Thermoelectric and Magnetic Properties of $CeRh_{1-x}M_xSn$ (M = Co, Ni, Ru)

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Abstract

The thermopower S, electrical resistivity ρ, and magnetic susceptibility χ are reported on $CeRh_{1-x}M_xSn$ (M = Co, Ni, Ru; $x \leq 0.25$). The Ni doping changes the valence-fluctuating behavior of $\chi(T)$ for $x = 0$ to the Currie-Weiss type, whereas the Ru one to the Pauli-type. Nevertheless, all the substitutions result in a decrease of the rather large maximum of $S = 60$ μV/K for $x = 0$.

Key words: CeRhSn; thermoelectric power; valence fluctuation

Valence-fluctuating Ce compounds such as $CePd_3$, CeRhSb and CeRhAs exhibit large positive thermopower, S∼100 μV/K, which coexists with small resistivity ρ [1,2]. The large S originates from the presence of a narrow band peaking at just above the Fermi level. The narrow band is formed by the hybridization of $4f$-electron states with a conduction band [1]. These compounds have been considered as the candidate for a p-type thermoelectric material [3], because the figure of merit is proportional to S^2/ρ. A valence-fluctuating compound CeRhSn with the hexagonal ZrNiAl-type structure [4] has the maximum of $S = 60$ μV/K at 150 K [5]. We expected that the maximum value would be further elevated by controlling the strength of c-f hybridization. The hybridization would be strengthened by replacing Co and Ni for Rh, because their atomic diameters are smaller than that of Rh. Replacement of Ru for Rh should decrease the number of $4d$ electrons, which may also increase the hybridization. Keeping this in mind, we have investigated the thermoelectric and magnetic properties of $CeRh_{1-x}M_xSn$ (M = Co, Ni, Ru).

The polycrystalline samples with x up to 0.25 were prepared by arc melting the constituent elements under a purified Ar atmosphere. All the samples were annealed at 900 °C for 5 days. Phase purity, crystal structure and lattice constants were checked by powder X-ray diffraction methods. Contrary to our expectation, it is found that the change in lattice parameters was less than 0.1% for all the substitutions up to $x = 0.25$. For M = Ru with $x = 0.25$, the hexagonal lattice shrinks along the a-axis by 0.1% but elongates along the c-axis by the same ratio. By using a SQUID magnetometer, $\chi(T)$ was measured in an applied field of 1 T from 2 to 370 K. The $\rho(T)$ was measured by a standard DC four-probe method in a range 1.4-290 K. A differential method was employed for the $S(T)$ measurement from 4.2 to 290 K.

Fig.1 shows the temperature dependence of χ for $CeRh_{1-x}M_xSn$ (M = Ni and Ru). For $x = 0$, $\chi(T)$ shows a weak hump around 170 K which is characteristic of valence-fluctuating Ce compounds. By Ni doping, $\chi(T)$ gradually changes to the Currie-Weiss behavior. With increasing x from 0 to 0.25, the effective moment μ_{eff} changes from 3.21 μ_B to 2.48 μ_B, being close to 2.54 μ_B expected for the trivalent Ce free ion. By contrast, Ru doping depresses the value of $\chi(T)$ and weakens the temperature dependence. These opposite effects imply that the intermediate-valent state of Ce ions is shifted to a trivalent state by Ni doping but to a tetravalent state by Ru doping. We note that a small amount of ferromagnetic impurities in the Co doped

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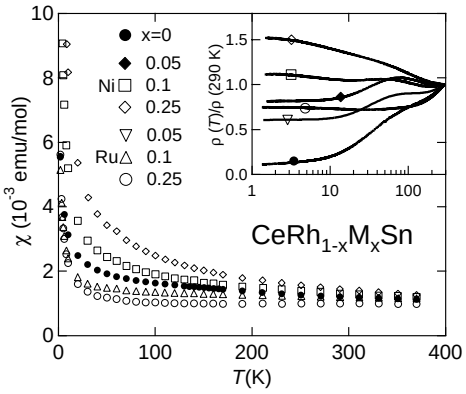

Fig. 1. Temperature dependence of magnetic susceptibility of $CeRh_{1-x}M_xSn$ (M = Ni and Ru) for $x \leq 0.25$. The inset shows the electrical resistivity.

samples did not allow such analysis.

The inset of Fig.1 shows the variations of $\rho(T)$ for $CeRh_{1-x}M_xSn$ (M = Ni and Ru). For M = Co, the results of $\rho(T)$ were very similar to that for M = Ni. Since the samples had many clacks, the ρ data were normalized to the room temperature value. For the doped samples, the significant increase in $\rho(T)/\rho(290\ \mathrm{K})$ is obvious at low temperatures. This is attributed to incoherent Kondo scattering from the Ce ions in the vicinity of substituted atoms, which violate the coherence in the hybridization between the $4f$ states and Rh $4d$ states. The increase of $\rho(T)/\rho(290\ \mathrm{K})$ in the Ni doped samples is stronger than in the Ru doped ones. The recovery of Kondo impurity scattering in Ni doped samples is consistent with the recovery of trivalent Ce state, as indicated by the Currie-Weiss behavior in $\chi(T)$.

The temperature variations of S for all the alloys are compared in Fig. 2. For $x = 0$, $S(T)$ exhibits the maximum of 60 μV/K at 150 K and a shoulder at 30 K [5]. These structures resemble those for $CePd_3$ [1]. It is believed that the high-T maximum originates from the incoherent Kondo effect and the low-T shoulder from the development of the coherent ground state [5]. The most noteworthy in Fig.2 is the gradual suppression of the maximum with increasing x for all the substitutions. An exception, *i.e.*, a tiny increase of the maximum, is seen for $x = 0.05$ and M = Ru. The temperature of the maximum shifts to higher temperatures for M = Ni and Co, but it stays at 150 K for M = Ru. The shoulder at 30 K is also gradually suppressed with increasing x for all the substitutions.

In the hope of increasing $S(T)$ of the valence-fluctuating compound CeRhSn, we studied magnetic and transport properties of substituted samples. The Rh site in CeRhSn was substituted with Co, Ni and Ru up to 25%. With Ni substitution, we found the recovery of the Kondo impurity scattering. By contrast, Ru doping changed the intermediate-valent state more

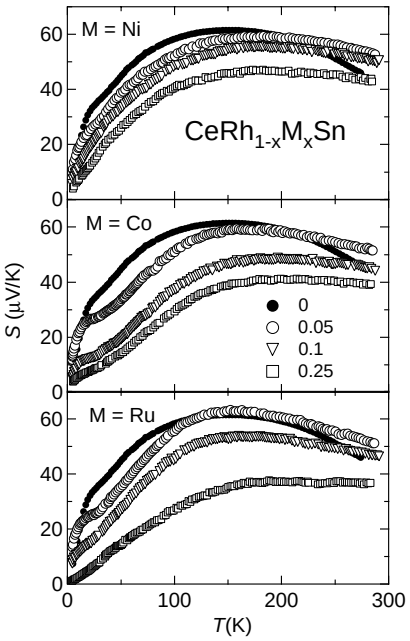

Fig. 2. Temperature dependence of thermopower of $CeRh_{1-x}M_xSn$ (M = Co, Ni, Ru) for $x \leq 0.25$.

or less to the tetravalent state. Nevertheless, all the substitutions resulted in decreasing the maximum of $S(T)$. This finding may imply that the coherence in the c-f hybridized band is necessary to maintain the large value of $S(T)$ in a given compound. This idea is supported by the fact that no enhancement of $S(T)$ for $CePd_3$ has been achieved by substitutions [6,7]. Pressure tuning of the hybridization would be more relevant to enhance $S(T)$ for a valence-fluctuating system.

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