Evidence for 4f-Ligand Dehybridization in the Evolution of Heavy-Fermion Behavior in the Series $CeCu_{2-x}Ni_xSi_2$

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Evolution of heavy-fermion behavior in $CeCu_2Si_2$ from strong mixed valence in $CeNi_2Si_2$ is demonstrated in the $CeCu_{2-x}Ni_xSi_2$ system. Heavy-fermion behavior, as probed by the low-temperature susceptibility, $\chi(0)$, is destroyed at $x \cong 0.65$. There is an anomalous increase in the Ce-ligand distances, without any anomaly in the Ce-Ce separation, for $x < 0.65$, tracking the x dependence of $\chi(0)$. This observation shows explicitly for the first time that the tendency for dehybridization of the ligand valence orbitals with the Ce 4f orbital is essential to attain the heavy-fermion ground state.

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The study of heavy fermions[1] (HF) in 4f and 5f systems, which are characterized by an unusually large value of the linear coefficient of specific heat (γ) due to very high effective mass, has been an area of active research for the past few years. A broad spectrum of phenomena—superconductivity,[2-4] magnetic order,[5,6] strong Pauli paramagnetism,[7] coexistence of some of these phenomena[4]—have been observed in a number of HF systems. While the study of the origin of these phenomena is an area of active research, not much progress has been made in understanding all the factors leading to the formation of the heavy-fermion state itself.[8-11] It is pointed out by Meisner *et al.*[8] that, even beyond the Hill's limit[12] of the separation of f atoms where the f-f overlap is negligible, there is a correlation between f-f atomic separation and the values of γ. On the other hand, Koelling, Dunlap, and Crabtree[9] attribute the anomalous properties of HF to the f-ligand hybridization. Thus, the investigation of the factors enhancing the formation of heavy fermions is in itself very interesting. A systematic investigation of alloying at the ligand site, as emphasized by Koelling, Dunlap, and Crabtree, is warranted in order to explicitly show the influence of the ligands on the origin of heavy fermions.

In this paper, we report the results of our investigation in $CeCu_{2-x}Ni_xSi_2$, a new pseudoternary series with $ThCr_2Si_2$-type tetragonal structure. $CeCu_2Si_2$ is a well-known[2] HF system and $CeNi_2Si_2$ is a strongly mixed-valent compound (*vide infra*). This combination has the advantages that the f-f atomic separations are beyond the Hill's limit[12] and these values are not widely different between these two compounds. Hence the gradual replacement of Cu by Ni offers an ideal opportunity to identify the exact role of the ligands alone in heavy-fermion materials. We find that the substitution of less than 30% of Cu by Ni destroys the HF character of $CeCu_2Si_2$, as probed by the low-temperature magnetic susceptibility, $\chi(0)$, measurements. The new finding is that there is an abnormal increase in the lattice parameter c (in other words, Ce-ligand distances) at the same concentration where $\chi(0)$ increases significantly as one proceeds towards the Cu-rich end. In other words, c tracks the variation of $\chi(0)$ as a function of x. This observation, in our opinion, proves conclusively that the dehybridization of ligand valence orbitals with Ce 4f, besides the criteria on Ce-Ce separation,[8] is essential to form the heavy-fermion ground state. The identification of the present pseudoternary series also offers an opportunity to study the evolution of the HF ground state in $CeCu_2Si_2$ continuously from the mixed-valent state by alloying without destroying the periodicity of the Ce sublattice; its advantages relative to the alloying at the Ce site are discussed later in this paper.

The polycrystalline samples of $CeCu_{2-x}Ni_xSi_2$ alloys ($x = 0$, 0.3, 0.5, 0.65, 0.8, 1.0, 1.5, and 2) were prepared by melting stoichiometric amounts of the constituent elements in an arc furnace in an atmosphere of argon. No attempt was made to anneal the ingots. The x-ray diffraction patterns confirm the single-phase nature of all the alloys ($ThCr_2Si_2$-type tetragonal structure). The lattice constants, a and c, were obtained from (220) and (116) diffraction lines. The magnetic susceptibility measurements were performed in a field of 6 kOe in the temperature interval 4.2–800 K with use of a Faraday balance.

The lattice parameters, a and c, are reported in Fig. 1 as a function of x. The value of a is an almost linear function of x within the limits of the experimental error, whereas there is a deviation from linearity for the values of c as $x \rightarrow 0.5$. c increases linearly with decreasing concentration of nickel till $x \cong 0.65$ and the observed increase of c for the lower values of x (Cu-rich side) is much more than what one would expect (see the dashed line in Fig. 1 obtained by joining the points at the nickel-rich side as well as from the known c values[13] of $PrCu_2Si_2$ and $PrNi_2Si_2$). The implications of this abnormal increase without any anomaly in a will be discussed along with the low-temperature sus-

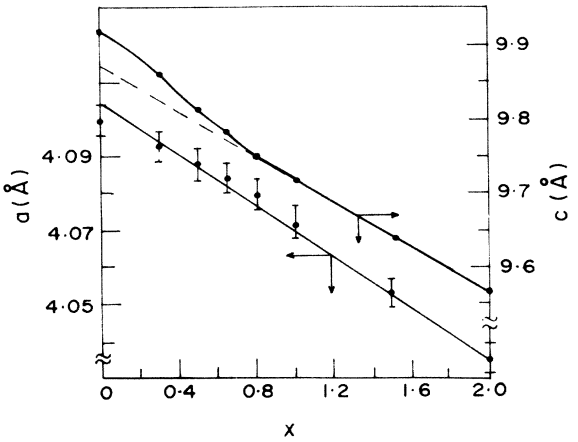

FIG. 1. The lattice constants (at 300 K), a and c, as a function of x in $CeCu_{2-x}Ni_xSi_2$. The solid lines are drawn through the experimental points. The dashed line in the case of c is obtained by the linear extrapolation from the nickel-rich end. The error in c is not more than the size of the dots.

ceptibility results.

The results of magnetic susceptibility studies are shown in Fig. 2. For $CeCu_2Si_2$, the values of χ are in good agreement with those reported in the literature,[1] taking into account the spread in the values of the low-temperature susceptibility, $\chi(0)$, which depends on the sample quality.[1] The values of χ over a wide temperature range 4.2–800 K for various values of x are plotted in Fig. 2(b) in order to illuminate the differences in their temperature-dependent behavior. The characteristic temperatures T_{max} (the point at which χ exhibits a maximum) which is a measure of the spin-fluctuation temperature[14] (T_{sf}) are about 600, 400, 300, 200, 150, and 100 K for $x=2$, 1.5, 1.0, 0.8, 0.65, and 0.5, respectively. We find that these values are in good agreement with those obtained from the respective $C/\chi(0)$ (here C is the Curie constant) values and this suggests the validity of scaling relation[14] over the entire range of solid solution. The observed values of T_{max} also agree with the general rule that as the lattice volume decreases, T_{sf} should increase.[15,16] T_{max} values can be taken to decide whether a compound is in the strongly mixed-valent regime ($T_{max} \gtrsim 100$ K) or in the Kondo-lattice regime ($T_{max} \lesssim 100$ K) as pointed out by Brandow.[17] Heavy-fermion materials are the extreme examples of Kondo lattices with $T_{sf} \lesssim 10$ K. Following these ideas, we infer that Ce is in a strongly mixed-valent state for $x > 0.5$, and in a heavy-fermion state for $x \lesssim 0.5$. Incidentally, the spectroscopic results[18] on $CeNi_2Si_2$ are also consistent with the strongly mixed-valent character of Ce in $CeNi_2Si_2$. Thus this work demonstrates the continuous evolution of the heavy-fermion ground state in $CeCu_2Si_2$ from the strongly mixed-valent state

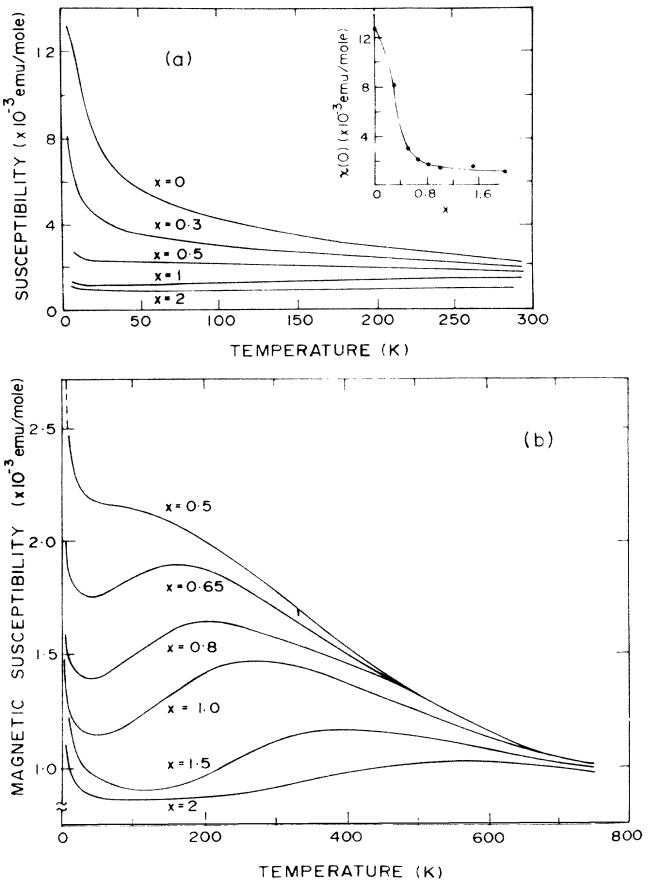

FIG. 2. (a) The magnetic susceptibility (χ) in the temperature interval 4.2–300 K for selected values of x. Inset shows the values of $\chi(0)$, assumed to be equal to $\chi(4.2\text{ K})$, as a function of x. (b) χ in the temperature range 4.2–800 K for various values of x in $CeCu_{2-x}Ni_xSi_2$.

by alloying. This may also imply that a single mechanism controls the low-temperature properties of all these phenomena, as shown by Zieglowski, Häfner, and Wohlleben[19] from volume-magnetostriction studies of a variety of Ce systems.

It should be remarked that alloying studies in $CeCu_2Si_2$ at the Ce site in the past were helpful in the understanding of competition between magnetism and Kondo effect.[20] Substitution at the copper site by nickel has some special advantages. Replacement of Ce by La or Y in $CeCu_2Si_2$ indicates that, in Kondo-lattice systems, there is a structure at the Fermi level which develops below 0.5 K due to the periodicity of Ce ions in the lattice.[21–23] In order to understand the evolution of this structure from the mixed-valent ground state, it is essential to maintain the periodicity of the Ce ions and in that respect the present pseudoternary series would be helpful. A mixed-valent ground state has also been proposed to occur under external pressure (above 20 kbar) in $CeCu_2Si_2$ by Bellarbi *et al.*[24]

and a correlation of such studies with chemical-pressure experiments would be helpful to understand various factors controlling the physical processes in a compound, as stressed by Schilling.[15]

Let us now turn to the behavior of the low-temperature susceptibility. As nickel is added, the value of χ is continuously reduced. For $x > 0.5$, the value of χ at 4.2 K, which serves as a measure of the zero-temperature susceptibility, $\chi(0)$ is diminished significantly relative to that of $CeCu_2Si_2$. As $\chi(0)$ is a quantity directly related[25] to γ, the results shown in the inset of Fig. 2(a) imply that the heavy-fermion state is destroyed as x approaches 0.5 as inferred from the values of T_{max} also. This observation emphasizes that the ligands play a vital role in the formation of heavy-fermion state. A further comparison of the x dependence of the lattice constants with that of $\chi(0)$ is very intriguing. As known in the literature,[18] in the compounds of $ThCr_2Si_2$ type, any anomaly in the valence of Ce is expected to influence the lattice parameter a predominantly and the anomalous Ce-ligand bonding effects will be reflected in the values of c. The observation that a is a smooth function of x implies that the dependence of Ce valence on x is linear. We recall[16,18,26,27] at this point that the overall variation of $4f$ occupation number is anyway not very large (< 0.2), as it is believed that the valency of Ce in any metallic environment is always close to three. Surprisingly, the value of c at the Cu-rich side increases much more sharply than the expected linear behavior, as discussed earlier. It is interesting to see that the Ce-ligand distance, as evidenced by the values of c, starts increasing anomalously at the same value of x at which $\chi(0)$ also increases (as one proceeds towards the Cu-rich side). In other words, $\chi(0)$ tracks the variation of c. We are, however, comparing the lattice constants at 300 K with the susceptibility at 4.2 K. This does not appear to be a serious defect in our reasoning, as the variation of c for $CeCu_2Si_2$ in the temperature interval 4.2–300 K is known[28] to be negligible relative to the magnitude of the deviation observed in this pseudoternary series. Bond distances being a measure of hybridization, our results, therefore, establish that the ligand valence orbitals tend to dehydridize the Ce $4f$ oribtals in order to favor the heavy-fermion ground state. Thus the study of the continuous evolution of heavy-fermion behavior from mixed-valent ground state in the alloys $CeCu_{2-x}Ni_xSi_2$ and its correlation with the lattice parameters place the role of the ligands in Kondo-lattice systems on a firm footing.

In our arguments above, the possible changes in the crystal-field ground state as a function of x and its consequences have not been taken into account. It is believed that $CeCu_2Si_2$ under ambient conditions has a crystal-field split $J = \frac{1}{2}$ ground state and that under pressure (or with the replacement of Cu by Ni) the ground state may be characterized by a sixfold degenerate $J = \frac{5}{2}$ multiplet.[29] This probable change in the ground state for $x > 0.5$ with the decreasing volume is obviously due to the stronger $4f$ hybridization relative to that in $CeCu_2Si_2$ and this is in any case consistent with our conclusion on the x dependence of hybridization strength. One consequence of the ground-state modification is that the ratio $\chi(0)/\gamma$ will also be a function of x, but it is not known experimentally how $\chi(0)$ and γ are related as J changes. However, theoretically,[25] this ratio is expected to increase as J is changed from $\frac{1}{2}$ to $\frac{5}{2}$. This means that the magnitude of the decrease in γ will be more dramatic than in $\chi(0)$ as a funciton of x till $x \cong 0.5$. Thus, such a variation of the ground state due to crystal fields does not alter our conclusions. In support of this, γ of $CeCu_2Si_2$ under pressure is known[30] to decrease dramatically.

Finally, we wonder whether x dependence of c plotted in Fig. 1 could help identify new heavy-fermion materials of $ThCr_2Si_2$-type structure. In other words, there may be a critical Ce-ligand distance (or c) separating the strongly mixed-valent regime from the heavy-fermion regime. In support of this proposal, we find that the value of c (~ 9.80 Å) for $CeRu_2Si_2$,[31] with a γ value[32] two or three times smaller than for $CeCu_2Si_2$ [about 400 mJ/(mole f-atom)$\cdot$K^2] lies at the border line in the plot of c vs x in Fig. 1). If this conjecture is found true from future experiments, it will contribute to a better theoretical understanding of heavy fermions.

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