Observation of the coherence transition into a collective dense Kondo state by resonant inverse photoemission spectroscopy

K. Kanai, T. Terashima, D. H. Eom, M. Ishikawa, and S. Shin

Institute for Solid State Physics, University of Tokyo, 7-22-1 Roppongi, Minato-ku, Tokyo 106-8666, Japan

(Received 2 June 1999)

By the resonant inverse photoemission spectroscopy (RIPES), we study the crossover from mixed-valent to heavy-fermion and Kondo regime in $CeCoGe_{3-x}Si_x$ ($0 \leq x \leq 3$). We have measured the RIPE spectra as functions of composition and temperature. The strong composition dependence of $4f$ state (''f^1 peak'') just above the Fermi level shows that the localized $4f$ electrons in the compound become itinerant due to the enhanced Kondo effect within the range $1.0 \leq x \leq 1.5$. Temperature dependence of the f^1 peak indicates a transition from the paramagnetic state at room temperature to a coherent Fermi-liquid regime at low temperatures where the Kondo effect dominates. The most remarkable variation of the spectra has been observed above 200 K with increasing temperature in $CeCoSi_3$ which has a very high Kondo temperature T_K of about 900 K. This suggests that the change in the $4f$-electronic state of $CeCoSi_3$ may be scaled by the coherence transition temperature rather than T_K. [S0163-1829(99)50638-3]

Many Ce- or U-based materials show several interesting physical properties, e.g., mixed valence, heavy fermion, superconductivity, and so on. The nature of those systems can be fairly well accounted for by following two competing effects. The first is an on-site Kondo effect that leads to a compensation of the localized moments through the exchange interaction J between the localized $4f$-electron and itinerant electrons. The second is the Ruderman-Kittel-Kasuya-Yoshida (RKKY) interaction that plays an important role in the magnetic ordering in heavy-fermion systems. This is an intersite interaction mediated by the polarized conduction electrons. Both are associated with the same coupling constant J. The competition of these two effects generates various phases of the system depending on the magnitude of J. The finite-temperature phase diagram for the Kondo lattice has been successfully studied by Doniach[1] in which the renormalized coupling $J = J/W$ (W stands for the bandwidth) is continuously varied. The long-range magnetic ordering emerges below a critical value of parameter J_c as the ground state and the critical line $[T_N(J)]$ exists in the finite-temperature region. In the noncritical region ($J \geq J_c$), on the other hand, the ''coherence transition'' from the paramagnetic state to the mixed-valent state in the Kondo lattice has been investigated in Ref. 7 using the scaling theory of critical phenomena. Continentino *et al.*, show that the coherence transition occurs at a temperature, the so-called coherence temperature T_{coh} below the single-impurity Kondo temperature T_K and marks the onset of the collective dense Kondo regime. They have predicted that the T_{coh} has a different dependence on J as compared with T_K, especially near the J_c.

The nature of the $CeCoGe_{3-x}Si_x$ series of compound has been investigated by measuring magnetic susceptibility, electronic resistivity, and specific heat.[2] Substitution of silicon for germanium produces the normal chemical pressure effect which reduces the unit-cell volume by about 10% from $CeCoGe_3$ to $CeCoSi_3$. The coupling constant J is thereby enhanced as the silicon concentration x increases and the

antiferromagnetism in $CeCoGe_3$ is suppressed around $x = 1.2$ by the enhanced Kondo effect. The overall behavior of this system is qualitatively understood within Doniach's magnetic phase diagram.[2] The present system is a good candidate for the investigation of quantum critical behavior in heavy fermion systems. In this work we study the crossover from the coherent Fermi-liquid to paramagnetic state on $CeCoGe_{3-x}Si_x$ by means of resonant inverse photoemission spectroscopy (RIPES), which is a very useful method to probe the $4f$-electronic structure in unoccupied states.[3,4] One of the advantages of this technique is a high sensitivity to the variation of the $4f$-occupancy, that is, the RIPES effectively detects the dependence of the $4f$ state on material and temperature. We have measured the RIPE spectra of $CeCoGe_{3-x}Si_x$ and found a remarkable reconstruction of the $4f$-electronic structure just above the Fermi level E_F with varying composition and temperature.

Measurements were performed in an ultrahigh vacuum chamber where the base pressure is always under 2×10^{-10} Torr. Samples are cooled by a closed cycle ^{4}He refrigerator. Clean sample surfaces were obtained by scraping with a diamond file in a high vacuum every ~60 min at the measurement temperature. A reproducibility of the spectra was checked out at both low and high temperatures. A BaO thermal cathode-type electron gun was used for the excitation source. It was confirmed that it does not give rise to an ascent of sample temperature by the electron-bombardment effect. The kinetic energy of the electron, E_{ex} was calibrated by the electron energy analyzer. The IPES was measured by the soft x-ray emission system which has a Rowland mounted-type spectrometer.[5] The E_F position was determined by referring to the Fermi edge in the IPE spectra of Au which was evaporated on the sample holder. The polycrystalline samples were synthesized by arc melting the stoichiometric amounts of the constituents on a water-cooled copper hearth under a purified argon atmosphere. To improve the homogeneity, the ingot was annealed in an evacuated quartz tube at 950 K for four days followed by an ad-
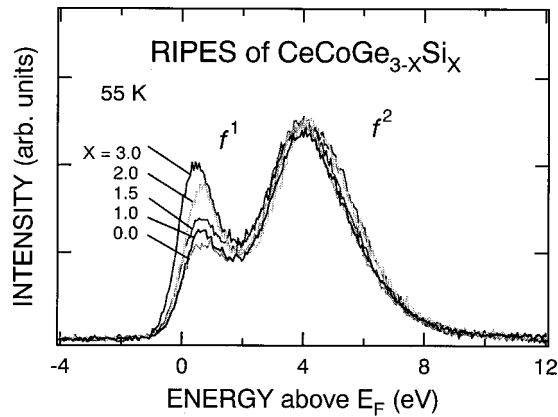
FIG. 1. The RIPES spectra of $CeCoGe_{3-x}Si_x$ $(0 \leq x \leq 3)$ measured at 55 K. The integrated backgrounds were subtracted from the spectra. The spectral intensities are normalized by the f^2 peak intensities.
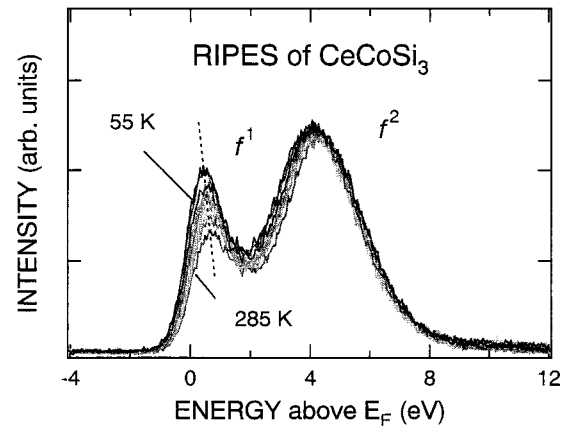

FIG. 2. The RIPES spectra of $CeCoSi_3$ as a function of the temperature. The spectral intensities are normalized by the f^2 peak intensities.

ditional annealing at 900 K for ten days. Conventional x-ray examination was carried out on these samples with Cu $K\alpha$ radiation and the crystal structure has been confirmed to be of the $BaNiSn_3$ structure type.

Figure 1 shows RIPES spectra of $CeCoGe_{3-x}Si_x$ ($x = 0, 1.0, 1.5, 2.0, 3.0$) measured at the Ce-$N_{4,5}$ absorption edge. The spectra were modified by subtracting the backgrounds. The excitation energy $E_{ex} = 122.2$ eV is selected by referring to the constant final-state spectra of $x = 0.0$ and 3.0 because the most resonant enhancements of the $4f$ structures occur approximately at this energy. The peak just above E_F is the so-called f^1 peak and the broad band at around 4 eV is the f^2 peak. The f^n peak ($n = 1, 2$) is almost caused by the $|4f^{n-1}, \underline{c}^{n-1}\rangle \rightarrow |4f^n, \underline{c}^{n-1}\rangle$ RIPE processes, that is to say, the $4f^1$ peak reflects the weight of the $|4f^{n-1}, \underline{c}^{n-1}\rangle$ state in the initial state. Here the $\underline{c}$ represents the hole in the conduction band. It is known that the f^1 peak structure contains the Kondo resonance located at $\sim k_B T_K$ within the framework of the impurity Anderson model.[6] However, in several excited states, the sidebands due to the spin-orbit and crystal-field splitting of the $4f^1$ final state are convoluted with the experimental energy resolution of the f^1 peak. Thus the present f^1 peak position in this experiment does not exactly show T_K. It is thought that the Kondo resonance is located at the lower energy side of the f^1 peak. However, the relative shift in the f^1 peak position should provide important information about the shift of T_K because the spin-orbit splitting of the $4f^1$ state which affects the spectral line shape is not a solid-state effect but an atomic one. The present study on $CeCoGe_{3-x}Si_x$ is thereby a unique test case for which T_K can be considerably varied by simply changing the composition x in a single system.[2] The results in Fig. 1 show the changes in the unoccupied $4f$ state with continuous rise of the J as x increases. The clear reduction of the f^1 peak is observed as x decreases (the spectral intensities are normalized by the f^2 peak) in Fig. 1. The intensity of the f^1 peak on $CeCoSi_3$ is reduced by $\sim 35\%$ as compared with that of $CeCoGe_3$. The reduction from $x = 3.0$ to $x = 1.5$ is most remarkable. The T_K which deduced from the Sommerfeld constant γ of $x = 1.5$ is reported to be 100 K[2], which is sufficiently higher than the measurement temperature (55 K). It

implies that we cross the ''coherence line'' in a range between $x = 1.5$ and 1.0 in the T/W vs J phase diagram.[7] The coherence line is associated with a coherence transition from the mixed-valent state of the collective Kondo regime to the paramagnetic state with the local moments in the nonmagnetic region. This is evidence of a scaling behavior of the Kondo resonance by the coherence temperature T_{coh} which will be discussed in more detail by referring to Fig. 3 below. Small variation of the f^1 peak intensity between $x = 0.0$ and 1.5 is caused by the stable valency in its paramagnetic state.

The f^2 peak has a poor compositional dependence in the energy position all over the range of x. On the other hand, it is strange that the f^1 peak of $x = 3.0$ is located at the lowest energy position in spite of the highest $T_K (\sim 900$ K).[2] As discussed later, the f^1 peak shifts to the higher energy side as temperature increases and coincides with the positions of the other x's. If the ground (Kondo) state in the $CeCoSi_3$ is attained at 55 K the high spectral intensity at the E_F cannot account for the small value of γ (37 mJ/K^2 mole) again.[2] This problem will be mentioned below in the discussion of Fig. 2.

The RIPE spectra of $CeCoSi_3$ are displayed as a function of temperature up to 285 K in Fig. 2. A continuous and striking reduction of the f^1 peak has been measured as temperature rises. We define the ratio r_f of the f peaks by the following equation as a direct indicator of the $4f$ occupancy n_f:

$$r_f = I[f^2]/(I[f^1] + I[f^2]).$$

Here, $I[f^n]$ represents the integrated intensities of the f^n peak. If the interference of the resonant processes having the f^1 and f^2 final states is disregarded, r_f is equivalent to n_f. In a realistic case, however, the configuration interaction in the intermediate and final states of the processes reconstructs the spectra, so that r_f does not represent the exact n_f.[6] But r_f still reflects n_f well and is a very useful quantity in the following discussion. The r_f's of the several compounds of $CeCoGe_{3-x}Si_x$ are plotted against temperature in Fig. 3(a). The r_f's except for $x = 3.0$ slightly rise with temperature up to 285 K. The relatively constant r_f's of $x = 1.0$ and 0.0
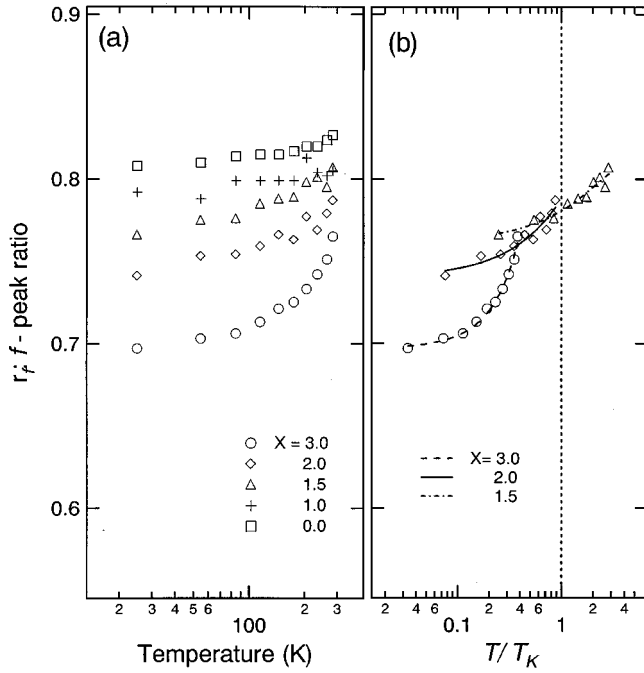
FIG. 3. (a)The f-peak ratio: r_f as a function of x plotted against temperature T. (b)r_f as a function of x plotted against T/T_K. The lines on the data are guides for the eyes and a vertical dotted line represents the point $T=T_K$.
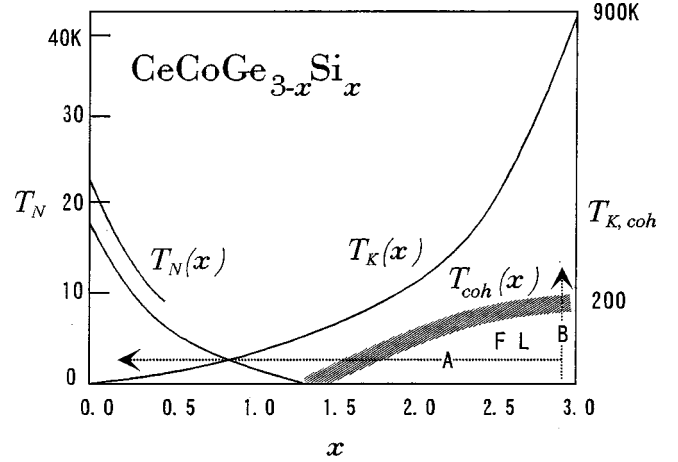

FIG. 4. The schematic phase diagram of the $CeCoGe_{3-x}Si_x$ series. The results measured along the lines ''A'' and ''B'' are displayed in Figs. 1 and 2, respectively.

reflect the stable $4f$-electron numbers $n_f \sim 1$, that is, the paramagnetic state with an effective magnetic moment close to the value of Ce^{3+}, $\mu_{eff}=2.54\mu_B$. On the other hand, r_f of $x=3.0$, for which the extremely high T_K (of the order of 900 K) has been reported,[2] shows a dramatic rise from about 200 to 285 K. As shown by Bickers *et al.*, the transport and thermodynamic properties of mixed-valence Ce systems are represented by universal functions scaled by T_K in the impurity systems.[10] And the scaling behaviors in the high-energy spectroscopic results of the several Ce compounds have been explained within the impurity model[8,9] and the Kondo effect which dominates the Ce-based heavy fermion systems is generally accepted to be well understood in the dilute limit. It should be noted, however, that the onset of the rise of the r_f sets in at a sufficiently lower temperature (~ 200 K) than the single-impurity T_K and the long-range coherence among the local singlets seems to be already destroyed at room temperature as indicated in Fig. 3(a). That is, the coherent dense Kondo state in $CeCoSi_3$ is strongly suppressed over the $T_{coh} \sim 200$ K. On the other hand, it is apparent from Fig. 3(b) that r_f's cannot be scaled by the T/T_K contrary to the prediction in an impurity approach. This result, we believe, gives a direct evidence for the basic energy scaling by T_{coh} which controls the dense Kondo system. This T_{coh} value appears to correspond to the temperature where the maximum value of magnetic susceptibility is found ($T^{\chi max}=230$ K).[2] The paramagnetic state with localized magnetic moments is sustained far below T_K. On the other hand, attention should be paid to the fact that the T_{coh} of $CeCoSe_{3-x}Si_x$ is much smaller than the single-impurity T_K though in the case of $CeRu_2(Ge_{1-x}Si_x)_2$, the T_{coh} is comparable to the T_K.[11] This strong material dependence of T_{coh}

suggests that the relationship between T_{coh} and T_K is not fixed and straightforward even in the spin-fluctuation systems with a large J.

We interpret our results by a schematic phase diagram as shown in Fig. 4, where included are the Néel temperature T_N and Weiss temperature θ_W as a function of x reported by Eom *et al.*[2] The θ_W is proportional to T_K which exponentially depends on the coupling constant J. We added the coherence line $T_{coh}(x)$ represented by a thick hatched line. The measurements in Figs. 1 and 2 were performed along the lines ''A'' and ''B'' respectively. It has been found that the lines ''A'' and ''B'' cross over the coherence line between $x=1.0$ and 1.5 at around 200 K, respectively. A saturation in r_f below about $x=1.5$ along the line ''A'' is evident in Fig. 3(a).

Although the clear shift of the f^1 peak position to the higher energy side with increasing temperature has been put into evidence in the present study, the cause for this temperature dependence is not fully settled at the moment and information about the band structure of $CeCoGe_{3-x}Si_x$ or the density of state near E_F around the coherence line would be of great importance for our understanding.

The results of the RIPES of the $CeCoGe_{3-x}Si_x$ ($0 \leq x \leq 3$) have been herein presented as a function of silicon concentration x and temperature. First, the f^1 peak which is associated with the f^1 final-state structure just above E_F, dramatically grows between $x=1.5$ and 3.0 with increasing x. This indicates that the localized $4f$ electron in $CeCoGe_3$ becomes itinerant due to the enhanced Kondo effect as x increases. Second, the f^1 peak in the spectra of $x=2.0$ and 3.0 dramatically diminishes as temperature rises above about 200 K. This fact suggests that a transition from the paramagnetic state to the coherent Fermi-liquid (mixed-valent) state occurs far below the Kondo temperature T_K, so that the $4f$ properties are scaled by the characteristic coherence transition temperature T_{coh} rather than T_K. It should be finally remarked that the energy shift of the f^1 peak with the composition x shown in Fig. 1 does not seem to scale with either T_{coh} or T_K as the impurity Anderson model predicts. This point should be more carefully examined both from experimental and theoretical points of view in the future.

[1] S. Doniach, Physica B & C **91B**, 231 (1977).

[2] D.H. Eom, M. Ishikawa, J. Kitagawa, and N. Takeda, J. Phys. Soc. Jpn. **67**, 2495 (1998).

[3] P. Weibel, M. Grioni, D. Malterre, B. Dardel, and Y. Baer, Phys. Rev. Lett. **72**, 1252 (1994); M. Grioni, P. Weibel, D. Malterre, F. Jeanneret, Y. Baer, and G. Olcese, Physica B **206 & 207**, 71 (1995); M. Grioni, P. Weibel, D. Malterre, Y. Baer, and L. Duo, Phys. Rev. B **55**, 2056 (1997); P. Weibel, M. Grioni, C. Heche, and Y. Baer, Rev. Sci. Instrum. **66**, 3755 (1995); P. Weibel, M. Grioni, D. Malterre, O. Manzardo, Y. Baer, and G.L. Olcese, Europhys. Lett. **29**, 629 (1995).

[4] K. Kanai, Y. Tezuka, M. Fujisawa, Y. Harada, S. Shin, G. Schmerber, J.P. Kappler, J.C. Parlebas, and A. Kotani, Phys. Rev. B **55**, 2623 (1997).

[5] S. Shin, A. Agui, M. Fujisawa, Y. Tezuka, T. Ishii, and N. Hirai, Rev. Sci. Instrum. **66**, 1584 (1995).

[6] O. Gunnarsson and K. Schönhammer, Phys. Rev. B **28**, 4315 (1983); J.W. Allen, S.J. Oh, O. Gunnarsson, K. Schönhammer, M.B. Maple, M.S. Torikachvili, and I. Lindau, Adv. Phys. **35**, 275 (1986).

[7] M.A. Continentino, G.M. Japiassu, and A. Troper, Phys. Rev. B **39**, 9734 (1989); M.A. Continentino, *ibid.* **47**, 11 587 (1993).

[8] F. Patthey, W.-D. Schneider, Y. Baer, and B. Delley, Phys. Rev. Lett. **58**, 2810 (1987).

[9] K. Kanai, Y. Tezuka, H. Ishii, S. Nozawa, S. Shin, A. Kotani, G. Schmerber, J.P. Kappler, and J.C. Parlebas, J. Electron Spectrosc. Relat. Phenom. **92**, 81 (1998).

[10] N.E. Bickers, D.L. Cox, and J.W. Wilkins, Phys. Rev. B **36**, 2036 (1987).

[11] S. Süllow, M.C. Aronson, B.D. Rainford, and P. Haen, Phys. Rev. Lett. **82**, 2963 (1999).