Kondo screening of uranium in the dilute system $(U_xLa_{1-x})Ru_2Si_2$

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Kondo screening is found in dilute uranium compounds $(U_xLa_{1-x})Ru_2Si_2$ ($x \leqslant 0.15$). At high temperatures, the susceptibility with a large magnetic anisotropy is explained by the crystal field model with the non-Kramers doublet ground state. On the other hand, the low-temperature behaviors of the high-field magnetization, susceptibility, and specific heat are well described by the Kondo model. The γ value and Schottky anomaly are nearly the same as those observed for URu_2Si_2. These results suggest that single-site Kondo screening is important for understanding the Fermi liquid state in URu_2Si_2. [S0163-1829(96)03341-3]

I. INTRODUCTION

Several uranium-based heavy fermion systems have attracted much interest due to their unconventional properties. Many experimental and theoretical studies have been done intensely to clarify the ground state of these systems. In these studies, URu_2Si_2 is one of the most interesting systems, because it exhibits the coexistence of a type-I antiferromagnetic order ($T_N=17.5$ K) with an unusual small ordered moment ($\sim 0.04\mu_B$) and non-BCS-type superconductivity ($T_c=1.2$ K).[1–4] Much experimental study has been done extensively to understand this system with various measurements.[5–11] The mechanism of the phase transition at T_N, however, is still controversial. Moreover, it has not yet been cleared whether the $5f$ electrons of this system are itinerant or well localized. In the itinerant electron picture, the weak-antiferromagnetic ordering was ascribed to the formation of a spin density wave (SDW) due to itinerant heavy electrons.[12,13] In the well-localized electron picture, these magnetic properties have been studied theoretically by the crystalline electric field (CEF) model with the singlet ground state.[14–16] For the phase transition at T_N, the contribution of the quadrupolar coupling between $5f$ electrons of the uranium atoms was suggested by the study of the nonlinear susceptibility.[17–19] However, it seems that a complete explanation for the experimental results has not yet been given.

One of the complications for understanding the magnetism of URu_2Si_2 is the competition between the Kondo effect and the RKKY interaction.[20–22] In order to clarify this situation experimentally, and to understand the role of the uranium crystalline field, we have carried out the magnetic measurements on $(U_xLa_{1-x})Ru_2Si_2$ ($x=0.05$, 0.07, and 0.15) reported here. After identifying the single-site properties on the dilute uranium system, this competition should be analyzed on the samples with more uranium concentration.

In the dilute uranium compounds $(U_xLa_{1-x})Ru_2Si_2$, the temperature dependence of the magnetic susceptibility at high temperatures and the large magnetic anisotropy were analyzed by means of the CEF model.[23] It is derived from this analysis that the CEF ground state is the Ising-type non-Kramers doublet ($\Gamma_{t5}^{(2)}$ or $\Gamma_{t5}^{(1)}$). The experimental results at low temperatures below about 25 K suggest a single-site screening of the localized magnetic moment. In the temperature dependence of the magnetic susceptibility, $(U_xLa_{1-x})Ru_2Si_2$ is quite different from the dilute uranium compounds $(U_xTh_{1-x})Ru_2Si_2$ which indicates a logarithmic temperature dependence.[24] The study of $(U_xTh_{1-x})Ru_2Si_2$ shows the non-Fermi-liquid behavior and suggests the possibility of the two-channel Kondo effect, which are quite different from the Fermi liquid behavior observed in URu_2Si_2.

The aim of this paper is to study the origin of the screening of the localized moment of the uranium atom in $LaRu_2Si_2$. We performed a high-field magnetization measurement to study the magnetic field effect to this screening and also measured the specific heat to study the thermodynamical properties of the screening in the low-temperature region. The analysis of the single-site properties of the uranium atom is important to understand the relation between the heavy fermion state and the Kondo effect in URu_2Si_2.

II. EXPERIMENTAL PROCEDURE

We prepared the single-crystalline and polycrystalline samples of $(U_xLa_{1-x})Ru_2Si_2$ ($x=0.0$, 0.05, 0.07, and 0.15). The polycrystalline samples were fabricated by arc melting and this melting procedure was repeated about 7 times to ensure the sample homogeneity. The single crystals were grown by the Czochralski method with a tri-arc furnace.

The high-field magnetization measurements up to 30 T were performed at the high magnetic field laboratory of Research Center for Extreme Materials, Osaka University. The magnetization measurements up to 7 T and the magnetic susceptibility measurements between 1.8 K and 300 K were

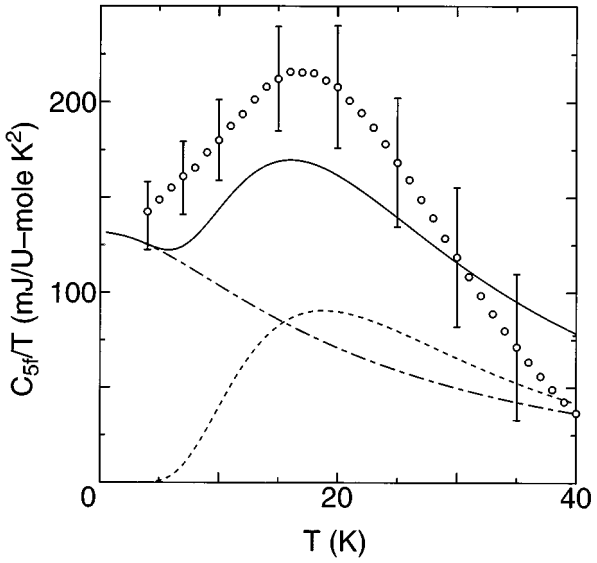

FIG. 1. C_{5f}/T vs T plot of the electronic specific heat of $(U_{0.15}La_{0.85})Ru_2Si_2$. The dash-dotted and dashed lines show the fitting results for the temperature dependence of C_{5f}/T by using the Kondo model and the CEF splitting, respectively. The solid line shows the sum of the fitting calculations by the Kondo model and the CEF splitting.

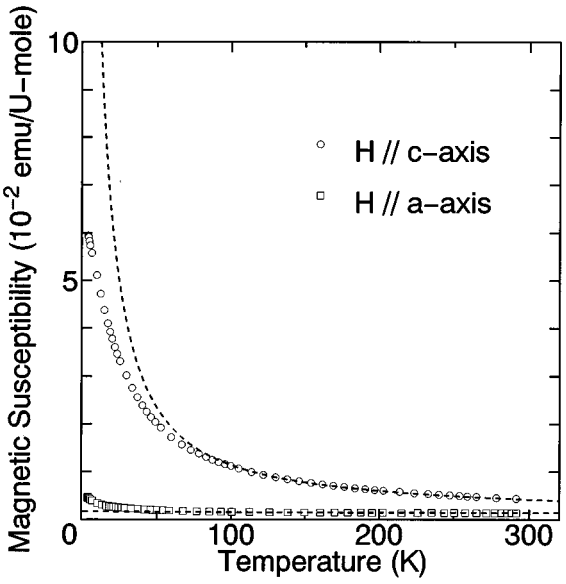

FIG. 2. Temperature dependence of the magnetic susceptibility of $(U_{0.05}La_{0.95})Ru_2Si_2$ along the c and a axes. The dashed lines show the temperature dependence of the calculated magnetic susceptibility based on the CEF model.

performed by a superconducting quantum interference device (SQUID) and the Faraday balance magnetometers. The magnetic susceptibility measurement down to 350 mK was performed using a Hartshorn bridge ac method with a dilution refrigerator. The specific heat measurements between 4.2 K and 40 K were performed by a standard adiabatic method.

III. RESULTS AND DISCUSSIONS

In Fig. 1 we show the C_{5f}/T vs T plot of the electronic specific heat for the $(U_{0.15}La_{0.85})Ru_2Si_2$ polycrystal. The contribution of $5f$ electrons is obtained from the total specific heat by subtracting the lattice part using the reference compound $LaRu_2Si_2$. The lines in Fig. 1 show the calculated electronic specific heats, which are explained later. As shown in Fig. 1, the C_{5f}/T vs T curve shows a broad maximum at around 17 K, which corresponds to the CEF splitting of about 60 K between the ground and first excited states. This anomaly is similar to the one observed for URu_2Si_2. Although the total specific heat is measured with an experimental error of about 0.7% in our measurement, the absolute value of the electronic specific heat per uranium mole has some ambiguity above 10 K, which is mainly due to the small electronic specific heat in the dilute system compared with the lattice part. For example, the contribution of the electronic part to the total specific heat is only about 3% at 40 K. In addition, there is an inaccuracy of about 10% arising from the nominal uranium concentration. This inaccuracy is estimated from the susceptibility and magnetization measurements for the samples with $x=0.05$, 0.07, and 0.15. The estimate of systematic errors is shown by the error bars in Fig. 1. The electronic specific heat of the three compounds $(U_xLa_{1-x})Ru_2Si_2$ ($x=0.05$, 0.07, and 0.15) shows a similar broad maximum at around 25 K and the qualitative behavior of the Schottky anomaly is independent of the uranium concentration. On the other hand, below 10 K the electronic specific heat coefficient $\gamma(=C_{5f}/T)$ has been estimated rather accurately, for $(U_xLa_{1-x})Ru_2Si_2$ ($x=0.05$, 0.07, and 0.15), to be about 130 ± 20 mJ/K^2 U mol, which is almost the same value as that of URu_2Si_2.

In our early study, the magnetic susceptibilities in this concentration region were analyzed by assuming the CEF splitting which has the non-Kramers doublet ($\Gamma_{t5}^{(2)}$ or $\Gamma_{t5}^{(1)}$) ground state and a singlet excited one located at around 10^3 K.[23] These CEF levels, however, are not appropriate to explain the Schottky anomaly in the specific heat at around 25 K. Therefore, the susceptibility and magnetization data are reanalyzed in detail by the exact calculation of the CEF theory so as to satisfy the specific heat data.

Figure 2 shows the magnetic susceptibilities of the $(U_{0.05}La_{0.95})Ru_2Si_2$ single crystal along the c and a axes. The contribution of $5f$ electrons is estimated by subtracting the susceptibility of $LaRu_2Si_2$. It is noted that a large uniaxial magnetic anisotropy is observed for the susceptibility measurement, as similarly observed for URu_2Si_2. The susceptibility along the c axis obeys the Curie-Weiss law above about 100 K, while the susceptibility along the a axis is almost constant down to the lowest temperatures measured. The dashed lines in Fig. 2 are the fitting results of the CEF calculation to the experimental data. The CEF splitting determined here is as follows. The ground state is the magnetic non-Kramers doublet with the strong Ising property and the first excited one is the nonmagnetic singlet located at around 60 K. The wave functions of the ground and first excited states are $\Gamma_{t5}^{(2)}$ and $\Gamma_{t1}^{(1)}$ (or $\Gamma_{t5}^{(1)}$ and $\Gamma_{t1}^{(2)}$), respectively. The J_X matrix element between these two states is very small, so that this energy splitting could not be determined by the CEF fitting calculation for susceptibility measurement in the previous paper.[23] The fitting curves are almost the same as the ones obtained in Ref. 23, because the singlet excited state is nonmagnetic. As shown in Fig. 2, the

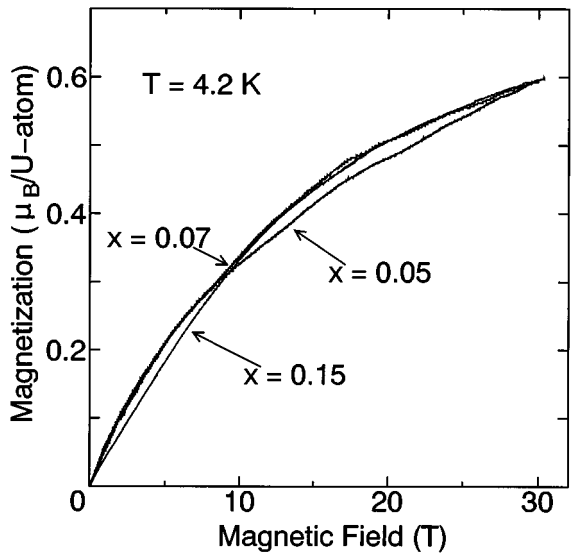

FIG. 3. High-field magnetization curves of $(U_xLa_{1-x})Ru_2Si_2$ ($x=0.05$, 0.07, and 0.15) at 4.2 K.

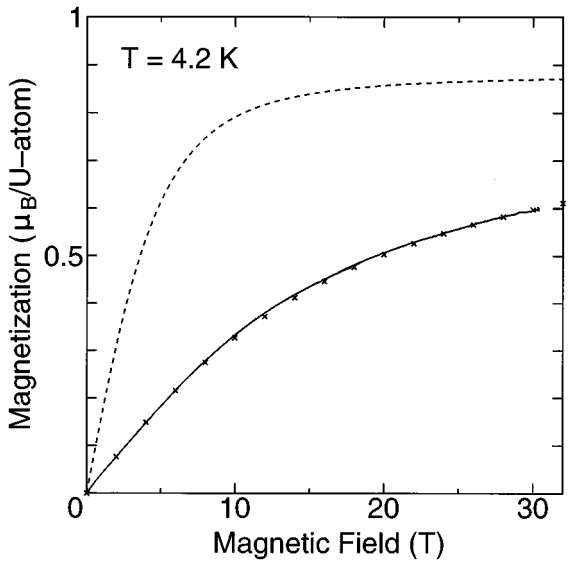

FIG. 4. High-field magnetization curve of $(U_{0.15}La_{0.85})Ru_2Si_2$ at 4.2 K. The dashed line and the crosses show the magnetization curves calculated by the CEF and Kondo model, respectively.

experimental result along the c axis deviates from the calculated susceptibility below about 100 K. In another paper,[23] the uranium concentration dependence was discussed for the susceptibility. The Curie-Weiss constant $\Theta=11\pm1$ K is obtained for the samples with $x=0.05$, 0.07, and 0.15, and it is independent of the uranium concentration. The RKKY interaction has only a minor effect on the suppression of the susceptibility in the samples with $x\leqslant0.15$. This deviation between the experimental data and the fitting curve indicates that the single-site screening of the localized magnetic moment is the major effect on the suppression of the susceptibility in this dilute system as discussed before.[23]

The high-field magnetization measurements were performed on the polycrystalline sample to clarify this deviation observed in the low-temperature region. The magnetization per uranium atom is obtained for three $(U_xLa_{1-x})Ru_2Si_2$ with $x=0.05$, 0.07, and 0.15, within the errors of 10% using the nominal concentrations. As shown in Fig. 3, the magnetizations of the various uranium concentrations increase gradually and do not saturate, even at 30 T.

The dashed line in Fig. 4 shows the calculated magnetization based on the CEF model using the same fitting parameters as the high-temperature susceptibility. The saturated moment along the c axis is estimated to be about $1.8\mu_B$ by this CEF fitting. This value is almost the same as the one obtained by the high-field magnetization measurement on URu_2Si_2.[11] The large anisotropic g values seen in Fig. 2 are averaged by integrating the direction cosine to the magnetic field. The calculated magnetization shows a saturation at about 15 T, which is quite different from the experimental data (solid line). This means that at low temperatures, the CEF model is not valid to understand the magnetic properties.

To explain this magnetization data, the Kondo model is used. The experimental results are compared with the exact Bethe ansatz results found in Schlottman's review article.[25] The fitting calculation is made for the $S=1/2$ case, because the CEF ground state is considered to be a doublet. The fitting parameter is the Kondo temperature T_K.

The fitting result is given by the crosses in Fig. 4. The Kondo model[26] is applied to only along the c axis in the calculation of the magnetization, because the susceptibility along the a axis is negligibly small compared with that along the c axis and the screening is detected only for the c axis susceptibility. The saturated moment used in this fitting is the same as the one used in the CEF calculation. The Kondo temperature T_K is estimated to be 13 ± 2 K, which definition follows the paper of Desgranges and Schotte.[28] The magnetization calculated by the Kondo model agrees fairly well with the experimental results over the whole range of the measurement.

The magnetic susceptibility is also fitted by the Kondo model using the same parameters.[27] The calculated susceptibility of this model has a finite value at zero temperature and the overall behavior of this fitting quantitatively agrees with the experimental results over the whole temperature range. This is clearly seen in the plots of $-Td\chi/dT$ as a function of the temperature (see Fig. 5). The value of this plot is that it eliminates the constant component of the susceptibility, leaves the term of $1/T$ unchanged, and converts the term of $\ln T$ to a constant. The magnetic susceptibility for $(U_{0.15}La_{0.85})Ru_2Si_2$ was measured by using the powdered sample, but for $x=0.05$ and 0.07, the susceptibility data as the powdered sample are obtained by averaging the data for the single crystals. The temperature dependence of the susceptibilities for the single crystal and powdered sample are the same as each other except for the absolute value, because the susceptibility along the a axis is constant. As is seen in Fig. 5, the experimental data show almost no uranium concentration dependence, reach a maximum at around 25 K, and decrease in the low-temperature region. The susceptibility increases more steeply than the slope of $-\ln T$ above 25 K while it increases weakly below 25 K. It becomes nearly constant below about 10 K as shown in the inset of Fig. 5, which means the formation of the Kondo singlet state. The solid line in Fig. 5 shows the fitting result for the susceptibility by using the Kondo model, which traces well the ex-

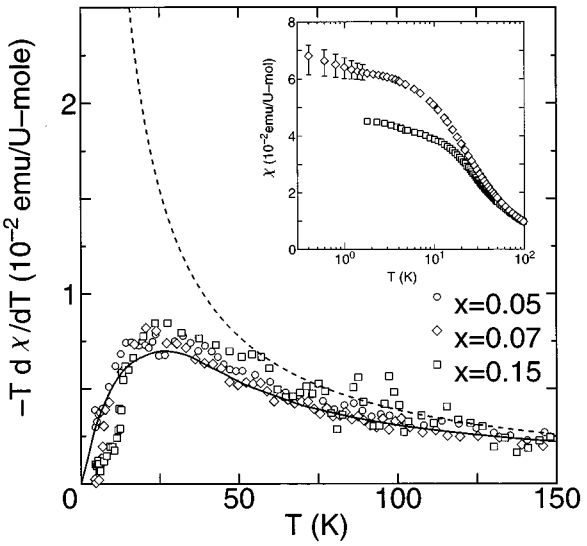

FIG. 5. Temperature dependence of the $-Td\chi/dT$ plot for $(U_xLa_{1-x})Ru_2Si_2$ ($x=0.05$, 0.07, and 0.15). The dashed and solid lines show the CEF and Kondo model calculations, respectively. Inset: Temperature dependence of the magnetic susceptibility of $(U_xLa_{1-x})Ru_2Si_2$ ($x=0.07$ and 0.15) along the c axis. The data for $x=0.15$ are estimated from the experimental value for the powdered sample.

perimental data. The value as powder sample is obtained in the same way mentioned above. On the other hand, the susceptibility calculated by the CEF model, which is indicated by the dashed line, deviates from the experimental value below 100 K, because this CEF model has a susceptibility with the term of $1/T$. These analyses have ignored the effect of the interactions between the dilute magnetic moments, because $-Td\chi/dT$ vs T plots are almost independent of the uranium concentration.

The experimental data of the electronic specific heat at low temperatures are also fitted qualitatively well by the calculation which takes account of both the Kondo model[28,29] and the CEF splitting. The fitting results are shown by the lines in Fig. 1. The dash-dotted and dashed lines show the specific heat calculated by the Kondo model and the CEF splitting, respectively. The solid line shows the total calculated specific heat. The fitting parameters are the Kondo temperature T_K, which is estimated to be 67 ± 10 K using the same definition as before, and the CEF excitation energy Δ, which is estimated to be 60 ± 6 K. From these results, it is concluded that the Kondo behavior does exist in the dilute uranium system $(U_xLa_{1-x})Ru_2Si_2$ and the Kondo screening reduces the magnetic moment of the uranium atom at low temperatures. The observation of the enhanced γ value is the evidence to show that the ground state of the $5f$ electrons at low temperatures is the Kondo singlet state which is described as the Fermi liquid.[30]

The difference between the Kondo temperatures estimated from the specific heat fitting and the magnetization and susceptibility fitting is caused by the difference of the Wilson ratio for the dilute uranium compound $(U_xLa_{1-x})Ru_2Si_2$ and the exact solution of the $S=1/2$ Kondo model. If the Wilson ratio formula $(\chi_{\rm imp}/g_J^2J(J+1)\mu_B^2)/(\gamma_{\rm imp}/\pi^2k_B^2)$ with $J=4$ is used, the Wilson ratio of our system is estimated to be about 8.5, which is quite different from the value of 2 for the exact solution of the $S=1/2$ Kondo model. The Wilson ratio of 2 was obtained for the exact calculation of the isotropic $S=1/2$ Kramers doublet ground-state system. Our system is the Ising-type non-Kramers doublet ground-state system, and so it is not necessary that the Wilson ratio of our system should be 2. Therefore, T_K may be adjusted for the specific heat and the susceptibility, because the $S=1/2$ Kondo model is used. The exact calculation of the thermodynamics properties for the system with the doublet-singlet CEF splitting has not yet been performed so far.

As mentioned in the Introduction, the study of the dilute uranium compounds $(U_xTh_{1-x})Ru_2Si_2$ suggests the possibility of the two-channel Kondo effect.[24] According to their work, the CEF ground state is the same as the one obtained in the present study. However, C_{5f}/T increases logarithmically and does not approach a constant value. Moreover, the specific heat shows no Schottky anomaly. These results are quite different from those of URu_2Si_2 and are considered to be a non-Fermi-liquid behavior. On the other hand, the present results show the similarity of the γ value and Schottky anomaly between these dilute uranium compounds $(U_xLa_{1-x})Ru_2Si_2$ and URu_2Si_2. Therefore, we suspect that the present results indicate the fundamental interactions important for URu_2Si_2. The difference between $(U_xLa_{1-x})Ru_2Si_2$ and $(U_xTh_{1-x})Ru_2Si_2$ may be explained by the shift of the singlet excited energy level. The theoretical study shows that the singlet excited state plays an important role in stabilizing the Fermi liquid state over the non-Fermi-liquid state.[31]

IV. CONCLUSION

We have analyzed the magnetic and thermodynamical properties of the dilute uranium system by the crystalline electric field (CEF) and Kondo models. In the high-temperature region above 100 K the CEF model with the non-Kramers doublet ground state is a good picture, while at low temperatures the Kondo model shows good agreement with the experimental data. This means that there is the single-site Kondo screening of the uranium atom and the Fermi liquid state occurs at low temperatures. The γ value $(=C_{5f}/T)$ and Schottky anomaly are nearly the same as those observed for URu_2Si_2. From these results, it is suggested that the single-site Kondo screening is important for understanding the Fermi liquid state in URu_2Si_2. Further study of the samples with more uranium concentration is necessary to clarify the role of the RKKY interaction in the formation process of the heavy fermion state in URu_2Si_2.

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