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The effect of La substitution and magnetic field on non-Fermi-liquid behaviour in $CeRu_4Sb_{12}$

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Abstract

$CeRu_4Sb_{12}$ with the filled skutterudite structure exhibits a novel non-Fermi-liquid (NFL) behaviour in the low-temperature specific heat and electrical resistivity at ambient pressure. We investigated the effect of La substitution and magnetic field on the NFL state and found that it can be easily destroyed either by the application of a magnetic field or by a small degree of La substitution. In magnetic fields, C/T becomes strongly depressed and nearly constant below 1 K and $\rho(T)$ turns to following a T^2-law, implying that the Fermi-liquid state recovers in high magnetic fields. The type of critical fluctuation is discussed on the basis of the results of magnetic susceptibility, electrical resistivity and specific heat measurements.

1. Introduction

The filled skutterudite compounds with a general formula RT_4X_{12} (R = alkaline earth, rare earth, Th and U; T = Fe, Ru and Os; X = P, As and Sb) crystallize in the body-centred cubic structure of space group $Im\bar{3}$ (No 204). In this structure, the lanthanide atoms fill the voids of the $CoAs_3$ (skutterudite) structure which consists of distorted octahedra of pnictogen atoms centred on a transition metal atom [1–3]. These compounds exhibit various interesting physical properties at low temperatures, such as superconductivity, magnetic order, semiconducting behaviour and metal–insulator transition [4–6]. Furthermore, these compounds have attracted much attention as new thermoelectric materials for applications [7, 8]. We previously reported the superconductivity for R = La and Pr, and magnetic order for R = Nd and Eu in RRu_4Sb_{12} [9]. In this series of compounds, $CeRu_4Sb_{12}$, which is a metallic intermediate-valence compound with a Kondo temperature (T_K) of about 100 K, shows particularly interesting properties, exhibiting a non-Fermi-liquid (NFL) behaviour similar to quantum critical phenomena near the magnetic–nonmagnetic transition [9–11]. The specific heat is fairly well represented by either $C/T = \gamma + \alpha \ln(T) + A/T^3$ or $C/T = \gamma + \beta T^{1/2} + A/T^3$, where A/T^3 is interpreted as the nuclear contribution of ^{121}Sb and ^{123}Sb, and the electrical resistivity by $\rho(T) \propto T^n$, where $n = 1.6$–1.7 [10]. From the theoretical point of view, the temperature dependence of the above quantities depends on the type of critical fluctuation, i.e. $C/T \propto -\ln(T)$ and $\rho \propto T^{5/3}$ for ferromagnetic fluctuations or $C/T \propto -T^{1/2}$ and

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$\rho \propto T^{3/2}$ for antiferromagnetic ones [12]. It has to be clarified which type of critical fluctuation is dominant for the NFL behaviour. In this paper, we present the effects of La substitution and of magnetic field on the NFL behaviour and discuss the types of critical fluctuation occurring in $CeRu_4Sb_{12}$.

2. Experimental procedure

The samples were prepared by the Sb-flux method with an excess of Sb (1:4:20). The mixture of constituents was sealed in an evacuated quartz tube, kept at 950 °C for five hours, cooled at a rate of 3 °C h^{-1} down to 650 °C, and then cooled in a furnace. Excess Sb was eliminated using aqua regia. The x-ray diffraction examination reveals a small peak of $RuSb_2$. The lattice constant is determined to be 9.273 Å which is slightly larger than the reported value of 9.2657 Å [3]. The magnetic susceptibility $\chi(T)$ was measured with a commercial Quantum Design SQUID magnetometer (MPMS) in a field of 5 kOe between 2 K and 400 K. The electrical resistivity was measured by a conventional dc four-probe method. The specific heat was measured by a semi-adiabatic heat-pulse method in a commercial dilution refrigerator (S.H.E.).

3. Results and discussion

The temperature dependence of the normalized magnetic susceptibility of $Ce_{1-x}La_xRu_4Sb_{12}$ ($x = 0.0$, 0.02, 0.05 and 0.1) is shown in figure 1. $\chi(T)$ above 150 K for all values of x obeys a Curie–Weiss law and passes through a broad maximum around 100 K, characteristic of intermediate-valence (IV) compounds; this is followed by an upturn below 20 K. We measured the ac magnetic susceptibility for $x = 0.0$ and 0.02 down to about 30 mK and found neither a magnetic nor a superconducting phase transition. $\chi(T)$ above 60 K scales well with the Ce concentration and the peak position around 100 K does not shift upon La substitution. This fact implies that the local Kondo temperature of about 100 K does not change with the La substitution and the 4f electrons are well localized at high temperatures. On the other hand, the low-temperature susceptibility does not scale with the Ce concentration and the La substitution strongly depresses the low-temperature upturn as can be seen in the inset. This systematic depression may be intrinsic and reflect the suppression of NFL behaviour, as described below.

The temperature dependence of the electrical resistivity normalized at 300 K is displayed in figure 2(a). The $\rho(T)$ for all samples are qualitatively similar above 20 K, and decrease very slowly down to 80 K and then show a steep decrease. The temperature where $\rho(T)$ decreases steeply shifts slightly toward lower temperatures with the La substitution as observed in different Kondo materials. $\rho(T)$ is reminiscent of that for Kondo compounds rather than that for IV compounds, which usually shows a monotonic temperature dependence. In $CeRu_4Sb_{12}$, a large distance between nearest-neighbour Ce ions, of 9.27 Å, may stabilize the localized 4f state albeit with a high T_K. This may also result in the scaling law for $\chi(T)$ mentioned above. $\rho(T)$ for $x = 0.1$ below 20 K is nearly constant and shows a shallow minimum. For $x = 0.0$, 0.02 and 0.05, however, $\rho(T)$ exhibits anomalous decrease below 8 K. The temperature where $\rho(T)$ starts to decrease shifts to lower temperatures as x increases. The temperature dependence of $\rho(T)$ for $x = 0.0$ and 0.02 below about 5 K (as shown by arrows in figure 2(b)) is well represented by a relation $\rho(0) + aT^{1.65\pm0.02}$. The value of 1.65 is very close to the value 5/3 for the SCR theory at a quantum critical point for ferromagnetic critical fluctuations but differs from the value 3/2 for antiferromagnetic ones [12].

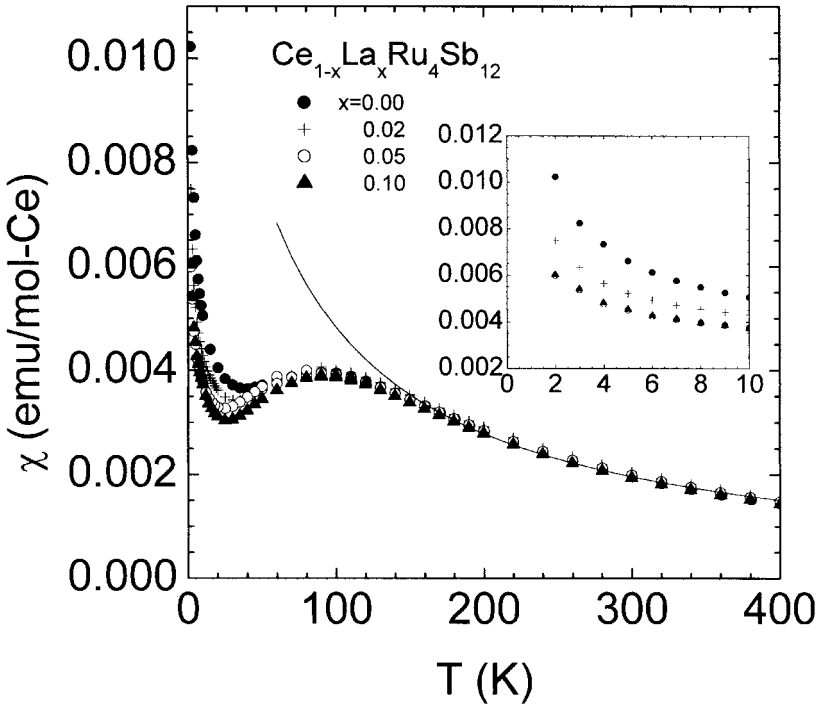

Figure 1. The magnetic susceptibility normalized by the Ce concentration. The solid line shows a Curie–Weiss fit with $\mu_{\rm eff} = 2.3\ \mu_{\rm B}$ and a Weiss temperature of -36 K. The inset shows the low-temperature part. χ is systematically depressed by La substitution.

Figure 3 displays C/T for $Ce_{1-x}La_xRu_4Sb_{12}$ for $x = 0.0$, 0.02, 0.05 and 0.10. The phonon part of $LaRu_4Sb_{12}$ has already been subtracted from these data [9]. C/T is strongly depressed by the La substitution. Although C/T for all values of x increases with decreasing temperature, only the data for $x = 0.1$ are approximately described by $C/T = \gamma + A/T^3$, where γ is the nearly temperature-independent linear specific heat coefficient and the second term is interpreted as a nuclear contribution. $Ce_{0.9}La_{0.1}Ru_4Sb_{12}$ does not show any NFL behaviour in the resistivity and hence is expected to show a normal temperature dependence of C/T. Our interest is in deducing the electronic part of C/T and we first analyse it for $x = 0.10$ to estimate the nuclear contribution. We have measured C/T for $x = 0.10$ under magnetic fields. The data for all magnetic fields were analysed using the formula $C/T = \gamma + A/T^3$ below 0.4 K and the field dependence of γ and A determined is shown in figure 4. The γ-value at zero field is determined to be about 52 mJ mol^{-1} K^{-2}, which is 40% larger than the value of 37 mJ mol^{-1} K^{-2} for $LaRu_4Sb_{12}$, and decreases about 40% at 40 kOe. It is worth noting that the reduction of 40% at 40 kOe is very large, which is in contrast with the usual case for IV compounds and rather comparable to that for typical Kondo-lattice compounds such as $CeCu_6$ [13]. This fact may reflect that the system is close to a magnetic instability and the magnetic field tends to suppress the critical fluctuations. On the other hand, A is nearly independent of magnetic field. The nuclear specific heat consists of the contributions due to dipole moments interacting with the effective magnetic hyperfine field and quadrupole moments interacting with the electric field gradient. Because the specific heat of a dipole moment is proportional to H^2, the present experimental result, which is independent of the magnetic field, is ascribed to the nuclear quadrupole contribution. The nuclei which

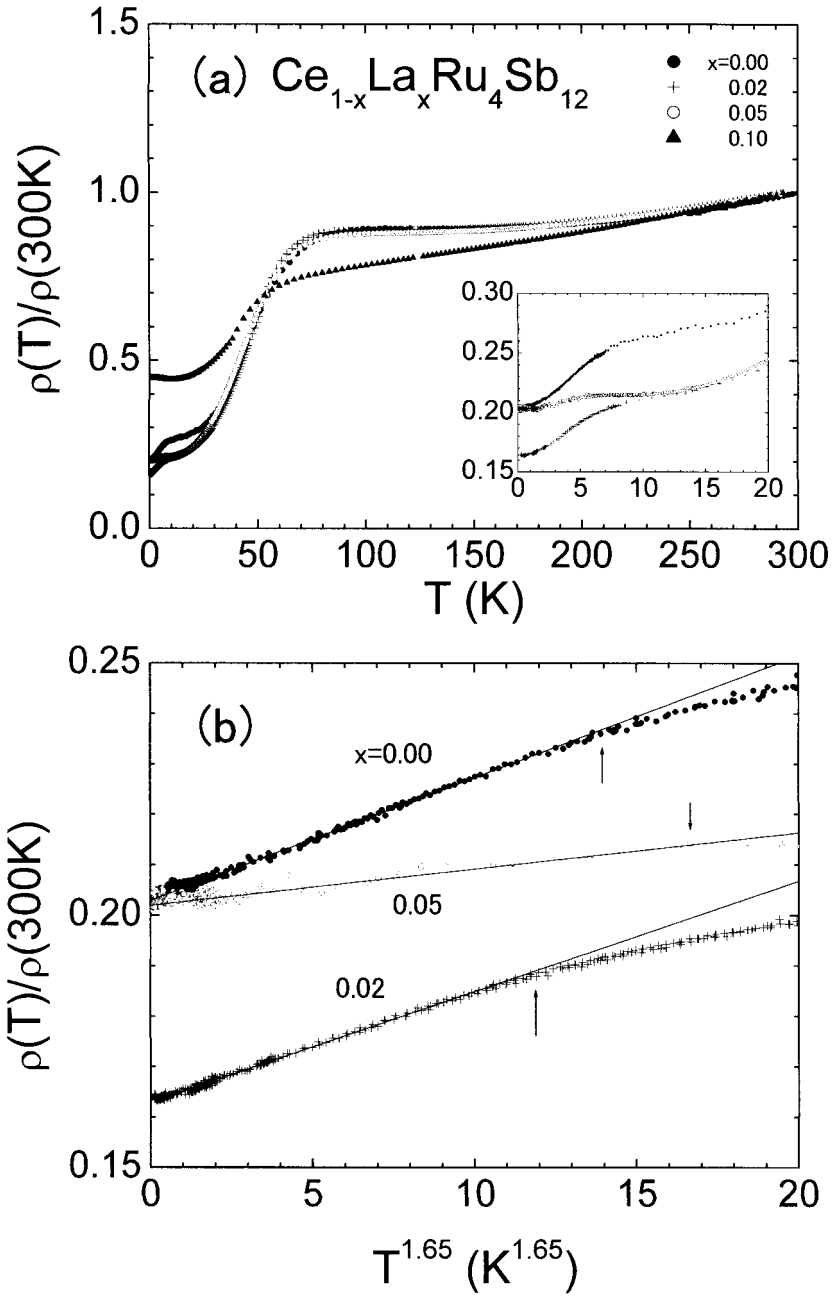

Figure 2. (a) The electrical resistivity normalized at 300 K for $x = 0.0$, 0.02, 0.05 and 0.10. The inset shows the anomalous decrease at low temperatures. (b) A $\rho(T)/\rho(300\ \mathrm{K})$–$T^{1.65}$ plot indicating a linear relation below about 5 K.

have a quadrupole moment are ^{121}Sb, ^{123}Sb and ^{139}La, but ^{139}La occupies a site with cubic symmetry and the electric field gradient vanishes. Therefore we conclude that the resultant contribution is due to the quadrupolar moments of ^{121}Sb and ^{123}Sb. In the following analysis,

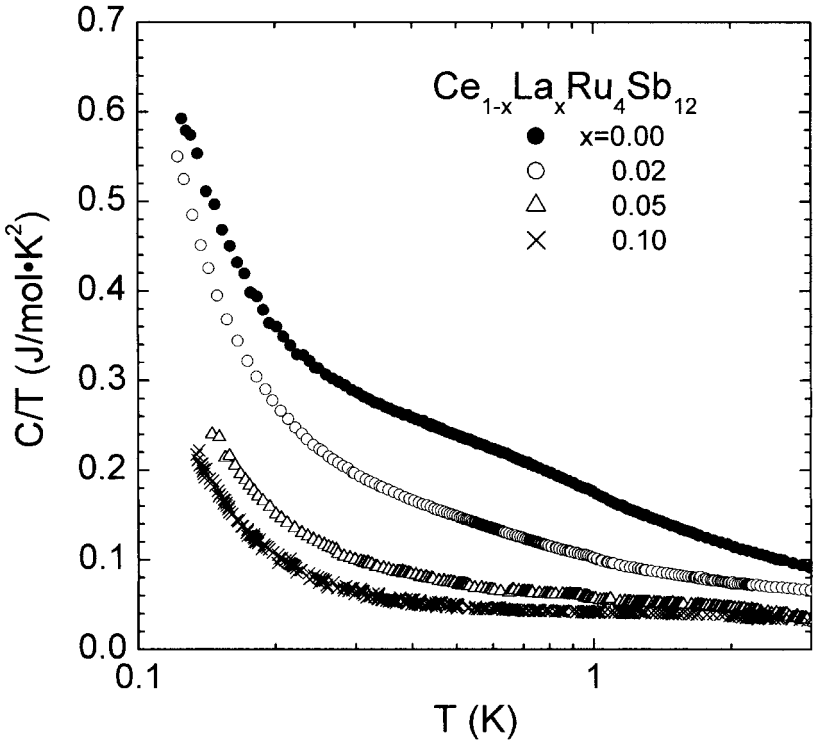

Figure 3. The temperature dependence of C/T. The phonon part of $LaRu_4Sb_{12}$ has already been subtracted.

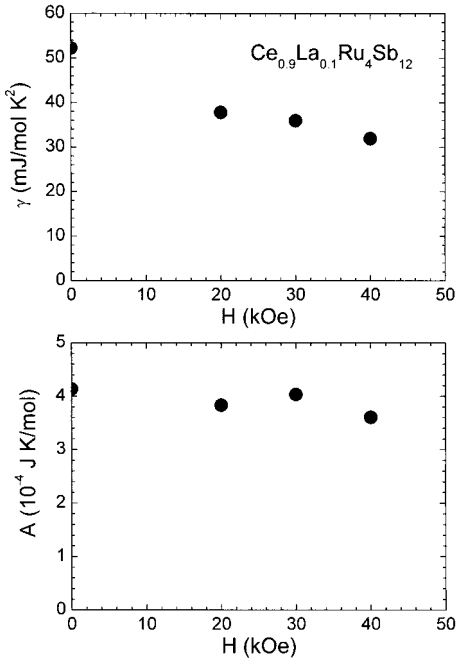

Figure 4. The magnetic field dependence of (a) γ and (b) A for $Ce_{0.9}La_{0.1}Ru_4Sb_{12}$.

$A = 4.1 \times 10^{-4}$ J K mol^{-1}, independent of the magnetic field, is assumed for all values of x, but this assumption may not always be correct because A would be affected by the electronic state.

Figure 5 displays $C_e/T = (C - C_{nuclear})/T$, the electronic part of the specific heat. There is a slight upturn below 0.2 K for $x = 0.0$ and 0.02 even after subtraction of the nuclear part. It is not known at present whether this upturn is intrinsic or due to an improper correction of the nuclear contribution, but one has to bear in mind that in the NFL system $U_{0.2}Y_{0.8}Pd_3$ there is a large excess C/T proportional to T^{-3}, which is not a nuclear contribution but of unknown origin [14]. As clearly seen, C_e/T is strongly depressed by the La substitution. These results indicate that a substitution of only a few per cent destroys the NFL behaviour of C_e/T and the Fermi-liquid state is already recovered at $x = 0.10$. This fact strongly suggests that the coherence of the Ce sublattice plays a crucial role in the NFL behaviour of $CeRu_4Sb_{12}$. Recently, an increasing number of studies on NFL behaviour have been reported. Most of them were performed near the magnetic–nonmagnetic instability region by controlling composition or applying high pressure, i.e. by changing J, the constant of coupling between local moments and conduction electrons. The magnetic–nonmagnetic transition in many f-electron systems results from quenching of local moments by the Kondo effect. Therefore it

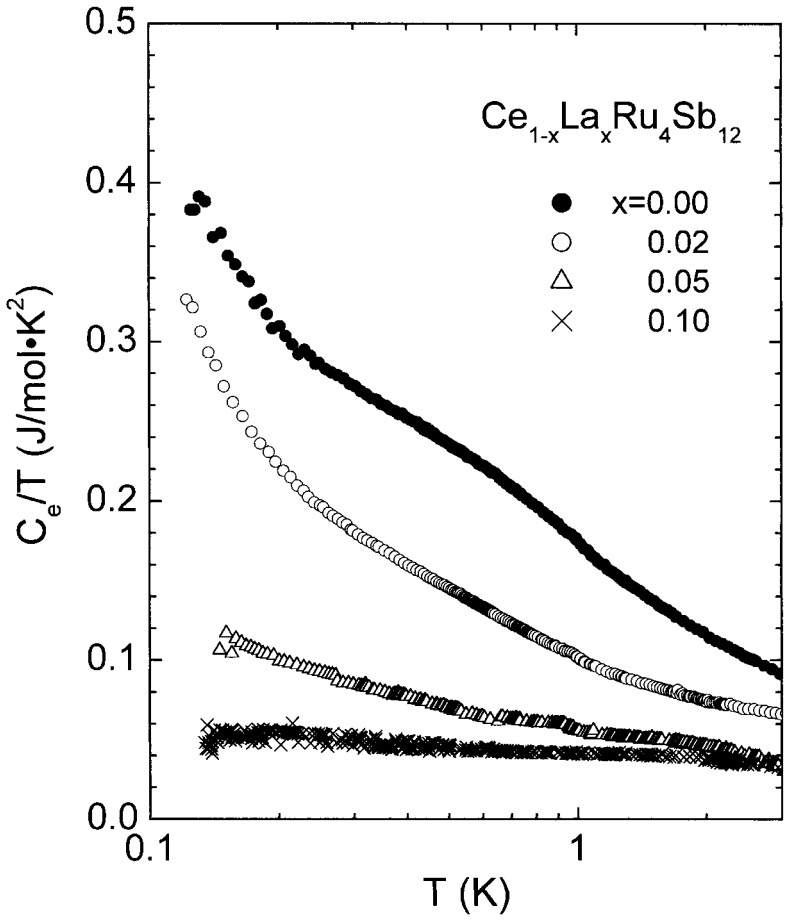

Figure 5. The electronic part of C/T.

would be difficult to envisage such an ordinary magnetic instability in intermediate-valence compounds with a stable nonmagnetic ground state, which is usually described by the band theory at low temperatures [15]. On the other hand, magnetic–nonmagnetic transitions are also observed in itinerant-d-electron metals such as MnSi [16]. Hence it is conjectured that the NFL behaviour of $CeRu_4Sb_{12}$ results from a magnetic instability similar to the one found in itinerant-d-electron systems.

Figure 6 shows C_e/T for $x = 0.0$ under magnetic fields up to 40 kOe. In contrast to the case for $x = 0.10$, C_e/T is strongly depressed below 1 K by the magnetic field. For $H \geqslant 30$ kOe, C_e/T becomes nearly constant except for the upturn below 0.3 K, implying that the Fermi-liquid behaviour is recovered in large magnetic fields. The similar field dependence and recovery of the Fermi-liquid state are also observed at the magnetic instability point in $CeCu_{0.9}Au_{0.1}$ [17].

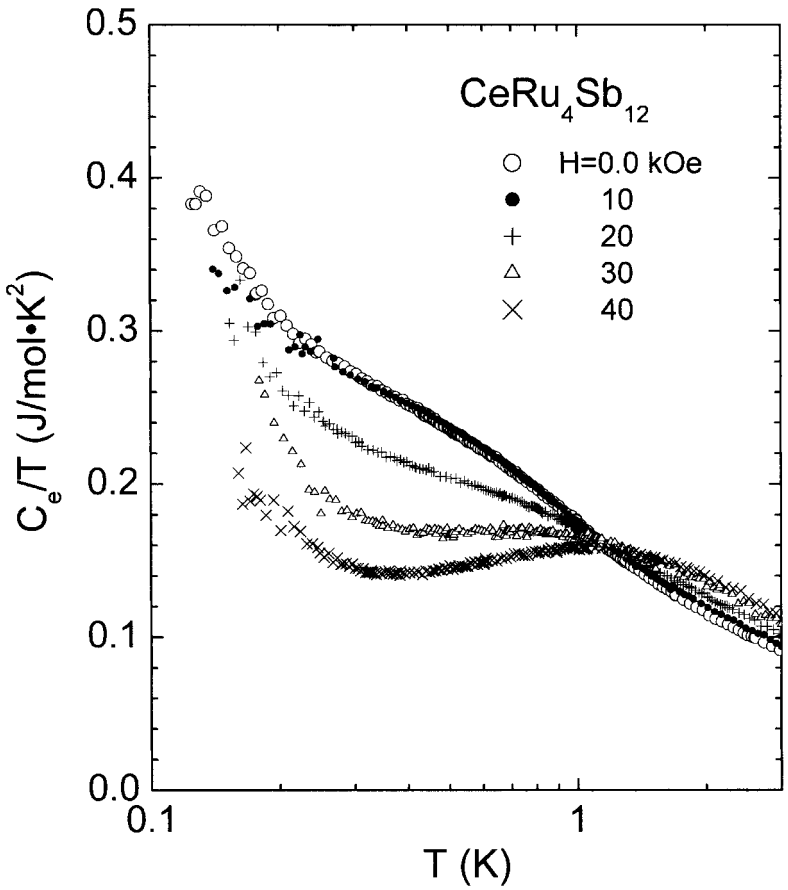

Figure 6. The magnetic field dependence of C_e/T for $CeRu_4Sb_{12}$.

As described in the introduction, the temperature dependence of C_e/T for $x = 0.0$ at zero field can be well analysed using either $C/T = \gamma - \alpha \ln T + \delta/T^3$ ($T < 0.7$ K) or $C/T = \gamma - \beta\sqrt{T} + \delta/T^3$ ($T < 1.3$ K). The term proportional to $\sqrt{T}$ gives a very slight curvature with a negative $d^2(C_e/T)/dT^2$ above 0.7 K, which can be seen only for $x = 0.0$, and this shifts smoothly to higher temperatures and turns into a broad peak with increasing magnetic fields (see figure 6). On the other hand, the data for $x = 0.02$ and 0.05 do not exhibit

such a structure at zero field. Figure 7 shows the magnetic field dependence of C_e/T for $x = 0.02$. It should be noted that a structure appears around 0.4 K at $H = 10$ kOe, which is quite similar to the case for $x = 0.0$ at zero field. This structure shifts to higher temperatures and changes to a broad peak with increasing magnetic fields, similarly to the $x = 0.0$ data. This finding suggests that the small curvature above 0.7 K is due to an evolution of some internal field as the magnetic instability is approached. C_e/T proportional to $\ln(T)$ is consistent with ferromagnetic instability [12]. $\chi(T)$ at low temperatures is also consistent with a ferromagnetic case, i.e. the upturn below 20 K is enhanced by increasing the Ce concentration.

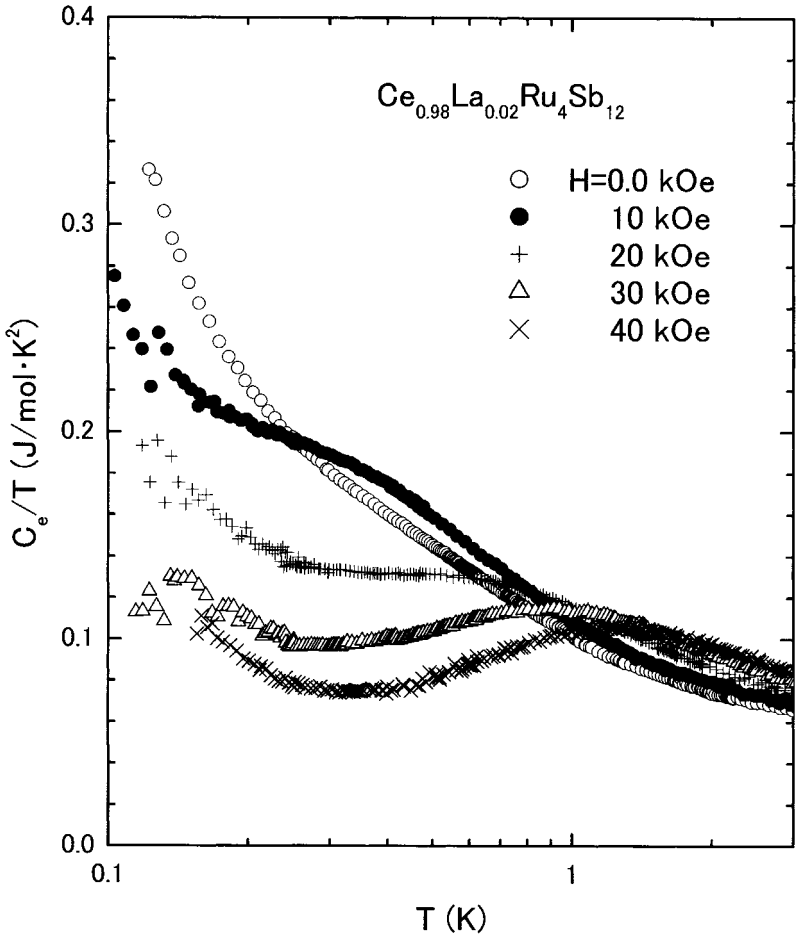

Figure 7. The magnetic field dependence of C_e/T for $x = 0.02$.

In order to confirm the Fermi-liquid behaviour, we measured the electrical resistivity for $x = 0.0$ under magnetic fields and the result is shown in figures 8(a) and 8(b). The $T^{1.65}$-dependence at $H = 0.0$ kOe, which is well demonstrated for a wide T-range below about 5 K in figure 2, changes in magnetic fields to a T-dependence between 1 and 6 K and a T^2-dependence below 1 K[1]. This result suggests that the NFL behaviour is destroyed and the Fermi-liquid behaviour is recovered by application of the magnetic field.

[1] Unfortunately we cannot discuss the precise T-dependence of the zero-field data below 1 K, because of the scatter of the data points.

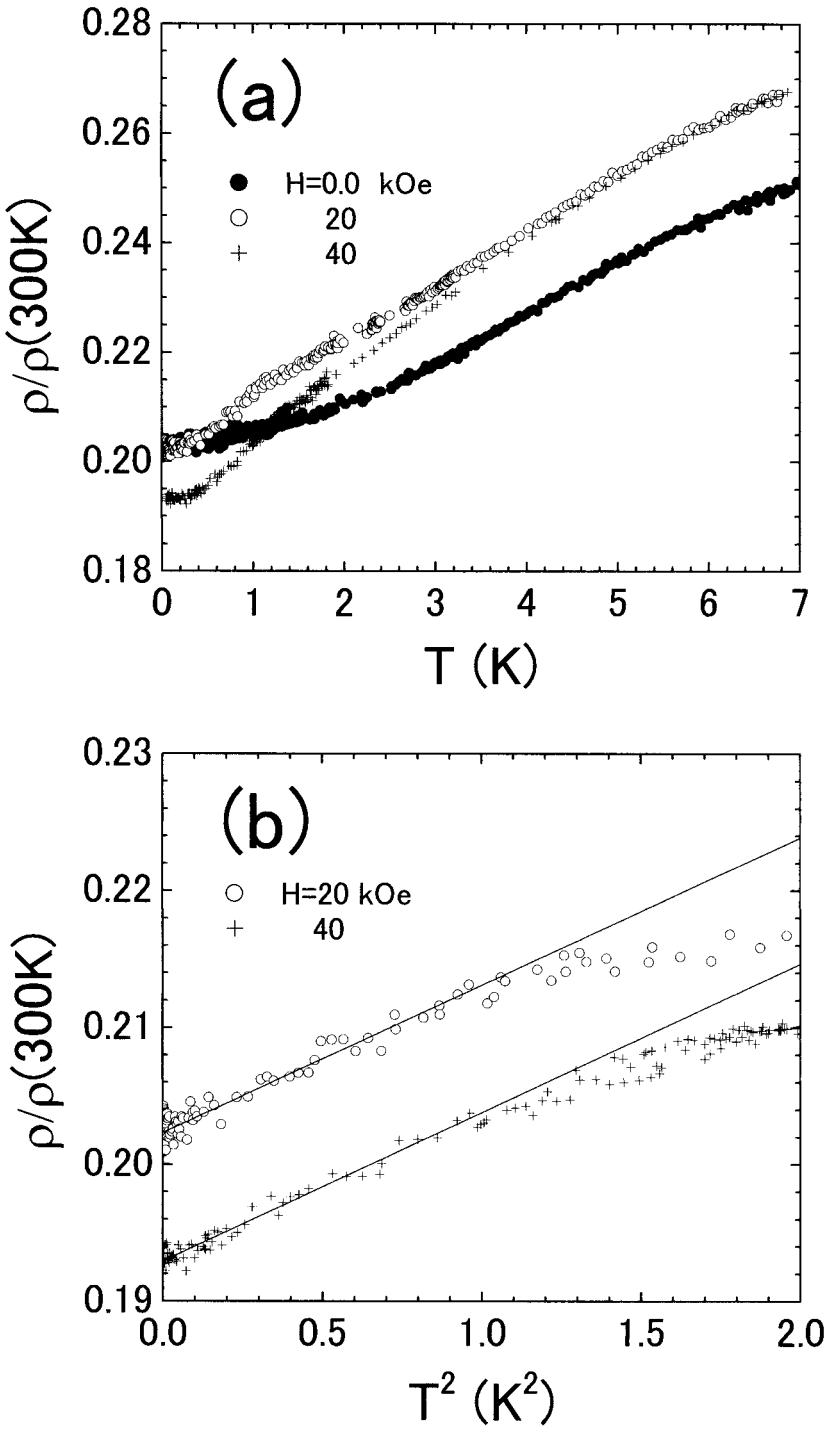

Figure 8. (a) The temperature dependence of $\rho(T)/\rho(300\ \mathrm{K})$ under a magnetic field for $CeRu_4Sb_{12}$. (b) A $\rho(T)/\rho(300\ \mathrm{K})$–$T^2$ plot at low temperatures indicating a linear relation.

4. Summary

We have investigated the effect of La substitution and the magnetic field on the NFL behaviour in $CeRu_4Sb_{12}$. The results obtained by La substitution clearly show that NFL behaviour is easily destroyed by impairing the coherency of the Ce sublattice. It was also revealed that the NFL behaviour is strongly depressed and the Fermi-liquid behaviour is recovered by application of a magnetic field as for other NFL materials near a magnetic instability. The present experimental results on magnetic susceptibility, electrical resistivity and specific heat consistently revealed that the system approaches a ferromagnetic instability as x decreases.

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