in-gap state at $E_F$. These behaviours are consistent with the gap structures in the DOS calculated on the basis of the periodic Anderson model which takes into a slight dispersion in the $f$-band in the orthorhombic Kondo semiconductors [16].

The temperature dependences of $dI/dV$ vs $V$ are shown in Fig. 2 for three selected compositions $y = 0, 0.02$ and 0.1. For $y = 0$, we present the data obtained with the single crystal [8] because the gap structures are clearer than that obtained with the polycrystal. We note that there is little difference in the gap structures between the two. The voltage difference between the shoulders at ±200 mV at 78.5 K is denoted as $V_1$. On cooling, the shoulders change to peaks. Below $T_N$, other peaks develop at ±100 mV, whose peak-to-peak voltage is denoted as the AFM gap $V_{AF} = 200$ mV. On further cooling below 16 K, additional peaks appear at ±50 mV, whose peak-to-peak voltage is denoted as $V_2$.

In the spectra for $y = 0.02$, the $dI/dV$ at 40 K displays shoulders at $V_1/2$. The shoulders change to peaks at 35 K, and transform into shoulders again at $T < 30$ K. On cooling below 27 K ($> T_N = 23$ K), other shoulders appear at $V_{AF}/2$. At low temperatures, the $dI/dV$ exhibits a cusp at $V = 0$, which develops.

![Figure 1](image_url) **Figure 1.** Tunneling conductance spectra $dI/dV$ vs the bias voltage $V$ normalized by the values at $V = -400$ mV for Ce(Os$_{1-y}$Re$_y$)$_2$Al$_{10}$ ($y = 0, 0.02$ and $0.05$) at 4.4 K. The arrows on the spectrum for $y = 0$ indicate the structures $V_1$, $V_{AF}$ and $V_2$, respectively.
into a peak on cooling. The spectra for \( y = 0.1 \) is characterized by one cusp at \( V = 0 \). The development of a cusp at \( V = 0 \) is a characteristic of a metallic heavy fermion state \[17\]. It indicates that the 4f state in CeOs\(_2\)Al\(_{10}\) becomes more itinerant by 5d hole doping. With increasing \( y \), in fact, the behavior of \( \rho(T) \) changes from the Kondo semiconducting one to that for the valence fluctuating Ce compounds \[10\].

The temperature dependences of the gap widths \( V_{P-P} (= V_1, V_{AF} \text{ and } V_2) \) are plotted in Fig. 3(a). For \( y = 0 \), the black and blue data are obtained with a single crystal and a polycrystal, respectively, whose temperature variations are essentially same. The gap width \( V_1 \) for \( y = 0 \) decreases from 430 to 400 mV at around 36 K, which is still above \( T_N = 28.5 \) K. We recall that the CDW-like charge gap develops in CeOs\(_2\)Al\(_{10}\) on cooling below 36 K \[18\]. Similarly for \( y = 0.02 \), \( V_1 \) decreases on cooling from 50 to 27 K (> \( T_N = 23 \) K). It is reminiscent of the CDW gap in CeTe\(_2\) which decreases on cooling below 6.1 K, where a short-range ferromagnetic order develops \[6\]. By analogy, the reduction in \( V_1 \) occurring above \( T_N \) in Ce(Os\(_{1-y}\)Re\(_y\))\(_2\)Al\(_{10}\)\((y = 0, 0.02)\) may be attributed to the onset of a short-range magnetic correlation.

The gap \( V_{AF} \) for \( y = 0 \) increases gradually below \( T_N \), whereas that for \( y = 0.02 \) seems to appear suddenly at 27 K. The gap \( V_2 \) for \( y = 0 \) appears below 16 K, but corresponding anomaly is absent for \( y = 0.02 \).

Figure 3(b) displays the temperature dependences of normalized zero bias conductance, \( \{NZBC\}^{1/2} = \left[\frac{\partial I}{\partial V}(V = 0)\right] / \left[\frac{\partial I}{\partial V}(V = -400 \text{ mV})\right] \). We note that the NZBC is proportional to the square of the DOS at the Fermi level, \( N(E_F) \). The NZBC for \( y = 0 \) gradually decreases and bends at around 36 K, which occurs simultaneously with the sudden decrease in \( V_1 \). It suggests that a part of Fermi surface is lost by the development of the short-range correlation. Besides, the significant change in the Fermi surface on cooling from 36 K manifests in the sharp decrease in the thermopower, which is very sensitive to the energy derivative of quasiparticle density of states at \( E_F \), sharply decreases only along the \( b \)-axis \[19\]. For \( y = 0.02 \), the decrease in NZBC turns to an increase below 27 K due to the development of in-gap states at \( E_F \). For \( y = 0.1 \) with no AFM transition, the NZBC increases monotonically on cooling.

Figure 4(a) displays the \( y \) dependences of gap widths \( V_1, V_{AF} \) and \( V_2 \) as well as \( \{NZBC\}^{1/2} \). The increase in \( \{NZBC\}^{1/2} \) with \( y \) is consistent with that in the \( \gamma \) value as shown in Fig. 4(b). The inverse correlation between \( T_N \) and \( \gamma \) in Fig. 4(b) indicates that the increase of \( N(E_F) \) suppresses the AFM order.
Figure 3. (a) Temperature dependences of gap widths $V_1$, $V_{AF}$, $V_2$ and (b) the square root of normalized zero bias conductance $\langle NZBC \rangle^{1/2} = ([dI/dV (V = 0)] / [dI/dV (V = -400 \text{ mV})])^{1/2}$ for Ce(Os$_{1-y}$Re$_y$)$_2$Al$_{10}$ ($y = 0$, 0.02 and 0.1). For $y = 0$, the data in black and blue are obtained with a single crystal and a polycrystal, respectively. $T_N$ denotes the AFM ordering temperature determined by the specific heat measurements.

Moreover, the $T_N$ and the gap widths $V_1$ and $V_{AF}$ are largely suppressed at a small hole-doping level $y = 0.02$, and all disappear at $y = 0.05$. Therefore, the AFM transition is strongly correlated with the hybridization gap $V_1$. This relation supports our previous argument that the presence of the hybridization gap $V_1$ is necessary for the unusual AFM order [10]. Here, let us compare the $c$-$f$ hybridization gap $V_1$ with the spin gap which was observed by inelastic neutron scattering [12]. The spin gap exists at 11 meV in the undoped sample with $y = 0$. For $y = 0.03$, $T_N$ is decreased to 21 K, but the spin gap still exists at the same energy 11 meV while the excitation intensity is much reduced. On the other hand, the spin gap disappears in the 5$d$ electrons doped systems Ce(Os$_{1.92}$Ir$_{0.08}$)$_2$Al$_{10}$ with $T_N = 21$ K. It is highly required to examine by the BJTS wherever or not the hybridization gap $V_1$ is correlated with the spin gap.

4. Summary
We have performed the BJTS measurements for the Ce(Os$_{1-y}$Re$_y$)$_2$Al$_{10}$ ($y \leq 0.1$) to study how the two hybridization gaps $V_1$, $V_2$ and the AFM gap $V_{AF}$ change by doping of the 5$d$ holes in CeOs$_3$Al$_{10}$ with $T_N = 28.5$ K. For the undoped sample, both the hybridization gap $V_1$ and the magnitude of $N(E_F)$ decrease on cooling below 36 K. These reductions occurring above $T_N$ are attributed to a short-range correlation. For $y = 0.02$, in-gap states develop at $E_F$ with concomitant disappearance of $V_2$. With increasing $y$ to 0.1,
the in-gap states at $E_F$ develops further. We found a strong correlation between the variations of $T_N$, $V_1$ and $V_{AF}$. Thus, we conclude that the presence of the hybridization gap $V_1$ above $T_N$ is necessary for the unusual AFM order.

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