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Low-temperature specific heat and resistance for the heavy-electron metals $CeCu_{6-x}M_x$ (M=Ni,Zn)

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The specific heat and resistance of $CeCu_{6-x}M_x$ (M=Ni,Zn) have been studied in the concentration range where they still retain the orthorhombic structure. The coefficient c of -ln$T$ term in resistance $R = R_0+bT$-$c\ln T$, as well as the γ, have been found to vary in opposite directions with increasing x for Ni and Zn substitutions. The physical mechanism is discussed.

Keywords: heavy fermion system, low-temperature specific heat, low-temperature resistance
PACC: 7127, 7128

1. Introduction

The heavy-electron metal (also known as heavy-fermion system) is an important member of the strongly correlated electron systems, following the discovery of the heavy-electron materials $CeAl_3$ and UBe_{13}.[1] So far, there have been ten heavy-fermion systems found with the Sommerfeld coefficient γ of the electron specific heat larger than 400mJ/mol·K^2, of which $CeCu_6$ has a γ value as high as 1600mJ/mol·K^2. It is known that γ is proportional to the electronic density of states at the Fermi surface and the effective mass m^* of an electron. The γ value of noble metals, for example Au, Ag, Cu, is about 1mJ/mol·K^2, so the effective mass of the electrons in heavy-electron metals is 2–3 orders of magnitude larger than that of the common metals. Most heavy-electron metals contain rare-earth Ce or actinide U atoms whose f-electrons are localized and thus they possess net magnetic moments. At low temperatures, the density of states increases rapidly due to the hybridization of the local f-electrons with conduction electrons, and the local moment is partly compensated due to the exchange interaction. $CeCu_6$ is nowadays considered to be a paramagnetic Fermi-liquid state at above 3mK.[2] When impurity concentration x is over the critical value x_c, $CeCu_{6-x}M_x$ (M= Ag, Au, Pd, Pt) will show a long-range antiferromagnetic order at low temperatures. The experimental results of the Löhneysen group have testified that the critical values x_c are 0.1, 0.09 and 0.05 for Au, Ag, and Pd respectively, under normal pressure without external magnetic filed.[3−13] They attributed the existence of critical value x_c to the "size effect". As some Cu atoms are replaced by larger atoms M (M=Ag, Au, Pd, Pt), the mean distance between two Ce atoms gradually increases, and therefore the exchange coupling constant J decreases.

But why is the critical value x_c for Pd smaller than that for Au, even though the radius of Pd atom is smaller than that of Au? It is contemplated that the metal Pd is a nearly ferromagnetic element with very large Stoner enhancement factor (about 10), and therefore Pd atom as an impurity would affect the magnetism of Ce atoms seated near Pd. In the case of Au, both Au and Cu are non-magnetic, and there is only "size effect" for Cu if replaced by Au. However, once Cu is replaced by Pd, both magnetic and size effect have contributions.

In order to clarify the magnetic effect of impurities on the low-temperature properties of $CeCu_6$, we introduce the magnetic Ni atom and non-magnetic Zn atom as impurities, which have nearly the same atomic radius as the Cu atom. Considering that

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Ni is a ferromagnetic metal, while Zn is nonmagnetic, $CeCu_{6-x}Ni_x$ and $CeCu_{6-x}Zn_x$ should have different behaviours. In this work, we study the temperature-dependence of specific heat and resistances for $CeCu_{6-x}M_x$ (M=Ni, Zn) systems for several concentrations x at low temperatures.

2. Experiment

Polycrystalline $CeCu_{6-x}Ni_x$ (x=0.0, 0.05, 0.1, 0.15, 0.2) samples were arc-melted under high-purity argon from appropriate amounts of ingots (Ce 3N,Cu 5N, Ni 5N). X-ray diffraction measurement shows that they are all single-phase materials.

$CeCu_{6-x}Zn_x$ (x=0.05, 0.1, 0.15, 0.2, 0.3) samples were quite difficult to prepare, owing to the very low boiling temperature of Zn. We prepared $CeCu_{6-x}$ by the arc-melting method first, and after being annealed at 850°C for 150h,the samples were ground into powder, and then thoroughly mixed with Zn powder (purity 99.5 percent). The mixed powder was sealed in a high vacuum quartz tube and annealed at 850°C for 150h, then melted at 950°C for 5h. X-ray diffraction showed the good single-phase orthorhombic p_{nma} structure of $CeCu_{6-x}Zn_x$ up to the concentration x_s=0.3. X-ray analysis showed that $CeCu_{6-x}Zn_x$ has nearly the same molar volume as that of $CeCu_6$.

The resistances of $CeCu_{6-x}M_x$ (M=Ni, Zn) were measured by the standard four-probe method, and the current was kept low enough to avoid self-heating of the samples. A dilution refrigerator was used to achieve temperature below 1.5K for the measurement of resistance versus temperature of $CeCu_{6-x}Ni_x$ (down to 100mK). The specific heat of $CeCu_{6-x}M_x$ (M=Ni, Zn) was measured using the adiabatic method in the range between 4.2 and 80K.

The resistances of $CeCu_{6-x}M_x$ (M=Ni, Zn) are plotted in Fig.1, in which the resistances mainly consist of three parts: Kondo scattering part, phonon scattering part and residual resistance, namely $R = R_0 + bT - c\ln T$[14] in the low-temperature range above T^*, which corresponds to the maximal resistance of $CeCu_{6-x}M_x$ (M=Ni, Zn). At low temperatures, the phonon scattering is negligible, while the Kondo scattering is the dominant factor. All the resistances of these samples change linearly against $-\ln T$ below 40 and 55K for $CeCu_{6-x}Ni_x$ and $CeCu_{6-x}Zn_x$ respectively (see inset of Fig.1). From Fig.1 (a), we observe that the resistances of the $CeCu_{6-x}Ni_x$ have a negative temperature coefficient up to 250K, the highest measured temperature, while from Fig.1 (b), we notice that the resistances of $CeCu_{6-x}Zn_x$ show a positive temperature coefficient in the temperature range above 150K, indicating that the phonon scattering is more important than Kondo scattering at higher temperatures. From the two insets of Fig.1, we can calculate the coefficient c for samples $CeCu_{6-x}M_x$ (M=Ni, Zn) with different x by the $R = R_0 + bT - c\ln T$, which shows the strength of the Kondo scattering (see Fig.2). From Fig.2, we can find that the coefficient c of $-\ln T$ increases in $CeCu_{6-x}Ni_x$ and decreases in $CeCu_{6-x}Zn_x$ with increasing x. This phenomenon shows that impurity Ni enhances the Kondo scattering, while the impurity Zn weakens it.

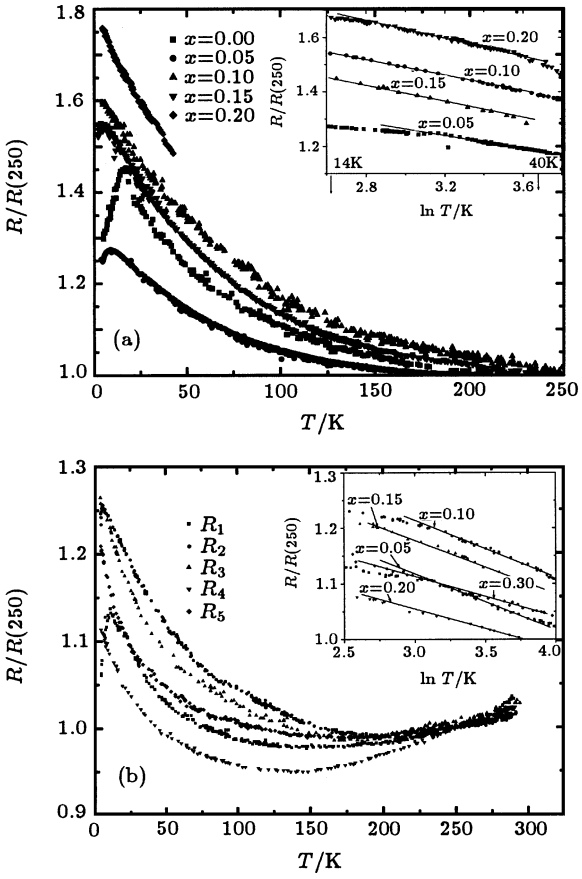


Fig.1. The temperature dependence of the renormalized resistances of the $CeCu_{6-x}M_x$ (M=Ni,Zn) plotted as $R/R(250)$ vs T, $R(250)$ being the resistance at temperature 250K; the inset shows the temperature dependence of resistance $R/R(250)$ in $\ln T$. (a) $CeCu_{6-x}Ni_x$ (x=0.0, 0.05, 0.1, 0.15, 0.2). (b) $CeCu_{6-x}Zn_x$ (x=0.05, 0.1, 0.15, 0.2, 0.3).

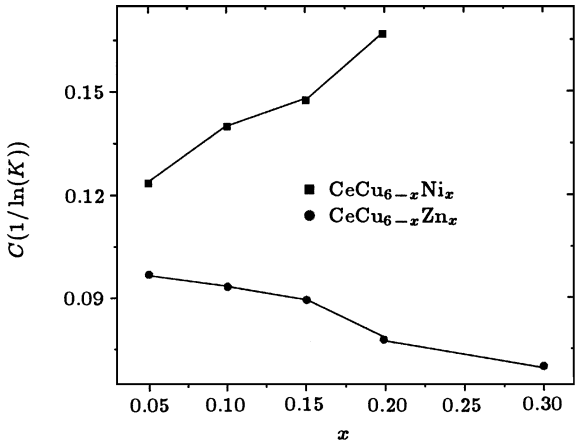


Fig.2. The coefficient c of -ln$T$ term for different x in $CeCu_{6-x}M_x$ (M=Ni, Zn) plotted as c vs x.

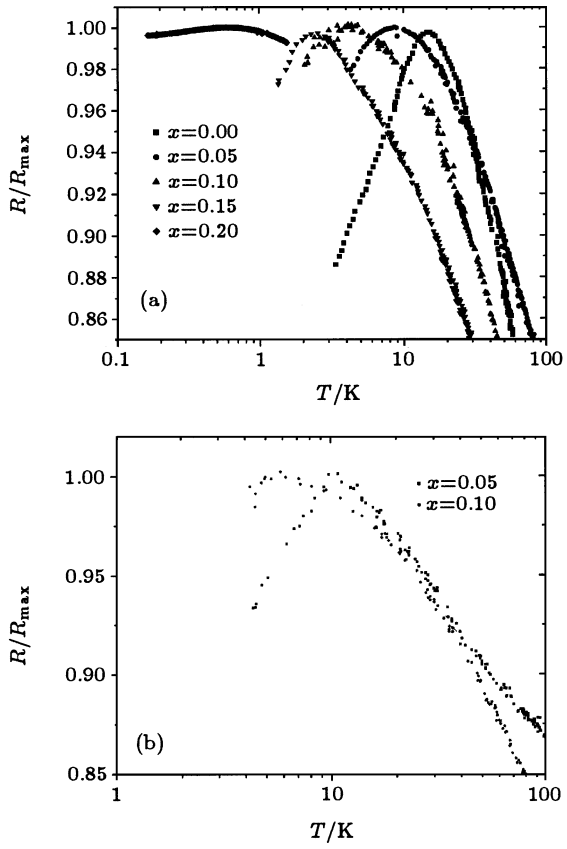


Fig.3. The temperature dependence of R/R_{max} around T^* for (a) $CeCu_{6-x}Ni_x$ (x=0.0, 0.05, 0.1, 0.15, 0.2), (b) $CeCu_{6-x}Zn_x$ (x=0.05, 0.1), where T^* corresponds to the peak of the resistance.

The results plotted in Fig.3 (a) show that there exists a peak temperature T^* corresponding to the maximal resistance in each R–T curve of the polycrystalline $CeCu_{6-x}Ni_x$ (x=0.0, 0.05, 0.1, 0.15, 0.2) and the temperature T^* decreases rapidly with the increase of Ni concentration x. The T^* of $CeCu_6$ is 14K, which is in agreement with the result in Ref.[10] Fig.3 (b) shows the R–T curves of the polycrystalline $CeCu_{6-x}Zn_x$ (x= 0.05, 0.1) near T^*.

All the observed T^* values have been plotted in Fig.4. We can see that T^* of $CeCu_{6-x}Ni_x$ is lower than that of $CeCu_{6-x}Zn_x$ when x is the same. In other words, the change of T^* with increasing x in Zn-doped samples is not so sensitive as that in Ni-doped samples. For a better comparison in Fig.4, we also plot the T^* values of Au-doped $CeCu_{6-x}Au_x$ samples cited from Ref.[10].

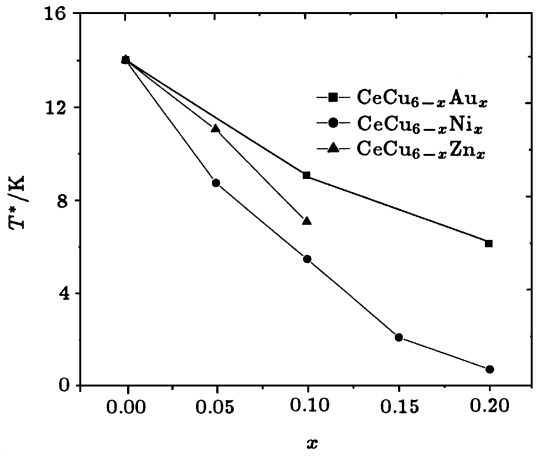


Fig.4. T^* for $CeCu_{6-x}M_x$ (M=Au, Ni, Zn).

The temperature dependences of specific heat C_p are plotted in Figs.5(a) and (b) as C_p/T vs T^2. The measurement accuracy is better than 2 percent in the measured temperature range. Figures 5 (a) and (b) show that the electron specific heat coefficient γ increases rapidly below 8K. The temperature of the minimal C_p/T value, T_{min}, is about 8K for both $CeCu_{6-x}Ni_x$ and $CeCu_{6-x}Zn_x$ samples. The minimal C_p/T values of $CeCu_{6-x}Ni_x$ become slightly smaller with increasing x, while those of $CeCu_{6-x}Zn_x$ are not affected by impurity concentration x as much as that of $CeCu_{6-x}Ni_x$.

From Figs.5 (a) and (b), we can clearly find that the Sommerfeld coefficient γ=C_v/T at 4.5K has a tendency to decrease with increasing x in $CeCu_{6-x}Ni_x$, and a tendency to increase with increasing x in $CeCu_{6-x}Zn_x$.

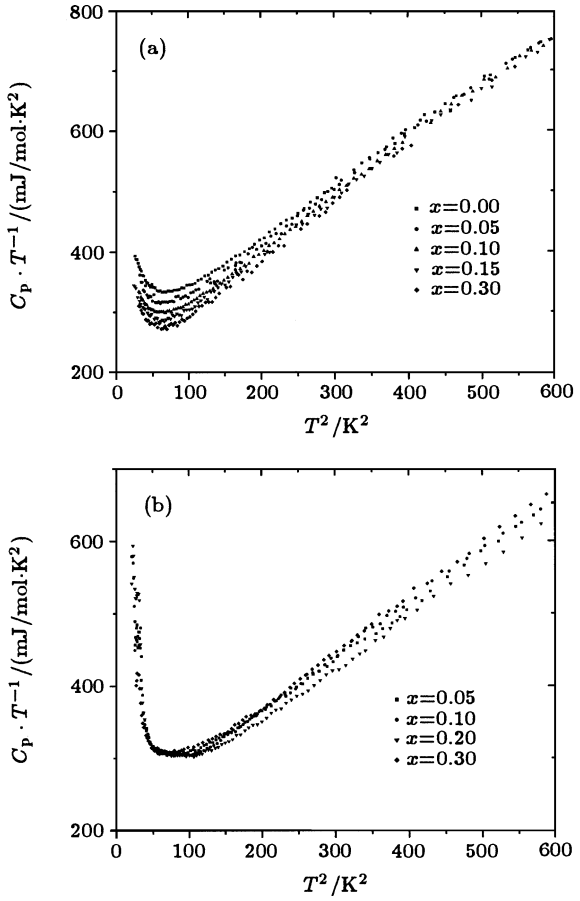


Fig.5. C_p/T versus T^2 curves at low temperatures for (a) $CeCu_{6-x}Ni_x$ with x=0.0, 0.05, 0.1, 0.15, 0.2. (b) $CeCu_{6-x}Zn_x$ with x=0.05, 0.1, 0.2, 0.3.

3. Discussion

The existence of long-range antiferromagnetic order ground state has been clearly observed in the archetypal heavy-electron system $CeCu_6$ by substituting some Cu with Au, Ag or Pd; the Néel temperature T_N decrease with decreasing x for $x > x_c$ (x_c, the critical concentration) and the magnetic order is suppressed. In these cases, the Néel temperature T_N tends to zero, and non-Fermi-liquid (NFL) behaviour can be observed.[4,13,15] As observed in the insets in Figs.1 (a) and (b), there exists a temperature range above T^* where the resistances of all $CeCu_{6-x}M_x$ (M=Ni, Zn) samples vary in the $-\ln T$ law. This phenomenon shows that the moments of the Ce-ions are available for Kondo scattering and contribute to the resistances. The correlation between f-electrons of neighbouring Ce ions is very weak in this temperature range. In heavy-electron systems, the competition between on-site Kondo interaction and inter-site RKKY (Ruderman, Kittel, Kasuya and Yosida) interaction allows of various ground states in different samples. In the Doniach model, this competition is governed by a very important parameter, the effective exchange interaction J between conduction electrons and local f-electrons (which is responsible for local magnetic moments).[16] The characteristic energy scales $k_B T_K \propto \exp(-1/N(E_F)J)$ and $k_B T_{RKKY} \propto J^2 N(E_F)$ are for Kondo interaction and RKKY interaction respectively. Here $N(E_F)$ is the electron density of states at the Fermi level. Numerous examples can be found in the literature where this important concept has worked quite well on a qualitative level. The strength of the exchange interaction J is usually tuned by composition, pressure or magnetic field etc. Actually, impurities change the local environments of some Ce ions near impurities, according to the formula of $T_K^i \approx E_0(J_i\rho_F)^{1/2}\exp(-1/J_i\rho_F)$ by Bhatt,[17] where E_0 is of the order of the bandwidth, and ρ_F is the density of states at the Fermi level; it is noticed that J_i and ρ_F are local values at the i site. Therefore, those Ce ions near impurities have different T_K from that of most other Ce ions. That means that there exists a distribution of T_K in the doped samples. In most works reported, T_K denoted an average value for the whole sample. When Cu is replaced by different elements, for example Au, Ni or Zn, the local environments of Ce-ions are not quite consistent with one another, and thus the local magnetic moments and T_K of Ce-ions near impurities will be changed. In this way, the contributions to the resistances from the little portion of Ce-ions with lower Kondo temperature T_K, in some cases, can extend to much lower temperatures.

From the comparison of the curves c versus x for different x in $CeCu_{6-x}M_x$ (M=Ni, Zn) plotted in Fig.2, we find that the coefficient c gradually increases in Ni-doped samples and decreases in Zn-doped samples with increasing x. The Kondo scattering is caused by magnetic scattering centres (i.e. Ce ion in this work), hence qualitatively it can be said that the larger the magnetic moment of Ce ion, the stronger the Kondo scattering for the conduction electrons. According to the experimental results, we suppose that doping with Ni will increase the local moments of those Ce ions near the atom Ni, and then strengthen the Kondo scattering of the conduction electrons; while in the Zn-doped samples, the coefficient c decreases with increasing x, indicating that when some Cu atoms are replaced by Zn, every Zn atom provides one more conduction electron than the Cu atom; in the principle of electric neutrality, the

conduction electron number for screening the positive charge near every Zn^{+2} is greater than that of every Cu^{+1} nearby, which may slightly weaken the magnetic moments of those Ce ions near the Zn atom and decreases the Kondo scattering.

The resistance–temperature curves show a maximum for $CeCu_{6-x}Ni_x$ (x=0.0, 0.05, 0.1, 0.15, 0.2) and $CeCu_{6-x}Zn_x$ (x=0.05, 0.1) at the temperature T^* (see Figs.3 (a) and (b)). The appearance of resistance maximum comes from the competition between Kondo scattering and the coherent effect: as the temperature of the sample becomes lower, the Kondo scattering causes resistance to increase, while the coherent scattering of conduction electrons by Ce ion sub-lattice causes resistance to decrease. The T^* of different samples are dependent on x, as shown in Fig 4.

While T^* is often understood as the onset temperature of the coherent scattering in the literature, the phenomenon of the decrease of T^* with increasing x mainly depends on two factors: the weakening of the coherent effect and the decreases of the Kondo temperature T_K. As observed for $CeCu_{6-x}M_x$ (M=Ni, Zn) in Figs.3 and 4, the effects on T^* for Ni- and Zn-doped samples are much stronger than those by the same concentration of Au. When part of Cu is replaced by Au, due to the increase of the distance of Ce–Ce ions near Au, namely "size effect", the magnetic moments become stronger and make T_K decrease; meanwhile, due to the element substitution, the periodicity of the Ce ion-sublattice is slightly destroyed to some extent depending on x; in this way, the coherent scattering is weakened at low temperatures. When replaced by Ni, considering the fact that the radius of Ni is nearly the same as that of Cu, the "size effect" is not significant, we suppose that the lowering of T^* is mainly caused by the increase of Kondo scattering by those Ce ions near Ni sites, which is stronger than that of Au-doped situation.

From Fig 4, we find that the effect of Zn substitution on T^* is also stronger than that of Au substitution, but weaker than that of Ni substitution. The physical mechanism for this phenomenon is not clear yet. Obviously, the "size effect" is not important here, and non-magnetic Zn ions seems not to induce bigger magnetic moments of Ce ions next to Zn sites. It is probably due to the impurity Zn that makes the coherent scattering much weaker than pure $CeCu_6$.

As the temperature is lowered close to the Kondo temperature T_K, the process that compensates the f-electron local magnetic moments is accompanied by the hybridization between f-electron and conduction electrons. It is the hybridization that increases the electron effective mass and is directly reflected by the low-temperature electron specific heat. The C/T vs T^2 plots(see Fig.5) show a rapid increase in γ-coefficient of the electron specific heat at temperatures below T_{min}, corresponding to the rapid increase of effective mass of electrons in each sample. We could imagine that only a few percent of Cu are replaced by impurities, which do not affect the T_K for most of the Ce ions, that is why the average electron effective mass is roughly the same for all samples, and T_{min} is almost not affected by impurities. But, if one looks at Figs.5(a) and (b) closely, it can be found that the T_{min} of C/T curves for Zn-substituted samples are slightly higher than those of Ni substitution. We suggest that the magnetic moments of Ce ions next to the Zn sites have already been partly screened and consequently result in a higher T_K.

From the comparison between the values of Sommerfeld coefficients γ of the electron specific heat for $CeCu_{6-x}Ni_x$ and $CeCu_{6-x}Zn_x$ (Fig.5), we find that, at 4.5K, with increasing x, the values $\gamma=C_v/T$ for Ni-doped sample increase and those for Zn-doped sample decrease. These phenomena show that the hybridization for the Zn-doped sample is stronger than that of the Ni-doped one. At 5K, the anomalies of specific heat for Zn- and Ni-doped samples are still an open problem for us.

4. Conclusion

From the measurements of low-temperature resistances and specific heats of $CeCu_{6-x}M_x$ (M=Ni, Zn), we can conclude that, with increasing concentration x of impurities, the T^* decreases rapidly and the linear term coefficient γ of the electron specific heat at low temperatures has nearly the same behaviour for Ni- and Zn-doped $CeCu_6$.

The resistance can be described as $R = R_0 + bT - c\ln T$ for every measured sample, including residual resistance, phonon scattering term and Kondo scattering term. At low temperatures, with increasing x, the coefficient c of the Kondo scattering term increases for $CeCu_{6-x}Ni_x$ and slightly decreases for $CeCu_{6-x}Zn_x$; it is reasonable to interpret this phenomenon as due to the magnetism of Ce near the impurities having opposite turning due to their different change of local environment. By comparing the case of $CeCu_{6-x}M_x$ (M=Ni, Zn) with that of $CeCu_{6-x}Au_x$, when some Cu atoms are replaced by Ni or Zn, due to the radius

of Ni or Zn being nearly the same as the radius of Cu, the "size effect" can be neglected. This is contrast to the case of Au substitution, in which "size effect" is dominant. The impurity Ni leads to the increase of the moments of Ce-ions near an Ni atom, while impurity Zn contributes one more conduction electron when it replaces Cu, which may weaken the moments of Ce-ions nearby.

Because the maximum substitution of Cu in the $CeCu_{6-x}M_x$ (M=Ni, Zn) is only about 3.3 percent, the hybridization of most Ce-ions by conduction-electron is not affected, and the low-temperature electron specific heat coefficient γ is, as a whole, not sensitive to the impurity concentration x.

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