# Competition between the Kondo effect and exchange interactions in the system $CeSi_x$

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Precision electrical resistivity measurements on twelve alloys in the series $CeSi_x$ ($1.60 \leq x \leq 1.90$) reflect the smooth progression from a magnetically ordered dense Kondo system ($x \leq 1.85$) to compositions where the conventional single-impurity Kondo effect dominates the exchange interaction, resulting in a ground state which is not magnetically ordered. The variations of the Kondo temperature and the magnetic ordering temperature are determined as a function of Si content and found to agree well with the theoretical Kondo-lattice model.

## INTRODUCTION

The nature of the low-temperature states of alloys in the series $CeSi_x$ ($1.60 \leq x \leq 2.00$) has been the focus of numerous recent experimental studies.[1-14] $CeSi_2$, which crystallizes in the $\alpha$-$ThSi_2$-type structure ($I4_1/amd$), admits considerable vacancies on the Si sublattice while still retaining its tetragonal symmetry. At room temperature below a silicon concentration of $x = 1.75$, a crystallographic distortion occurs and the alloys have the orthorhombic $GdSi_2$-type structure *(Imma)*. The variation in composition also directly affects the low-temperature properties of these alloys resulting in magnetic order at lower Si concentrations ($x \leq 1.85$).

Yashima and co-workers[1,3] proposed that for $CeSi_{1.70}$ and $CeSi_{1.80}$, the magnetically ordered state may be understood on the basis of a ferromagnetic dense Kondo system in which the regular sublattice of Ce atoms orders via the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction while the Kondo effect reduces the magnetic moment ($\sim 0.3 \mu_B$/Ce atom). The preservation of an intact, periodic array of Ce atoms across the entire series $CeSi_x$ makes this system ideal for studying the competition between the Kondo effect and magnetism which occurs through the RKKY interaction. Both of these effects arise from the exchange interaction between the conduction and $4f$ electrons.

The electrical resistivity has been shown to be especially sensitive to the development with temperature of the single-impurity Kondo resonance as well as the RKKY-interaction strength. In this paper we present a detailed experimental study of the temperature dependence of the electrical resistivity for 12 alloys in the system $CeSi_x$ ($1.60 \leq x \leq 1.90$). Few resistivity measurements have been reported for these materials, and then only on isolated compositions.[2,9,10] The preponderance of experimental data focuses on magnetic susceptibility and heat-capacity experiments. Since Kondo-type behavior is evident in these materials, a comparative, self-consistent set of resistivity data is necessary to fully understand the nature of the low-temperature states of Ce in the series $CeSi_x$.

## EXPERIMENTAL DETAILS

The samples in the Ce-based system were prepared by arc melting stoichiometric amounts of the elements. These large ingots ($\sim 10$ g) were then drop cast into right circular cylinders suitable for heat-capacity experiments. Each sample was sealed under vacuum in a tantalum crucible and heat treated in a vacuum furnace at 1100 °C for 18 days. After this time period, the furnace power was turned off and the samples allowed to cool to room temperature. The cooling process lasted about one hour. Small rectangular parallelpipeds of approximate dimensions $1 \times 1 \times 5$ mm$^3$ were cut from these master ingots using a slow-speed diamond wheel and used for the resistivity measurements. Some corresponding samples in the $LaSi_x$ series were also prepared by arc melting. These smaller ingots ($\sim 1$g) were annealed at 1000 °C for 20 days.

The lattice parameters of the unit cell were determined from powder x-ray diffraction patterns by the method of least squares using 12 reflections and including an internal silicon standard ($a = 0.543\,083$ nm). Except for $CeSi_{1.60}$, no impurity reflections were observed. In the case of $CeSi_{1.60}$ we have exceeded the limit of the homogeneity range for this phase. Photomicrographs taken on the Ce-based alloys confirm the single-phase nature of these samples for $1.67 \leq x \leq 1.90$. The $CeSi_{2.00}$ alloy was also prepared, but it was found by metallography to consist of two phases and thus no physical property measurements were made on this sample. Table I presents the lattice parameters of all samples used in this study along with other experimental quantities discussed below. Yashima and Satoh[5] have reported the variation of the lattice parameters as a function of the Si concentration from $x = 2.00$ to $x = 1.70$. Their values for the $a$ parameter are in good agreement, but their $c$ parameters differ by $\sim 0.02$ nm, our values being larger. More disturbing is the fact that their $c$ parameters increase with decreasing $x$, while our values show a decrease as a function of decreasing $x$. Since this material becomes deficient in Si as the $x$ value decreases, a decreasing $c$ with decreasing $x$ would more reasonably be the expected trend. The variation of the

 

crystallographic parameters as a function of composition for the $CeSi_x$ alloys is shown in Fig. 1. The tetragonal-to-orthorhombic transformation which occurs between $x = 1.75$ and 1.80 is readily detected. It is also evident that as the number of Si vacancies increases (i.e., as the Si content decreases) the Ce-Ce distances along the $c$ axis decrease from 0.4056 nm for $CeSi_{1.90}$ to 0.4044 nm for $CeSi_{1.80}$ to 0.4039 nm for $CeSi_{1.67}$ (considering only the shortest distance in the orthorhombic cell). The corresponding distances in the basal plane are 0.4191, 0.4175, and 0.4115 nm respectively. In $CeSi_{1.67}$ the various distances are 0.4039 nm in the $c$ direction, $a$ face; 0.4059 nm in the $c$ direction, $b$ face; 0.4115 nm in the $b$ direction; 0.4190 nm in the $a$ direction.

Electrical resistivity measurements (dc) were made between 2.4 and 300 K using a standard four-probe technique in a system fully automated for temperature stability and data acquisition.[15] Data were taken with the current applied in both directions to eliminate possible thermal effects. All data presented are for the warming curves. The magnetic ordering temperatures were determined from ac susceptibility measurements on powdered samples placed in either a standard $^4He$ cryostat or a dilution refrigerator[16] for temperature below 1.1 K.

## RESULTS AND DISCUSSION

Normalized resistivity data for 12 alloys with distinct Si concentrations are presented in Figs. 2 and 3. Data for $CeSi_{1.80}$ appear in both figures to provide a comparison between the graphs. Data for the $LaSi_x$ compounds are not presented since they are devoid of any interesting features. For examples, $LaSi_{1.90}$ has a monotonic resistivity versus temperature that varies essentially linearly from a residual value of 44 $\mu\Omega$ cm at 10 K to 140 $\mu\Omega$ cm at 300 K. Referring to Fig. 2, we note that the presence of a sharp cusp in the $\rho$ versus T data corresponds directly to the onset of magnetic order. The magnitude of this peak grows as $x$ approaches 1.80. With one exception, the position of this peak is in excellent agreement with the magnetic transition temperature detected from ac susceptibility measurements (see Table I). Only $CeSi_{1.60}$ fails to display a cusp in the resistivity data. This is probably due to the presence of secondary, impurity phases in this sample which dilute any sharp features in the transport properties.

In the concentration range shown in Fig. 2

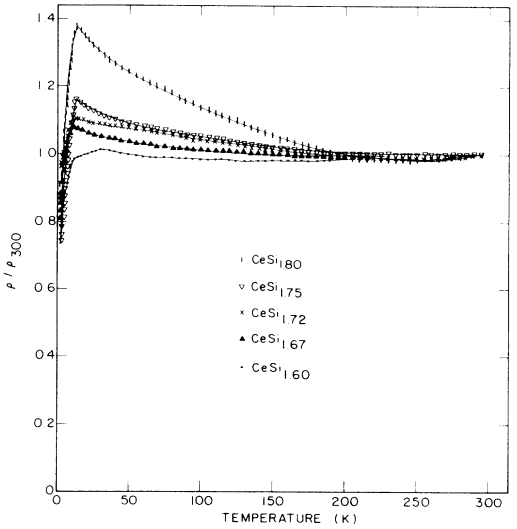


FIG. 2. Electrical resistivity normalized to the value at room temperature as a function of temperature for five alloys in the system $CeSi_x$.

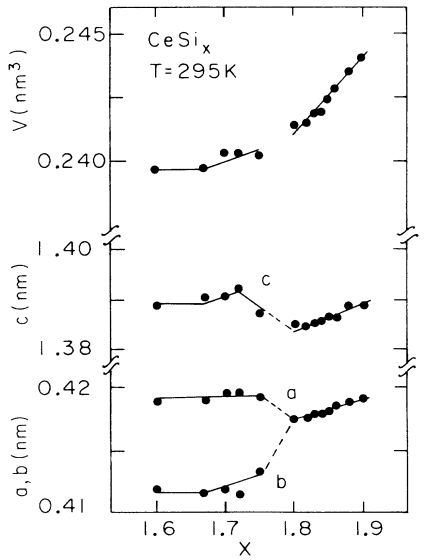


FIG. 1. The room temperature lattice parameters and unit-cell volume for alloys in the series $CeSi_x$.

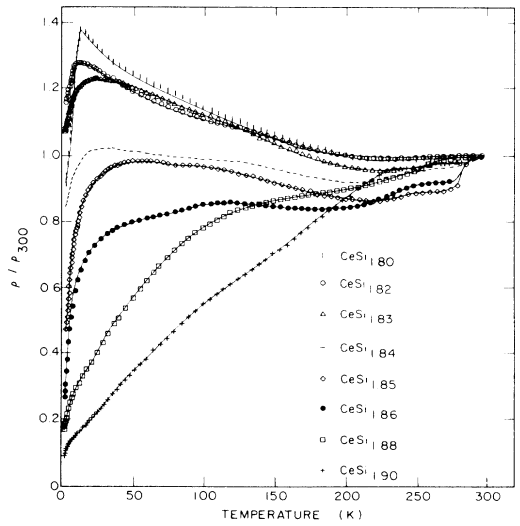


FIG. 3. Electrical resistivity normalized to the value at room temperature as a function of temperature for eight alloys in the system $CeSi_x$.

TABLE I. Lattice parameters, magnetic ordering temperatures, and resistivity values for $CeSi_x$ compounds.

| Composition (x) | $a$[a] (nm) | $b$[a] (nm) | $c$[a] (nm) | $V$[a] ($nm^3$) | $T_m$ (K) | $\rho$ (300 K) ($\mu\Omega$ cm) |
|---|---|---|---|---|---|---|
| 1.90 | 0.4191(2) | | 1.3889(6) | 0.2440(2) | b | 910 |
| 1.88 | 0.4188(1) | | 1.3886(4) | 0.2435(1) | b | 640 |
| 1.86 | 0.4185(1) | | 1.3865(4) | 0.2428(1) | b | 374 |
| 1.85 | 0.4181(1) | | 1.3866(5) | 0.2424(1) | 1.0 | 2136 |
| 1.84 | 0.4178(1) | | 1.3856(4) | 0.2419(1) | 5.1 | 910 |
| 1.83 | 0.4178(1) | | 1.3854(3) | 0.2418(1) | 5.5 | 730 |
| 1.82 | 0.4176(2) | | 1.3848(5) | 0.2415(1) | 8.4 | 630 |
| 1.80 | 0.4175(2) | | 1.3852(7) | 0.2414(1) | 12.6 | 390 |
| 1.75 | 0.4192(2) | 0.4132(3) | 1.3870(8) | 0.2402(3) | 11.9 | 188 |
| 1.72 | 0.4196(1) | 0.4114(3) | 1.3920(4) | 0.2403(2) | 11.6 | 737 |
| 1.70 | 0.4195(2) | 0.4119(2) | 1.3905(6) | 0.2403(2) | 11.6 | 265 |
| 1.67 | 0.4190(2) | 0.4115(3) | 1.3904(7) | 0.2397(2) | 11.8 | 410 |
| 1.60 | 0.4189(5) | 0.4119(2) | 1.3886(14) | 0.2396(3) | 11.8 | 370 |

[a]The number given in parentheses is the standard deviation in the least significant digit(s) of the reported value.
[b]Does not order down to 50 mK.

$(1.67 \leq x \leq 1.80)$, the magnetic ordering temperature remains essentially constant (see Table I). This may be due to the fact that in the orthorhombic phase the average Ce-Ce distance in the $c$ direction (0.4049 nm) increases slightly from that in $CeSi_{1.80}$ (0.4044 nm) which has the tetragonal structure. Although one Ce-Ce distance in the $c$ direction ($a$ face) decreases, the other Ce-Ce separation ($c$ direction, $b$ face) increases, and it may be this competition which keeps $T_m$ constant. The effect of this competition is illustrated clearly in Fig. 4 where $T_m$ is plotted against the shortest Ce-Ce separation distance. For the tetragonal phase there is a definite correlation between this distance and $T_m$ which is exceptionally sensitive to the Ce-Ce separation. Indeed, the data indicate that if the orthorhombic transformation were not present, one would expect the ordering temperature to continue to increase as the Ce-Ce distance was reduced. The onset of the orthorhombic phase arrests this sensitivity since $T_m$ remains

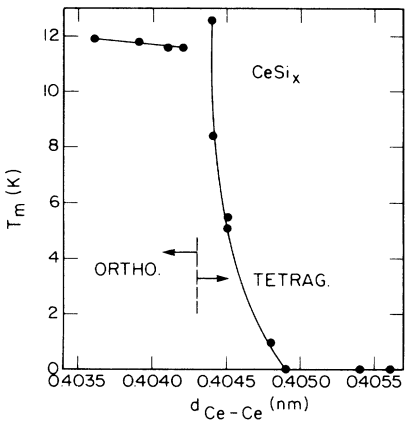


FIG. 4. Magnetic ordering temperature, $T_m$ vs the shortest Ce-Ce separation distance.

essentially constant for the orthorhombic alloys while the shortest Ce-Ce separation continues to decrease. However, as noted above, there are two Ce-Ce separations along the $c$ axis and they compensate for each other. As the Si content is increased beyond $x = 1.80$, the magnetic interactions responsible for ordering weaken, resulting in a rapid decrease in the ordering temperature, $T_m$. This again can be correlated with the increasing Ce-Ce separation as the Si content increases (from 0.4044 nm for $CeSi_{1.80}$ to 0.4056 nm for $CeSi_{1.90}$ in the $c$ direction). This loss of magnetic order is reflected in the resistivity data of Fig. 3 where the sharp peak for the $CeSi_{1.80}$ sample gives way to an increasingly rounded maximum which becomes less pronounced as Si content increases above $x = 1.80$. The position of the maximum resistivity also increases with increasing $x$ so that it no longer corresponds to the value of $T_m$. Indeed, the highest Si concentration which exhibits magnetic order ($x = 1.85$, $T_m = 1.00$ K) shows a resistivity maximum which occurs at about 45 K, well above the ordering temperature. Therefore, while the presence of a low-temperature maximum in the resistivity data exists in the presence of magnetic order, it is only a sharp peak in the resistivity that accurately marks the correct magnetic ordering temperature.

To illustrate the competition between the RKKY exchange interactions which are responsible for long-range magnetic order in this system and the Kondo-type interactions which favor a nonmagnetic ground state, we plot the values of the magnetic ordering temperature, $T_m$, and the Kondo temperature, $T_K$ in Fig. 5. We obtain a self-consistent estimate of $T_K$ by using the temperature of the maximum in the resistivity versus temperature curve. This method may overestimate values of $T_K$ for the compounds where $T_k \sim T_m$ (i.e., $x \leq 1.80$) since the sharp drop in the resistivity that marks the onset of magnetic order at low temperatures tends to obscure the Kondo maximum. However, for these compositions $T_K$ is small, and any uncertainty introduced by this method is unimportant

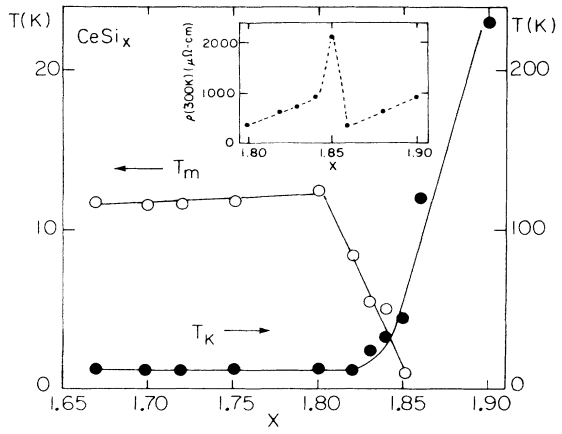


FIG. 5. Kondo temperature, $T_K$(●), and magnetic ordering temperature, $T_m$(○), vs composition for alloys in the system $CeSi_x$. Inset shows the room temperature resistivity for the tetragonal alloys.

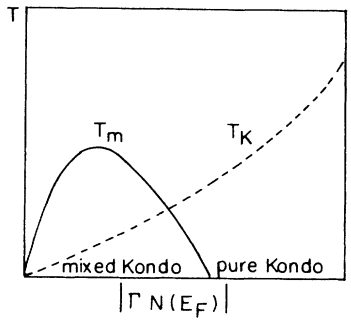


FIG. 6. Schematic dependence of the Kondo temperature, $T_K$, and magnetic ordering temperature, $T_m$, on the interaction strength $|\Gamma N(E_F)|$ after Ref. 18.

with respect to the overall conclusions. Using various expressions involving the magnetic susceptibility and heat capacity, Yashima and co-workers[1] obtain estimates of $T_K$ for five alloys in the series $CeSi_x$. While their estimates vary considerably depending on the method used, their overall trend of $T_K$ versus composition agrees with our data presented in Fig. 5.

The room temperature resistivity versus composition dependence in the tetragonal phase region shows a sharp maximum at $x=1.85$, see inset of Fig. 5. Because microcracks may be present in these samples (which could be formed by anisotropic contraction during the cooling of the samples to room temperature or possibly when cutting the samples for resistivity measurements), the peak in $\rho$ (300 K) versus composition may not reflect the intrinsic properties of the samples. However, for the $x=1.85$ composition, we measured this exceptionally high resistivity on two distinct pieces cut from a master ingot. In addition, low-temperature heat-capacity data show a broad peak in the electronic specific heat constant versus composition plot at $x=1.85$.[6,17] This confirms our belief that the sharp maximum in $\rho$ (300 K) which occurs at the composition where magnetic order appears is real. This high resistivity sample marks the crossover from magnetic to nonmagnetic behavior of the heavy $4f$ electrons. It may be possible that a metal-insulator transition driven by the heavy electrons occurs near this composition.

We have also examined the effect of subtracting the resistivity data of $LaSi_x$ from those of $CeSi_x$ for a given concentration, thus obtaining the magnetic contribution to the resistivity. This procedure leaves the position of the resistivity maximum unchanged, while making the maximum itself more pronounced. For the highest concentrations, we have utilized this technique to obtain an accurate determination of the temperature at which the maximum in the resistivity occurs. Referring to Fig. 5, as the Si concentration increases, $T_m$ remains essentially constant for $x<1.80$, then decreases rapidly until no magnetic order is observed for $x>1.85$. For low Si concentrations ($x<1.82$) where long-range magnetic order is the stable low-temperature ground state, $T_K$ remains constant and small. For $x>1.82$ the RKKY exchange interaction weakens, as evidenced by the rapid drop in $T_m$, and the Kondo temperature increases rapidly. This behavior is consistent with the theoretical treatment of the Kondo lattice[18,19] which predicts a schematic dependence of $T_m$ and $T_K$ on the interaction strength $|\Gamma N(E_F)|$ as shown in Fig. 6, where $\Gamma$ is the coupling constant between the $4f$ and conduction electrons and $N(E_F)$ is the density of electronic states at the Fermi level. The similarity between the experimental data of Fig. 5 and the theoretical predictions of Fig. 6 illustrates that the interaction strength varies as the silicon concentration in the $CeSi_x$ system.

In conclusion, our systematic resistivity study of 12 $CeSi_x$ alloys clearly shows the competition between the Kondo effect and the RKKY exchange interaction which favors long-range magnetic order. For lower Si concentrations the alloys order magnetically and the resistivity data support the existence of a dense Kondo system. For $x>1.82$, the Kondo temperature increases rapidly, resulting in the dominance of the Kondo effect leading to the absence of magnetic order. This rapid increase of the Kondo temperature as the Si concentration increases in the tetragonal phase is accompanied by a volume increase as well. This is contrary to what is generally observed on the relationship between Kondo temperature and volume. Our data provide experimental evidence of the variation of $T_m$ and $T_K$ with the interaction strength $|\Gamma N(E_F)|$ which is responsible for both the exchange interaction and the Kondo effect.

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