Ce 4f-LIGAND DEHYBRIDIZATION IN CeT₂X₂-BASED KONDO LATTICE/HEAVY FERMION SYSTEMS

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The lattice parameters of two CeT₂X₂ (T = 3d transition elements and X = Si and Ge) based Kondo lattice systems, the CeNi₂₋ₓCuₓSi₂ and Ce(NiSi)₂₋ₓ(CuGe)ₓ, have been studied. The analysis of the Ce-ligand distances indicates that the variation of the a-parameter dominantly affects Ce 4f-X ligand orbital hybridization whereas the variation of c-parameter dominantly affects Ce 4f-T ligand orbital hybridization. The average Ce-ligand distance varies linearly with x across the whole series in spite of the abnormal increase of the c-parameter in the region 1.6 < x < 2.0. Thus, our analysis shows that the average Ce 4f-ligand orbital hybridization decreases uniformly with x across the entire range of x for the CeNi₂₋ₓCuₓSi₂ and Ce(NiSi)₂₋ₓ(CuGe)ₓ series. The means that the Ce 4f-ligand orbital dehybridization may not be a key factor to the formation of the heavy-fermion ground state in CeCu₂Si₂.

Keywords: Ce 4f-ligand hybridization; Kondo lattice; mixed valence; heavy-fermion; lattice parameters.

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1. Introduction

The study of the origins of heavy fermion (HF) ground-state formation in some cerium (Ce) and uranium compounds has been an area of substantial interest over the last two decades.1–5 In the past, some authors suggested that the hybridization between the f- and ligand-orbitals should be important to the formation of heavy fermion (high γ) ground state.6,7 The argument is that the γ values are correlated to the density of states (DOS) at the Fermi-surface which is partially determined by the f-ligand hybridization strength (associated with f-ligand spacing). At present, no sufficient experimental data are available for clarifying the role that f-ligand hybridization plays in the formation of heavy-fermion ground state.

The observed abnormal increase in the c-parameter for Kondo/HF series CeNi₂₋ₓCuₓSi₂ near x = 2.0 was used by Sampthkumaran et al.8 as evidence of the

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dehybridization of ligand orbitals with the Ce 4f orbitals. Based on the observed correlation between the c-parameter and low-temperature magnetic susceptibility,\(^8\) they concluded that such Ce 4f-ligand orbital dehybridization must be essential to the formation of the heavy-fermion ground state in CeCu\(_2\)Si\(_2\). Indeed, later an anomalous increase of the electronic specific heat \(\gamma\) was also observed in the 1.7 \(\leq x \leq 2.0\) region of the CeNi\(_{2-x}\)Cu\(_x\)Si\(_2\) series.\(^9\) However, since the relation between the c-parameter and the Ce 4f-ligand distance (which is related to Ce 4f-ligand dehybridization) in this series is complicated by both the tetragonal structure and the existence of two types of ligands (i.e. T and X ligands in Fig. 1) around the Ce atoms, whether or not the anomalous increase of c-parameter near \(x = 2.0\) represents an anomalous increase of the average Ce 4f-ligand distance (or dehybridization) is still an open question. As a consequence, how Ce 4f-ligand dehybridization is correlated to the anomalous increase of \(\gamma\) in the range of 1.6 \(\leq x \leq 2.0\) is also an open question. To clarify these important issues, we have analyzed the relationships among the lattice parameters, Ce-ligand distances, and f-ligand dehybridization strength for two Kondo lattice systems, CeNi\(_{2-x}\)Cu\(_x\)Si\(_2\) and Ce(NiSi)\(_{2-x}\)(CuGe)\(_x\).\(^{10,11}\) The latter serves as a good candidate for comparison with the former because the \(\gamma\) value at \(T \rightarrow 0\) for the end compound of this series, CeCu\(_2\)Ge\(_2\), is only 0.13 J/K\(^2\) mol. This \(\gamma\) value is almost an order of magnitude smaller than that for CeCu\(_2\)Si\(_2\).\(^{11,12}\)

![Fig. 1. ThCr\(_2\)Si\(_2\)-type crystal structure of CeT\(_2\)X\(_2\) compounds.](image)

2. Experimental

The polycrystalline samples used in this study were polycrystalline samples prepared by arc melting stoichiometric amounts of the constituent elements in an organ atmosphere. X-ray diffraction measurement were made using an automated SCINTAG-PAD-V powder diffractometer. All of the samples were confirmed to be single phase with the ThCr\(_2\)Si\(_2\) structure (see Fig. 1). The lattice parameters were obtained by least-square-fitting of the X-ray diffraction pattern in the range of 20° < \(2\theta\) < 80°.
3. Results and Discussion

Figure 2 shows the variation of lattice parameters $a$ and $c$ as functions of $x$ for both the CeNi$_{2-x}$Cu$_x$Si$_2$ and Ce(NiSi)$_{2-x}$(CuGe)$_x$ systems. It can be seen from Fig. 2 that both $a$ and $c$ deviated from Vegard’s law type linear behavior but with opposite signs. The $a(x)$ and $c(x)$ curves of the Ce(NiSi)$_{2-x}$(CuGe)$_x$ series manifest a very similar behavior to that of the CeNi$_{2-x}$Cu$_x$Si$_2$ series in the whole range of $x$. An anomalous bump in the region of $x \leq 1.6$ was observed for both series. These results are very similar to those reported by Sampathhumaran et al.\textsuperscript{8} for the CeNi$_{2-x}$Cu$_x$Si$_2$ series. A comparison between these two series indicates that the consequence of the Ge for Si substitution is an expansion of the lattice parameters, as observed previously in the CeMn$_2$Si$_{2-x}$Ge$_x$ series.\textsuperscript{13}

The layered ThCr$_2$Si$_2$-structure (see Fig. 1) material CeT$_3$X$_2$ ($T = 3d$ transition metal elements, here Ni and Cu, and $X = Si, Ge$) can be viewed as being formed by an insertion of the Ce layers between the tightly bonded $T_2X_2$ layers perpendicular to the $c$-axis.\textsuperscript{14} Thus, it appears that the $c$-parameter could be regarded as a dominant measure of the hybridizations between the Ce-4$f$ orbitals and the ligand orbitals (here the $T - 3d$ and $X - p$ orbitals) whereas the $a$-parameter should be
related only to the in-plane Ce 4f–Ce 4f overlapping and the hybridization between Ce 4f orbitals and the Ce 5dσs conduction bands. In the analysis below, however, we will see that while the Ce-T ligand dehybridization is dominated by the variation of the \( z \)-parameter, the Ce-X ligand dehybridization is actually dominated by the variation of the \( a \)-parameter.

The hybridization strength between Ce 4f and ligand orbitals (i.e. Si 3p, Ge 4p, T 3d, and T 4p, orbitals) can be evaluated by formula \( V_{l,l'} = d^{-\left(l+l'+1\right)} \), where \( V_{l,l'} \) is the hybridization matrix element, \( d \) is the separation between two neighboring atoms with orbital angular momentum \( l \) and \( l' \). Kang et al.\(^{15,16} \) used this formula to analyze their electron spectroscopy data for the heavy-fermion superconductor CeCu$_2$Si$_2$. In substituted CeT$_2$X$_2$ systems with ThCr$_2$Si$_2$ structure, as shown in Fig. 1, each Ce ion has eight nearest neighbor T-ligand atoms at a distance of \( d_1 = [(a/2)^2 + (c/4)^2]^{1/2} \) Å and eight nearest neighbor X-ligand atoms at a distance of \( d_2 = [a^2/2 + (1/2 - z)^2c^2]^{1/2} \) Å,\(^{17,18} \) where \( z \) is shown in Fig. 1. The parameter \( z \), currently unobtainable from our X-ray diffraction data, can be determined by certain techniques such as extended X-ray absorption fine-structure (EXAFS) or single-crystal X-ray diffraction measurements. The dependence of \( V_{l,l'} \) on parameters \( a \) and \( c \) is via \( d_1 \) and \( d_2 \). The variation of the \( f \)-ligand distances, i.e. \( \delta d_1 \) and \( \delta d_2 \), can be calculated by differentiating \( d_1 \) and \( d_2 \) with respect to \( a \) and \( c \). If \( \Delta_a \) and \( \Delta_c \) are used to represent the contributions to the variation of the \( f \)-ligand distances due to the variation of \( a \) and \( c \), respectively, then, one can easily find the ratio \( \Delta_c/\Delta_a = 1/4(c/a)(\delta c/\delta a) \) for \( \delta d_1 \) and \( \Delta_c/\Delta_a = 2(1/2 - z)^2(c/a)(\delta c/\delta a) \) for \( \delta d_2 \). The value of \( \Delta_c/\Delta_a \) determines which parameter, \( a \) or \( c \), dominates the change of \( f \)-ligand hybridization \( V_{l,l'} \) via the change of \( d_1 \) and \( d_2 \).

Godard et al.\(^{17} \) measured the \( z \)-parameter for some CeT$_2$Si$_2$ compounds by EXAFS and they found an interesting correlation between \( z \) and the Ce valence: \( z \approx 0.370 \) for strongly mixed-valent systems such as the T = Ni and Co compounds in which the Ce-L$_3$ valence (determined by Ce-L$_3$ edge spectra) is close to 3.2; \( z \approx 0.376 \) for nearly trivalent systems such as the CeT$_2$Si$_2$ compounds with T = Cu or Ru, in which the Ce valence is close to 3.0. Since the Ce valence values for both CeNi$_{2-x}$Cu$_x$Si$_2$ and Ce(NiSi)$_{2-x}$(CuGe)$_x$ fall into the same valence range,\(^{10,11,19} \) as these CeT$_2$Si$_2$ compounds, one can use the average value \( z = 0.373 \) for estimating \( \Delta_c/\Delta_a \) in these two compound series. The error induced by the uncertainty of the parameter \( z \) was estimated to be less than 0.04. For \( x \) varying from 0.0 and 2.0, our measured values of \( c/a \) and \( \delta c/\delta a \) are about 2.4 and 5.8, respectively, for the CeNi$_{2-x}$Cu$_x$Si$_2$ series, and about 2.4 and 4.4, respectively, for the Ce(NiSi)$_{2-x}$(CuGe)$_x$ series. The calculated \( \Delta_c/\Delta_a \) corresponding to \( \delta d_1 \) are 3.5 for the former and 4.4 for the latter series, respectively, whereas the \( \Delta_c/\Delta_a \) corresponding to \( \delta d_2 \) are 0.45 for the former and 0.34 for the latter series. Since \( d_1 \) is the Ce-T distance and \( d_2 \) is the Ce-X distance, our calculation thus clearly shows that in both of these two compound systems, the Ce 4f-T ligand dehybridization is dominantly controlled by the variation of the \( c \)-parameter whereas the Ce 4f-X ligand dehybridization is dominantly controlled by the variation of the \( a \)-parameter.
To see how the dehybridization of $f$-ligand distances (i.e. $d_1$ and $d_2$) vary with substitution concentration $x$ in CeNi$_{2-x}$Cu$_x$Si$_2$ and Ce(NiSi)$_{2-x}$(CuGe)$_x$, the parameter $z$ has to be known as a function of $x$ (because $d_2$ depends on $z$). The correlation\textsuperscript{17} mentioned previously between $z$ and Ce valence allows us to assume a $z$ value of 0.370 for CeCu$_2$Ge$_2$ because the Ce valence in this compound is nearly trivalent (similar to that of CeCu$_2$Si$_2$). Since the Ce valence was observed to be well correlated with $a$-parameter rather that $c$-parameter in all of the substituted CeT$_2$X$_2$ systems,\textsuperscript{10,11,13,20} it is reasonable to assume that $z$ depends on $a$ only. Thus for a very small change of $z$ in the whole $x$ range (i.e. $\delta z \approx 0.006$), one can reasonably assume a linear relation $z(x) = A + B a(x)$, where $A$ and $B$ are two constants to be determined by the values of $z$ and $a$ at $x = 0$ and $x = 2$. We found $A = 0.193$ and $B = 0.044$ for Ce(NiSi)$_{2-x}$(CuGe)$_x$, and $A = 0.008$ and $B = 0.090$ for CeNi$_{2-x}$Cu$_x$Si$_2$. The calculated $d_1$, $d_2$, and the average value of $d_1$ and $d_2$, i.e. $d_{av} = (d_1 + d_2)/2$, are plotted in Fig. 3 as functions of $x$.

Figure 3 clearly shows that $d_1(x)$ varies with $x$ in a similar manner as $c(x)$ (see Fig. 2), whereas $d_2(x)$ varies in a similar manner as $a(x)$. This indicates again that the variation of $d_1$ [or $d$(Ce-T)] is predominantly controlled by parameter $c$ and that the variation of $d_2$ [or $d$(Ce-X)] is predominantly controlled by parameter $a$. It is also seen from Fig. 3 that as $x$ increases, both $d_1$ and $d_2$ start to deviate...
from linearity at $x \approx 1.4$ but in opposite direction. This indicates that as the heavy-fermion CeCu$_2$Si$_2$ is approached, the rate of dehybridization between the Ce 4$f$-orbital and Si 3$p$-orbitals decreases. Also shown in Fig. 3 is that the average $f$-ligand distance $d_{av}(x)$ is almost linear in the entire range of $x$ for both compound series. If the Ce-T and Ce-X orbital hybridizations are equally important to the total $f$-ligand hybridization, then the linearity of $d_{av}(x)$ simply indicates that the average hybridization strength is varying with $x$ without the presence of anomaly. This implication holds even for the end compound CeCu$_2$Si$_2$.

As pointed out by some authors, the Ce 4$f$-Si 3$p$ hybridization in CeT$_2$X$_2$ compounds could actually be much stronger than the Ce 4$f$-T 3$d$ hybridization. This is due to the fact that compared with the T(3$d$)-ligands, the X-ligands usually have more spatially extended orbitals, a smaller quantum number $l'$, and smaller $f$-ligand distance. Indeed, Fig. 3 shows that $d_2$ is always smaller than $d_1$ at any $x$ value. For the heavy-fermion system CeCu$_2$Si$_2$, the narrow Ce 4$f$ band is degenerated with the broad Si 3$p$ band, whereas the Cu 3$d$ band is almost filled and far below the Ce 4$f$ level (as has been shown by band calculations and by 2$p$ XPS data). Thus, it is expected that the Ce-T hybridization strength should be further weakened as $x \to 2.0$ in both series. If the dominant contribution to the $f$-ligand orbital hybridization is from the Ce 4$f$-X $p$-hybridization, then it is the variation of the $a$-parameter (rather than the $c$-parameter) that manifests the change of the average strength of the Ce 4$f$-ligand hybridization. Thus, the Ce 4$f$-ligand dehybridization should have been slowed down slightly when the HF system CeCu$_2$Si$_2$ at $x = 2$ in the CeNi$_{2-x}$Cu$_x$Si$_2$ series is approached.

The last point we would like to make is about the correlation between the average Ce-ligand distance, $d_{av}$, and the cell volume in these two compound series. The cell volume as functions of $x$ for CeNi$_{2-x}$Cu$_x$Si$_2$ and Ce(NiSi)$_{2-x}$(CuGe)$_x$ series is shown in Fig. 4. Figure 4 clearly shows that the cell volume in these two series varies linearly with $x$ in exactly the same manner as $d_{av}$ (see bottom of Fig. 3).

![Fig. 4. The cell volume values as functions of $x$ for the Ce(NiSi)$_{2-x}$(CuGe)$_x$ and CeNi$_{2-x}$Cu$_x$Si$_2$ systems. The solid straight lines are guides to the eyes to show how the data points varies linearly with $x$.](image-url)
does. This correlation between the $d_{av}$ and the cell volume can be explained as the following: since both of them have contributions from both $a$- and $c$-parameters, the opposite effects on the cell volume and $d_{av}$ due to the opposite deviations of $a$- and $c$-parameter from Vegard's law type behavior (see Fig. 2) are effectively canceled, yielding the observed linearity for both cell volume and $d_{av}$. Since Ce valence in these 1:2:2 compounds is usually correlated with $a$-parameter (or Ce 4$f$-Ce 4$f$ spacing) due to the anisotropic ThCr$_2$Si$_2$-type tetragonal structure, the linear relationship between the average Ce-ligand distance, $d_{av}$ (as well as cell volume), and $x$ does not respond to the nonlinear variation of Ce valence with $x$ in these two series.$^{11,13,19}$

4. Conclusions

Our analysis on Ce-ligand distances for two substituted CeT$_2$Si$_2$ systems indicates that the Ce 4$f$-X ligand dehybridization is dominantly controlled by the variation of the $a$-parameter whereas the Ce 4$f$-T ligand dehybridization is dominantly controlled by the variation of the $c$-parameter. The average Ce-ligand distance $d_{av}$ depends on both $a$ and $c$ parameters, and varies linearly with $x$ over the entire range of $x$ for both compound series discussed. Thus, an abnormal increase in the $c$-parameter near the $x = 2.0$ end (including HF compound CeCu$_2$Si$_2$) of these two series does not induce an abnormal increase in $d_{av}$ as well as in the average Ce 4$f$-ligand orbital dehybridization. Thus, our results suggests that the Ce 4$f$-ligand orbital dehybridization probably is not a key factor to the formation of the HF ground state in CeCu$_2$Si$_2$.

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References
