Thermal Expansion in a diluted Ce system La$_{1-x}$Ce$_x$Cu$_6$

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Abstract. The thermal expansion of a diluted Ce system La$_{1-x}$Ce$_x$Cu$_6$ for (0 ≤ x ≤ 1) has been measured between 10 and 150 K to reveal the change from the coherent heavy Fermion state (0.9 ≤ x ≤ 1) to the incoherent Kondo state (0 ≤ x ≤ 0.73). The large Ce concentration x dependence of the linear thermal expansion coefficient along b-axis α$_b$(T) suggests that the coupling between the 4f$^1$ electron and the lattice strain is the largest along the b-axis in the three crystallographic axes. The maximum of the magnetic contribution to the volume thermal expansion coefficient β$_m$(T) at T = 50 K is retained in the x range of 0.6 ≤ x ≤ 1, suggesting the crystalline electric field (CEF) level for x = 1 doesn’t change by the substitution. Furthermore, the upturn in β$_m$(T) below 25 K, which should be a precursor of the maximum at T = 2.5 K reported for x = 1, is retained when we decrease x from 1 to 0.6. Because the ground state for x = 0.6 is the incoherent Kondo state, the robustness of the maximum at T = 50 K and upturn in the current x value implies that β$_m$(T) in 10 ≤ T ≤ 150 K is attributed to the CEF and Kondo effects rather than the formation of the heavy Fermion state.

1. Introduction

Cerium-based intermetallic compounds show a variety of phenomena arising from the strong hybridization between the 4f$^1$ electron and the conduction electrons (c − f hybridization), i.e., heavy Fermion states, non-Fermi-liquid behavior, and unconventional superconductivity [1, 2, 3]. Among them, an orthorhombic CeCu$_6$ is a well-known heavy Fermion compound exhibiting the large Sommerfeld coefficient γ ∼ 1.5 J/K$^2$-mol, the $T^2$ dependence in the electrical resistivity, and a maximum in the magnetic susceptibility, which is accompanied by the Kondo temperature $T_K$ ∼ 3 K [4, 5, 6, 7]. While CeCu$_6$ crystallizes in the orthorhombic structure with the space group Pnma (#62, D$_2h^5$) at room temperature, it shows a structural transition at $T_s$ ∼ 220 K, below which the space group changes to the monoclinic $P2_1$/$c$ (#14, $C_2h^5$) with a small angle modification δβ = 1.36°. The Au-substituted system CeCu$_6$$_{1-x}$Au$_x$ shows the non-Fermi-liquid behaviors, which have revealed the quantum criticality originating from the competition between the onsite Kondo effect and the intersite Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction [8]. The observation of the quantum criticality in CeCu$_6$$_{1-x}$Au$_x$ indicates that the non-substituted CeCu$_6$ is located near the quantum critical point. On the other hand, the electrical resistivity and magnetic susceptibility measurements on the diluted Ce system La$_{1-x}$Ce$_x$Cu$_6$ have revealed the consecutive change from the coherent heavy Fermion state to the incoherent Kondo state with a crossover concentration x ∼ 0.7 [9].

The thermal expansion of CeCu$_6$ have been reported in Refs. [10, 11]. The volume thermal expansion coefficient β(T) shows a maximum at $T = 2.5$ K, which temperature is close to $T_K$ ∼ 3 K. Because the maximum is observed in the other heavy Fermion compounds such as CeRu$_2$Si$_2$ [12] and EuNi$_2$P$_2$ [13], it would be attributed to formation of the heavy Fermion state. On the other hand, in our knowledge, the
thermal expansion arising from the Kondo effect has not been reported so far. Bearing this in mind, we measured the thermal expansion of the diluted Ce systems La$_{1-x}$Ce$_x$Cu$_6$ ($0.6 \leq x \leq 1$) down to 10 K in order to reveal the change of $\beta(T)$ from the heavy Fermion state ($0.9 \leq x \leq 1$) to the incoherent Kondo state ($0 < x \leq 0.73$).

2. Experiments

Single-crystalline samples of La$_{1-x}$Ce$_x$Cu$_6$ were prepared by the Czochralski method with boron nitride or tungsten crucibles as described in the previous papers [9, 14]. The thermal expansion was measured at 10–150 K by the active-dummy method with two strain gauges (Kyowa Dengyo, KFLB-12-120-C1-11). For the measurements, the laboratory-made dilatometer was installed on a commercial SQUID magnetometer (Quantum Design, MPMS) and operated with an external device control option.

3. Results and Discussion

Figure 1 shows the temperature dependences of the linear thermal expansion coefficients in La$_{1-x}$Ce$_x$Cu$_6$ for $0.6 \leq x \leq 1$ along three crystallographic axes, $\alpha_i(T)$ ($i = a, b, c$). The $\alpha_i(T)$ data for $x = 0$ (LaCu$_6$) [11] are plotted with the black solid curve for comparison. All of the $\alpha_i(T)$ data are derived by differentiating the relative length changes $dL_i(T)/L_i$ with respect to temperature. At first, we discuss the behavior of $\alpha_i(T)$ for the non-substituted system $x = 1$. The $\alpha_a(T)$ data for $x = 1$ monotonically decrease on cooling from 150 K to 12 K and the sign changes to negative below 12 K. The $\alpha_b(T)$ data, in contrast, remain constant in the temperature range of $40 \leq T \leq 150$ K and decrease on further cooling below 40 K. The $\alpha_c(T)$ data show a minimum at $T = 25$ K, and then an upturn in $T < 25$ K. The magnitude and the temperature dependences of $\alpha_i(T)$ are almost in good agreement with those of the previous reports [10, 11].

Next, we turn to the data of the diluted Ce system La$_{1-x}$Ce$_x$Cu$_6$ for $0.6 \leq x < 1$. The $\alpha_b(T)$ curves mostly decrease with decreasing the Ce concentration $x$ from 1 to 0.6. The $\alpha_a(T)$ and $\alpha_c(T)$ data, in contrast, hardly change in the current $x$ region. Rather, the $\alpha_a(T)$ data for $x = 1$ are almost identical to those for the nonmagnetic $x = 0$. The anisotropic change against $x$ would be attributed to the anisotropic coupling between the $4f^1$ electron and lattice strain. In particular, the large change in $\alpha_b(T)$ suggests that the coupling along the b-axis is the largest in the three crystallographic axes.

![Figure 1](image-url)
However, when we decrease the Ce concentration that the coupling between the $4f$ Ce system La$_1$ffi$_x$Ce$_y$Cu$_6$ for $0 \leq x \leq 1$, where $\beta(T)$ is derived by $\beta(T) = \alpha(T) + \alpha_c(T) + \alpha_e(T)$. Here, since the angle modification at $T_s$ is small as described in the introduction, we approximate that the system remains in the orthorhombic structure. All the $\beta(T)$ data monotonically decrease on cooling from 150 K. For $x = 1$, the $\beta(T)$ data exhibit a minimum at $T = 12$ K and an upturn on further cooling below 12 K. With decreasing $x$ from 1 to 0, the $\beta(T)$ curves gradually decrease, indicating the reduced magnetic contribution. At $x = 0$ [11], the $\beta(T)$ data monotonically decrease down to the lowest temperature of 10 K with no minimum.

In order to discuss the thermal expansion arising from the $4f^1$ electron, we estimated the magnetic contribution to $\beta(T)$, $\beta_m(T)$, by subtracting the data for $x = 0$ from the $\beta(T)$ data for $0.6 \leq x \leq 1$ as a phonon contribution, i.e., $\beta_m(T) = \beta_{\text{tot}}(T) - \beta_{\text{ex}}(T)$. Figure 2(b) shows $\beta_m(T)$ per molar cerium. For $x = 1$, the $\beta_m(T)$ data show a maximum at $T = 50$ K. The maximum was observed in the previous study as well [10], in which it was proposed that it may be due to crystal electric field (CEF) excitations with the level scheme 0–64–128K. In fact, similar maximum has been observed in the magnetic specific heat, which could be reproduced by the Schottky anomaly with the above CEF scheme. In the $x$ range of $0.6 \leq x \leq 1$, the maximum retains at the same temperature and magnitude, suggesting that the CEF scheme doesn’t change by the La-substitution.

Another feature in $\beta_m(T)$ for $x = 1$ is the upturn at $T < 25$ K. Since the upturn should be a precursor of the maximum at $T = 2.5$ K, we had initially expected that it might be attributed to the formation of the heavy Fermionic state. However, when we decrease the Ce concentration $x$ from 1 to 0.6 in which the ground state changes from the heavy Fermion state to the incoherent Kondo state, the upturn are retained. Therefore, the retaining of the upturn for $x = 0.6$ implies that it arises from the Kondo effect rather than the formation of the heavy Fermion state. To clarify the origin of the upturn accompanied by the maximum at $T = 2.5$ K, further low temperature measurements down to 1.8 K are desired. In particular, it is needed to confirm whether the maximum at $T = 2.5$ K exists or not at $x = 0.6$.

4. Summary
To reveal the change of the volume thermal expansion coefficients $\beta(T)$ from the coherent heavy Fermion state to the incoherent Kondo state, we performed the thermal expansion measurements on the diluted Ce system La$_1$ffi$_x$Ce$_y$Cu$_6$ for $0.6 \leq x \leq 1$ in the temperature range of $10 \leq T \leq 150$ K. The anisotropic Ce concentration $x$ dependence of the linear thermal expansion coefficients $\alpha_i(T)$ ($i = a, b, c$) suggests that the coupling between the $4f^1$ electron and the lattice strain along the b-axis is the largest in the three
crystallographic axes. The maximum in the magnetic contribution to the volume thermal expansion, $\beta_m(T)$, at $T = 50$ K is retained in the $x$ range of $0.6 \leq x \leq 1$, indicating that the crystalline electric field (CEF) levels for $x = 1$ don’t change with decreasing $x$. Moreover, the upturn below 25 K in $\beta_m(T)$, which should be accompanied by the maximum at $T = 2.5$ K reported for $x = 1$, is retained when $x$ is reduced from 1 to 0.6, which implies that $\beta_m(T)$ in $10 \leq T \leq 150$ K is attributed to the CEF and incoherent Kondo effects rather than the formation of the heavy Fermion state.

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