Fe substitution effect on the phase transition and hybridization gap in CeOs$_2$Al$_{10}$

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Abstract. We report on the magnetic susceptibility, electrical resistivity and specific heat measurements of the alloys Ce(Os$_{1-x}$Fe$_x$)$_2$Al$_{10}$ ($0 \leq x \leq 1$) in order to understand the anomalous phase transition in CeOs$_2$Al$_{10}$ at $T_0 = 28.5$ K. With increasing $x$, the unit cell volume decreases linearly and the $c$-$f$ hybridization is enhanced as indicated by the systematic change in the magnetic susceptibility. On the other hand, $T_0$ decreases slowly to 25 K at $x = 0.3$ then sharply to 20 K at $x = 0.5$, and eventually disappears at $x = 0.6$. However, the jump of $C_p$ at $T_0$, which is proportional to the entropy released by the phase transition, decreases quickly from 0.22 J/Kmol at $x = 0$ to 0.08 J/Kmol at $x = 0.3$, and then linearly to 0 at $x = 0.6$. These behaviours of $T_0$ resemble the pressure dependence of $T_0$ for CeOs$_2$Al$_{10}$ as well as the $x$ dependence of $T_0$ in Ce(Ru$_{1-x}$Fe$_x$)$_2$Al$_{10}$ for $0.25 \leq x$. This result suggests that the critical concentration where $T_0$ disappears depends strongly on the $c$-$f$ hybridization strength.

1. Introduction

Kondo semiconductors have been one of the central issues in the physics of strongly correlated $f$-electron system [1]. Kondo semiconductors display an activation-type behaviour in the transport properties at low temperatures because of the formation of a small energy gap at the Fermi level owing to the strong hybridization between the local $f$ state and conduction bands, so-called $c$-$f$ hybridization. This strong $c$-$f$ hybridization hinders magnetic order in the Ce-based Kondo semiconductors except CeOs$_4$Sb$_{12}$, which undergoes a spin-density-wave transition at 0.9 K [2].

Ternary Ce compounds CeT$_2$Al$_{10}$ (T=Fe, Ru and Os), which crystallize in the orthorhombic YbFe$_2$Al$_{10}$-type structure [3, 4], are a new series of Kondo semiconductors [5-9]. Especially, CeRu$_2$Al$_{10}$ and CeOs$_2$Al$_{10}$ display an unusual phase transition at $T_0 = 27$ K and 28.5 K, respectively, while CeFe$_2$Al$_{10}$ is a Kondo semiconductor without magnetic phase transitions akin to CeNiSn and CeRhSb [10]. The formations of hybridization gap below 80 K in CeT$_2$Al$_{10}$ (T=Ru and Os) are recognized in an activation-type electrical resistivity and the reduction of optical conductivity below 45 meV [11]. Below $T_0$, the resistivity shows a further increase which indicates opening of another energy gap on a part of Fermi surface by the phase transition. Moreover, the muon spin relaxation and neutron diffraction measurements revealed an antiferromagnetic order of $\sim 0.3$ $\mu_B$ of Ce 4f moments aligned along the orthorhombic $c$-axis [12-16]. Despite such a small value of Ce moment, $T_0$’s for CeT$_2$Al$_{10}$ are higher than the Néel temperatures of isostructural counterparts of Nd ($T_N$=2.4 K for T=Ru and $T_N$=2.2 K for T=Os) and Gd ($T_N$=17.5 K for T=Ru and $T_N$=18 K for T=Os) [7, 17]. In addition to anomalously high $T_0$, pressure dependence of $T_0$ for CeOs$_2$Al$_{10}$ shows a sudden decrease in the range of 0.26 GPa above the critical pressure $P_c$=2.54 GPa [18]. A similar behaviour is observed in
Ce(Ru1-xFe_x)2Al10 at 0.75 < x < 0.825 [19]. These behaviours are quite different from a gradual decrease of T_N observed in conventional Ce-based Kondo antiferromagnets by application of pressure or alloying. In this paper, we report the Fe substitution effect on T_0 of CeOs2Al10 by measuring the magnetic susceptibility, electrical resistivity and specific heat. We compare our results with the effects of pressure on CeOs2Al10 and alloying on Ce(Ru1-xFe_x)2Al10.

2. Experimental
Polycrystalline samples of Ce(Os1-xFe_x)2Al10 were prepared by arc-melting the constituent amount of pure elements of Ce, Os, Fe and Al. The obtained samples were annealed at 800 °C for one week. The least-square fitting of powder x-ray diffraction (XRD) patterns showed that the lattice parameters a, c, and unit-cell volume V of Ce(Os1-xFe_x)2Al10 decrease almost linearly with increasing x, while the parameter b shows significantly non-linear behaviour. A slight deviation from the linear extrapolation at x = 1 should result from the intermediate valency in CeFe2Al10. The electron-probe microanalyses (EPMA) and powder XRD indicate that Fe concentrations in the obtained samples agree well with the nominal compositions. The bottom of the ingot with x = 0.2 contained an impurity phase of CeOs3Al12, which was eliminated from the sample used for the physical measurements.

The magnetic susceptibility M/B was measured at 1 T by using a commercial SQUID magnetometer (Quantum Design MPMS) in the temperature range from 2 K down to 100 K. The electrical resistivity ρ was measured by the ac four probe method at 2.5 K < T < 300 K. The specific heat C_p was measured by the relaxation technique at 2 K < T < 300 K in the Quantum Design PPMS.

3. Results and Discussion
The inverse magnetic susceptibility B/M for Ce(Os1-xFe_x)2Al10 in the whole range 0 ≤ x ≤ 1 was found to obey a Curie-Weiss law from 300 K down to 100 K. With increasing x, the slope of B/M above 100 K decreases owing to the enhancement of c-f hybridization. This enhancement is also recognized by the increase of T'_{max}, which is the temperature at a maximum of M/B vs T. The x dependence of T'_{max} and the paramagnetic Curie temperature θ_p are shown in Fig. 1. Not only T'_{max} but also |θ_p| increase exponentially with increasing x. This behaviour agrees with that observed in the pressure study for CeOs2Al10 [18]. Therefore, the contraction of unit cell volume by Fe substitution strengthens the c-f hybridization.

Figure 2 displays the variations of ρ(T) for Ce(Os1-xFe_x)2Al10. For 0 < x < 0.6, a thermally activation behaviour is observed between 70 K and 30 K as shown by the dashed lines. The activation energy Δ is estimated as 30−50 K by the fitting of ρ(T) to the equation ρ(T) = ρ_0 exp(Δ/2k_BT). The values of Δ agree with that obtained for a single-crystal CeOs2Al10 [9]. Thus the activation behaviour

![Figure 1](image1.png)  
**Figure 1.** Variations of T'_{max} and |θ_p| versus Fe concentration x derived from the magnetic susceptibility. Solid lines are guide to the eye.

![Figure 2](image2.png)  
**Figure 2.** Temperature dependence of electrical resistivity for Ce(Os1-xFe_x)2Al10. Dashed lines for 0 ≤ x ≤ 0.6 represent the thermally activating behaviour.
in Ce(Os1-xFe)xAl10 originates from the formation of hybridization gap observed in the optical conductivity for CeOs2Al10 [11]. The constant behaviour of $\Delta$ in the range $0 < x < 0.6$ suggests that the gap size is independent of $x$. This result is inconsistent with the pressure dependence of $\Delta$ for CeOs2Al10 [18]. Because of the slow decrease of lattice parameter $b$, the anisotropic hybridization, especially that along the $b$-axis, should play an important role for the hybridization-gap formation.

Below 30 K, $\rho(T)$ shows a broad maximum and then increases with decreasing $T$ which is also observed in CeOs2Al10 [9]. The low-temperature upturn disappears at $x = 0.4$ and 0.6, but revives at $x = 0.8$ and 1. The reason of disappearance of upturn in $x = 0.4$ and 0.6 is unclear, but it may be related to the disappearance of phase transition because the low-temperature upturn disappears above $P_c$ for CeOs2Al10 [18]. The $\rho(T)$ for $x = 0.8$ resembles that of CeFe2Al10 for $I/\alpha$. Thus the phase transition should be absent at $x = 0.8$.

Figure 3 shows the specific heat divided by temperature $C/T$ versus $T$ for Ce(Os1-xFe)xAl10. A jump of $C/T$ by the phase transition is observed clearly for $x$ up to 0.3. For $x = 0.4$ and 0.5, a small but significant anomaly is recognized at 27 K and 21 K, respectively, as shown by an arrow in the inset of Fig. 3. Additional anomalies are observed at temperatures below 7 K for $x = 0.2$, 0.4, and 0.6. They can be attributed to the magnetic transition of CeOs3Al12 impurity phase because no anomalies are observed in $\rho(T)$ below 10 K as shown in Fig. 2. At $x = 0.6$, the values of $C/T$ below 40 K decrease with respect to those for $x = 0 \sim 0.5$. This decrease results from the suppression of the magnetic contribution of $C_p$ at $x = 0.6$ where the phase transition disappears and the c-f hybridization is enhanced.

The $x$ dependences of $T_0$ and the jump in $C/T$ at $T_0$, $\Delta(C/T)$, are plotted in Fig. 4. On going from $x = 0$ to 0.5, $T_0$ decreases gradually from 28.5 K to 21 K, then drops sharply to 0 K. On the other hand, $\Delta(C/T)$, which represents the contribution of phase transition for the entropy, decreases rapidly from $x = 0$ then vanishes at $x = 0.6$. These behaviours are very similar to the pressure dependences of $T_0$ and $\Delta(C/T)$ for CeOs2Al10 [18]. Moreover, as shown in Fig. 4, the dependences of $T_0$ and $\Delta(C/T)$, respectively, on $x$ for Ce(Os1-xFe)xAl10 coincides with those for Ce(Ru1-xFe)xAl10 [19] if the value of $x$ is shifted by 0.25. This feature indicates that the phase transition in CeT2Al10 results from the same origin. Moreover, this also suggests that the critical Fe concentration $x_c$ where the phase transition disappears depends not on the unit cell volume $V$ but on the c-f hybridization strength because the hybridization strength for T=Os is stronger than that for T=Ru despite $V$ of T=Os is only 0.3% larger than that of T=Ru. The importance of c-f hybridization for the phase transition is also suggested by the comparison between the result of Ce(Os1-xFe)xAl10 and pressure effects on CeOs2Al10; $T_0$ disappears
when $T_{\text{max}}$ is increased to 60 K in both cases. However, the discrepancy between $x$ dependence of $T_0$ and $\Delta(C/T)$, especially the sudden disappearance of $T_0$, cannot be explained solely by the enhancement of $c$-$f$ hybridization. Therefore, we have to consider following magnetic interactions in addition to the enhancement of $c$-$f$ hybridization: a superexchange interaction proposed by the pressure study [18], enhancement of on-site 4$f$-5$d$ mixing due to the lack of inversion symmetry at Ce site pointed out by the calculation of crystalline electric field effect [20], antiferromagnetic order driven by the formation of charge-density-wave along the $b$-axis proposed by the study of optical conductivity [11]. In order to clarify the origin of anomalous response of $T_0$ to pressure and Fe-substitution, we are doing neutron scattering experiment for Ce(T_{1-x}Fe_x)2Al10.

4. Summary
We studied Fe substitution effect on the magnetic transition in the Kondo semiconductor CeOs2Al10 by the measurements of magnetic susceptibility, electrical resistivity and specific heat for polycrystalline Ce(Os1-xFe)x2Al10. Exponential increases of paramagnetic Curie temperature and temperature at the maximum in the susceptibility indicate that the $c$-$f$ hybridization strength in Ce(Os1-xFe)x2Al10 increases with increasing $x$. The formation of hybridization gap in the range $0 < x < 0.6$ is manifested by the thermally activation behaviour in the resistivity between 70 K and 30 K. The weak variations of activation energy and lattice parameter for $b$-axis in the range $0 < x < 0.6$ suggest the importance of anisotropic $c$-$f$ hybridization for the gap formation. The specific-heat anomaly due to the phase transition is observed in the range $0 < x < 0.5$. The variations of transition temperature and the magnitude of specific-heat anomaly in Ce(Os1-xFe)x2Al10 agree with the pressure dependence of those for CeOs2Al10 and $x$ dependence in Ce(Ru1-xFe)x2Al10 at $x > 0.25$. This agreement suggests strongly that the critical point where the phase transition disappears is determined by the strength of $c$-$f$ hybridization.

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