Evolution of heavy-fermion behavior in the series $CePt_xSi$: A ferromagnetic dense Kondo system

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Evidence for a transition from heavy-fermion behavior to a ferromagnetically ordered state has been found in the system $CePt_xSi$ ($0.70 \leq x \leq 1.0$). The transition from a nonmagnetic state to a magnetically ordered state occurs around $x = 0.97$. Measurements of the lattice parameters, magnetic susceptibility, and resistivity on this system are reported. The magnetization measurements on $CePt_{0.7}Si$ reveal a large reduction of the Ce magnetic moment. These experimental results suggest that the Kondo effect coexists with the interionic ferromagnetic interaction.

The history of heavy fermions is a relatively young one. It has been only 12 years since the first known heavy-fermion system, $CeAl_3$, was discovered.[1] Interest in the research and characterization of such "heavy-fermion" systems increased dramatically after Steglich *et al.*[2] discovered superconductivity in the heavy-fermion ternary compound $CeCu_2Si_2$. A central issue in heavy-fermion systems (HFS) concerns the mechanism which leads to the enormous coefficient of electronic specific heat γ. However, due in part to the relatively few known heavy-fermion metals, a complete understanding of the origin of the heavy-fermion state has not been achieved. CePtSi, which crystallizes in the tetragonal LaPtSi-type crystal structure,[3] is a heavy fermion and coherent Kondo lattice compound with an enormous coefficient of the electronic specific heat $\gamma \sim 800$ mJ/mol K^2 (Ref. 4). This heavy fermion shows neither magnetic order nor superconductivity above 70 mK. Evidence also has been found for the transition from heavy-fermion behavior to mixed-valence state in magnetic resistivity and susceptibility in the series $Ce(Pt_{1-x}Ni_x)Si$.[5] In order to get a better understanding about the heavy-fermion state found in CePtSi, an investigation has been made on $CePt_xSi$ ($0.70 \leq x \leq 1.0$). According to our study, the LaPtSi-type crystal structure is stable over a wide range of nonstoichiometric compositions. With reference to the LaPtSi-type crystal structure it is reasonable to expect that a deficiency of Pt will cause a change of the number of electrons in the conduction band. Since the intermediate valence state is believed to originate from the proximity of the $4f$ level to the Fermi energy level, it is interesting to see how the paramagnetic behavior observed in CePtSi changes with Pt deficiency. In this paper, we report the results of our systematic investigation on crystal structure, magnetization data including hysteresis curves, magnetic susceptibility, and resistivity in the series $CePt_xSi$ where $0.70 \leq x \leq 1.0$.

All samples studied are polycrystalline specimens obtained by melting appropriate amounts of elements in an arc furnace under an argon atmosphere. The purities of the starting materials are $>99.9\%$ cerium, 99.999% platinum, and 99.999 999 9% silicon. Homogenization was achieved by repeated remelting. Weight losses were negligible ($< \frac{1}{10}\%$) in this process. Each sample ($x < 1.0$) was wrapped in molybdenum foil plus zirconium foil, sealed under argon in a quartz tube and annealed for 85 h at 1200 °C, followed by a water quench. To ensure that no contamination of samples occurred with Mo on the surface, samples were cleaned by using sandpaper. Powder x-ray diffraction patterns with Cu $K\alpha$ radiation indicated that each sample was single phase, with no impurity reflections. The only difference in the powder x-ray diffraction pattern among these samples is that the first two lines, (101) and (004), become relatively weaker as x decreases. We observe no evidence, such as x-ray line broadening, for a lattice distortion or structural change in the tetragonal unit cell. The lattice parameters of the unit cell were determined by the method of least squares[6] using the eight most intense reflections for $2\theta < 55°$ and including an internal silicon standard ($a = 0.543\,083$ nm). The lattice parameters thus obtained are listed in Table I. In Fig. 1, we show the monotonic decrease of the unit cell volume as Pt is removed from the lattice. Both lattice parameters vary smoothly as well. The uncertainty in each data point is smaller than the systematic variation across the composition range, thus supporting the claim of vacancy defect formation in the LaPtSi-type structure. In particular, the nearly linear decrease in unit-cell volume as x decreases unambiguously shows that the nonstoichiometry results from the vacancies. To complement the powder x-ray diffraction data, the microstructure of two samples ($x = 0.7$ and 0.9) was

TABLE I. Lattice parameters, magnetic ordering temperature T_m, and resistivity at $T=300$ K in the series $CePt_xSi$.

Composition (x)	a (nm)	c (nm)	V (nm^3)	T_m (K)	ρ(300 K) ($\mu\Omega$ cm)
1.00	0.4202(1)	1.4484(4)	0.2558(1)	a	675
0.97	0.4199(1)	1.4487(3)	0.2554(1)	b	
0.96	0.4199(1)	1.4478(4)	0.2553(1)	5.2	
0.95	0.4198(1)	1.4482(2)	0.2552(1)	4.5	
0.94	0.4198(1)	1.4481(4)	0.2552(2)	5.6	
0.90	0.4196(1)	1.4487(3)	0.2550(1)	5.5	
0.85	0.4192(1)	1.4495(3)	0.2547(1)	5.3	1670
0.80	0.4189(1)	1.4495(3)	0.2543(1)	5.8	455
0.75	0.4187(1)	1.4493(3)	0.2540(1)	5.7	
0.70	0.4184(1)	1.4496(4)	0.2538(1)	5.6	390

[a]No magnetic transition was observed above 70 mK (Ref. 4).
[b]No magnetic transition was observed above 1.26 K.

examined by optical metallography. For each sample, these optical investigations revealed a single dominant phase with a typical grain size of approximately 500 μm. A small amount of a secondary phase estimated at a maximum of 2% by volume may be present in the grain boundaries. This information is consistent with the powder x-ray patterns. The minimal amount of grain-boundary material confirms the stability of the LaPtSi-type structure in the presence of substoichiometric Pt concentration.

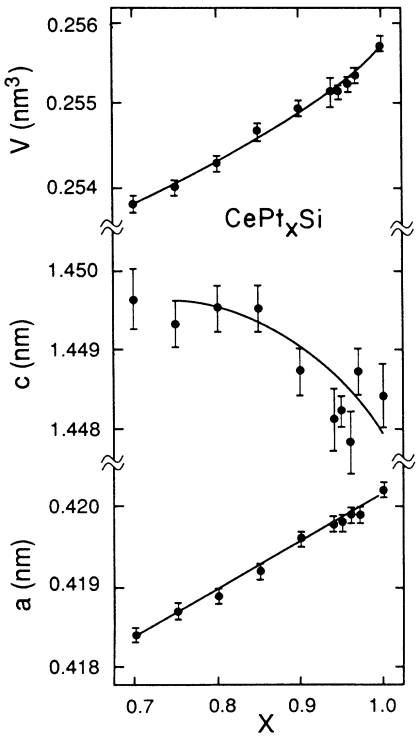

FIG. 1. Tetragonal parameters and unit-cell volume as a function of Pt concentration for compounds in the series $CePt_xSi$. Error bars represent uncertainty in determining the parameters from a least-squares fit. Lines are drawn as a guide to the eye.

The ambient pressure magnetic ordering transition temperatures, T_m of the samples were determined from low-frequency ($\sim$25 Hz) ac magnetic susceptibility measurements in a conventional ^{4}He Dewar for the temperature range between 1.26 and 30 K. In each case, temperatures were determined by means of calibrated Ge thermometers known to be accurate to within 0.1%. The peak point of the transition is taken as the magnetic ordering transition temperature. The data thus obtained are listed in Table I and plotted in Fig. 2. A very sharp transition in composition from nonmagnetic to magnetic ordering was found between $x=0.96$ and 0.97. For $x=0.97$ no magnetic ordering was observed down to 1.26 K and for $x=0.96$ the magnetic ordering transition temperature was found to be 5.2 K. In order to clarify the nature of the magnetic order found in $CePt_xSi$ ($x \leq 0.96$), the magnetization measurements of a polycrystal $CePt_{0.7}Si$ ingot (mass=64.1 mg) were taken in static fields up to 5.4 T at $T=2.0$ K. The magnetization curve and the hysteresis loop of the sample $CePt_{0.7}Si$, both taken at

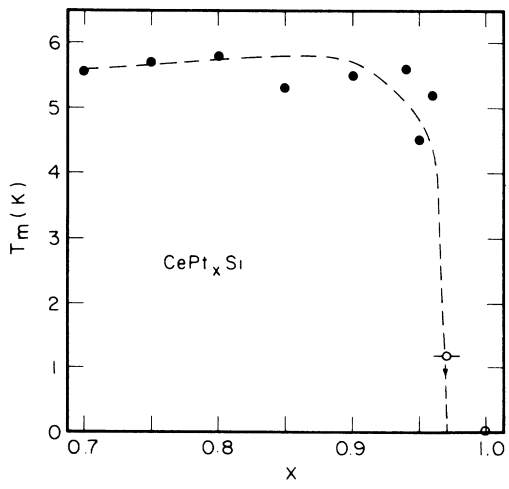

FIG. 2. Magnetic ordering temperature T_m as a function of Pt constituent in the system $CePt_xSi$.

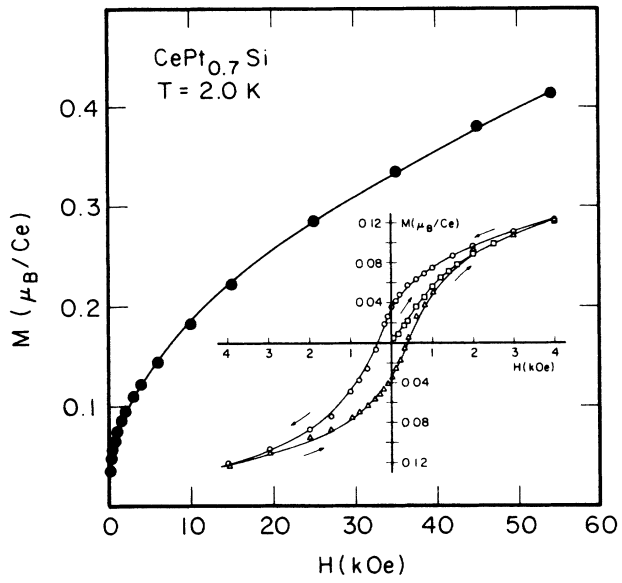

FIG. 3. Magnetization curve and hysteresis loop (inset) of $CePt_{0.70}Si$ at 2.0 K.

2.0 K, clearly demonstrate a ferromagnetically ordered state and are plotted in Fig. 3. At this temperature, a spontaneous magnetization appears; however, exact determination of the spontaneous magnetic moment is complicated by the presence of a field dependence of the magnetization even at the highest fields. Above an applied field of 35 kOe, the curvature in Fig. 3 is slight. To provide an estimate of the spontaneous magnetization, we extrapolate this high-field region to obtain a value of $\sim 0.18\mu_B$/Ce-atom. Additional data taken at still higher fields might alter this estimate slightly; however, the primary conclusion that the spontaneous magnetization of $CePt_{0.7}Si$ is an order of magnitude smaller than the free-ion value for Ce^{3+} ($g_J J\mu_B = 2.14\mu_B$), would remain unchanged. The known Ce-based ferromagnetic dense Kondo systems, e.g., $CeSi_x$,[7] CePt,[8] and $CeGe_2$,[9] also have a small spontaneous moment of $\sim 0.3\mu_B$/Ce-atom, $0.74\mu_B$/Ce-atom, and $0.75\mu_B$/Ce-atom, respectively. In the system $CePt_xSi$, there are at least two possible sources for this reduction. First, the experiments were done on a polycrystalline sample for which crystalline electric field (CEF) effects can remove the sixfold degeneracy of the $^2F_{5/2}$ Hund's-rule ground state of the Ce^{3+} ion, thus reducing the moment on the Ce sites. The atomic coordination of the Ce ion in the stoichiometric compound CePtSi consists of six Pt and six Si atoms, each arranged in groups of two plus four. No CEF energy levels or wave functions have been determined for this complex environment. We note that an effective-point-charge model[10] leads to a Γ_7 doublet and Γ_8 quartet state in the presence of a cubic or octahedral CEF environment. For Ce in CePtSi, the Γ_8 quartet should be split further due to the lower symmetry. Although crystalline electric fields are important in these materials, the CEF effect alone cannot account for the order of magnitude

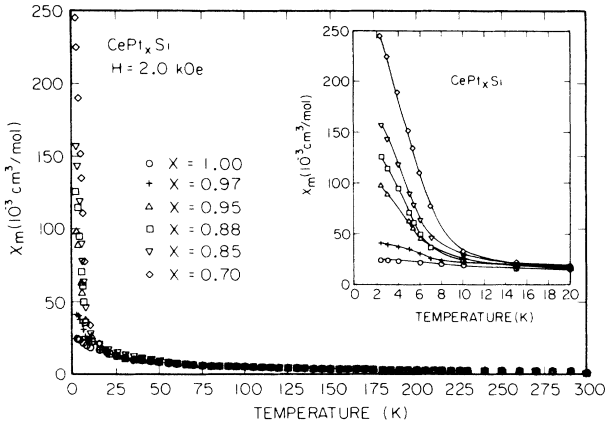

FIG. 4. Molar susceptibility χ_m vs temperature T for six alloys in the series $CePt_xSi$.

decrease in the Ce moment. The second source of the decrease in the Ce moment is that the Kondo effect reduces the magnetic moment and at lower temperatures the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction dominates to yield magnetic ordering. This interpretation is consistent with other Ce-based dense Kondo systems.[7-9]

The static magnetic susceptibility of each sample was measured in a field of 2.0 kOe between 2.4 and 300 K with a commercial SQUID magnetometer.[11] Figure 4 depicts the molar magnetic susceptibility χ_m versus temperature T for the $CePt_xSi$ alloys with $x = 1.0$, 0.97, 0.95, 0.88, 0.85, and 0.70. The high-temperature (> 70 K) susceptibility of all the samples can be fitted very well with the Curie-Weiss law $\chi_m = C'/(T+\Theta)$, where C' is the Curie constant and Θ may be considered as a temperature characteristic of the s-f mixing interaction. Below about 10 K, all samples for $x < 0.97$ show a rather sharp increase in the magnetic susceptibility (see inset of Fig. 4). We attribute these deviations from a Curie-Weiss law at low temperature to the combined results of the crystal field splitting of the $J = \frac{5}{2}$ multiplet level of Ce and the

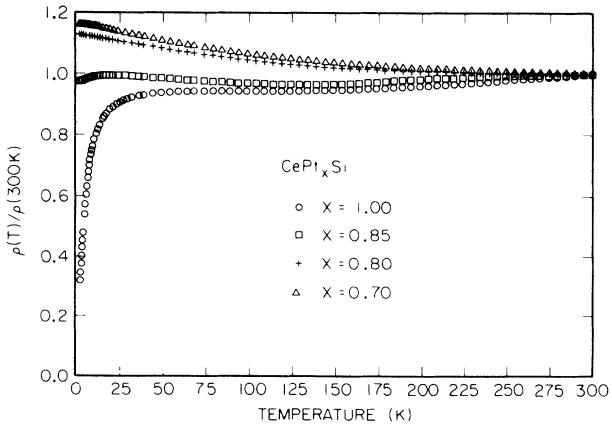

FIG. 5. Electrical resistivity normalized to 300 K vs temperature T for four alloys in the system $CePt_xSi$.

spin fluctuation (Kondo state) of the Ce $4f$ level.

Electrical resistivity measurements (dc) were made on rectangular samples of uniform thickness (approximate size $6\times1\times1$ mm^3) using a standard four-probe technique between 2.4 and 350 K. Data were taken with the current applied in each direction to eliminate possible thermal effects. Figure 5 presents the resistivity curves normalized at 300 K of the three ferromagnetic compounds $CePt_xSi$ ($x=0.70$, 0.80, and 0.85) along with the heavy-fermion compound CePtSi (Ref. 4). One striking feature of the resistivity curves is that the resistivity of $CePt_{0.7}Si$ decreases from 2.4 to 350 K. No local maximum or local minimum was observed in this range. For $x=0.8$, the maximum occurs around $T=3$ K and the local minimum occurs around $T=330$ K. When x increases, the T (ρ_{max}) value increases, but the T (ρ_{min}) value decreases. For $x=0.85$, the maximum occurs around $T=20$ K and the minimum occurs around $T=140$ K.

The development of a resistivity minimum is reminiscent of Kondo-like behavior. This implies the Kondo anomalies exist in the ferromagnetic regime. We attribute the small resistance ratio ($\rho_{300}/\rho_{4.2}$) to the increase in ρ at low temperatures because of Kondo scattering and magnetic ordering. Because there is no established theoretical treatment for a dense Kondo system, the T (ρ_{max}) value has been assumed by some authors[12–14] to be directly related to the value of the Kondo temperature T_K. However, Schilling believes that the RKKY interaction between Ce ions plays an important or even dominant role in determining the value of $T(\rho_{max})$.[15] In this $CePt_xSi$ system, we find that the ferromagnetic ordering temperatures T_m for $0.70\le x\le0.96$ are nearly the same (see Table I), indicating the strength of the RKKY interaction remains unchanged as the vacancy concentration increases from 4% to 30%. Although the RKKY interaction remains constant for this wide composition range, the value of $T(\rho_{max})$ changes significantly. Therefore, the Kondo effect plays an important role in determining the position of $T(\rho_{max})$ for the compounds $CePt_xSi$, consistent with work on other systems.[12–14] In conclusion, we report the crystal structure and results of measurements of magnetic susceptibility and resistivity for the $CePt_xSi$ system. The reduction in the magnetic moment and the resistivity-curve behavior suggest a Kondo effect. We have observed experimentally a transition from heavy fermion behavior to a ferromagnetically ordered state.

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