Crystal structure, resistivity, magnetic susceptibility and heat capacity of a new dense Kondo system: $CePtSi_2$

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We find that $CePtSi_2$ crystallizes in the $CeNiSi_2$-type orthorhombic structure with lattice parameters $a=0.4288(2)$ nm, $b=1.6718(4)$ nm, and $c=0.4238(2)$ nm. The magnetic resistivity data show that the Ce in $CePtSi_2$ has a doublet ground state according to the theory of Cornut and Coqblin. Above 100 K the inverse molar magnetic susceptibility follows a Curie-Weiss law, leading to an effective moment of $2.56\mu_B$ per cerium atom and a paramagnetic Curie temperature of -17 K. Down to 70 mK no sign of a transition into a state of long-range magnetic order or a superconducting state was detected by ac susceptibility measurements. The coefficient of the electronic specific heat has a maximum of about 1700 mJ/mol K^2 at 1.25 K.

INTRODUCTION

The problem of a single magnetic impurity in a metal known as the idealized "Kondo problem" has been of interest to both experimentalists and theorists since the early 1960's. Now the dilute Kondo system is understood in detail; however, there is still no established theoretical treatment for a dense Kondo system. Cerium compounds are frequently found to exhibit Kondo anomalies. For example, the saturation moments for Ce-based ferromagnetic dense Kondo systems are much smaller than the free-Ce^{3+}-ion value ($2.14\mu_B$).[1-5] The entropy $S_m(T_N)$ associated with a modulated magnetic structure for $CeAl_2$ is $(2R\ln 2)/3$, corresponding to a reduction of one-third of the cerium moment[6,7] and the existence of a nonsuperconducting peak (Kondoesque anomaly) in the C versus T data for the heavy-fermion superconductor $CeCu_2Si_2$ remain unexplained problems.[8,9]

In a recent study of ternary Ce-Pt-Si intermetallic compounds it has been established that there exist compounds of compositions CePtSi with the LaPtSi-type structure[10] and $CePt_2Si_2$ with a suggested $CaBe_2Ge_2$-type structure.[11] Both of these Kondo-lattice compounds show several interesting and novel properties.[12,13] During our research on the Ce-Pt-Si intermetallic compounds we have found another new compound $CePtSi_2$, which crystallizes in the $CeNiSi_2$-type[14] structure. In this paper, we report the lattice parameters, the temperature dependence of the electrical resistivity, dc magnetic susceptibility and heat capacity of single-phase, polycrystalline $CePtSi_2$. As determined from ac susceptibility measurements, no sign of a transition into long-range magnetic order or a superconducting ground state was detected above 70 mK. In addition to experiments on $CePtSi_2$, electrical resistivity measurements on the isostructural $LaPtSi_2$ have been made in order to estimate the phonon contribution to the resistivity of $CePtSi_2$.

EXPERIMENTAL DETAILS

Polycrystalline samples investigated for this work were synthesized by arc melting together with stoichiometric amounts of the constituent elements in a Zr-gettered arc furnace on a water-cooled Cu hearth under purified argon of about one atmosphere. The rare-earth elements of $>99.9\%$ (3N) purity were obtained from the Materials Preparation Center of the Ames Laboratory. The 5N purity Pt and 9N purity Si were purchased from Matthey Bishop, Inc., and Research Organic/Inorganic Chemical Corporation, respectively. Weight losses during arc melting were less than 0.1% due to the sufficiently low vapor pressures of these elements at the melting temperature of the ternary compounds. To ensure that no impurity phase was present in the sample, each sample was wrapped in tantalum foil and zirconium foil, sealed under argon in a quartz tube, and annealed for 4 to 5 d at 1200 °C. This heat treatment was followed by a water quench to room temperature. A microcomputer-controlled powder diffractometer equipped with copper target and graphite monochromator for Cu $K\alpha$ radiation was used to obtain the powder x-ray-diffraction patterns at a step scan rate 0.01°/sec. The dc electrical resistivity measurements were made on rectangular samples of uniform thickness (approximate dimensions $1\times1\times6$ mm^3) between 2.4 and 300 K in a system fully automated for temperature stability and data acquisition. The static magnetic susceptibility measurements were carried out in a field of 2.0 kOe between 2.0 and 300 K with a commercial[15] SQUID (superconducting quantum interference device) magnetometer in which the sample is moved slowly through the pickup coil. Low-frequency (~25 Hz) ac susceptibility measurements were performed in a conventional dewar for the 1.26–30-K temperature range and in a commercial[16] ^3He-^4He dilution refrigerator down to 70 mK. The specific heat was measured with a semiadiabat-

ic calorimeter using a standard heat-pulse technique in the temperature range from 0.66 to 30 K.

RESULTS AND DISCUSSION

Analysis of powder x-ray-diffraction patterns shows that the samples crystallize in an orthorhombic $CeNiSi_2$-type structure with space group *Cmcm*. No traces of secondary phases were observed. Four formula units of $CePtSi_2$ (or $LaPtSi_2$) are present in the unit cell. The refined lattice parameters of the unit cell were determined by the method of least squares[17] using the thirteen most intense reflections for $2\theta < 56°$ and including an internal silicon standard ($a = 0.543\,083$ nm). The lattice parameters $a = 0.4288(2)$ nm, $b = 1.6718(4)$ nm, $c = 0.4238(2)$ nm for $CePtSi_2$ and $a = 0.4335(1)$ nm, $b = 1.6823(5)$ nm, $c = 0.4260(2)$ nm for $LaPtSi_2$ were then obtained. In this refinement to determine lattice parameters, only the positions of the x-ray lines were required. A comparison of the calculated line intensities with those determined experimentally showed reasonable agreement, especially considering the nature of powder x-ray data for a quantitative determination of line intensities. In this comparison, we used standard atomic positional parameters for the atoms in the unit cell. Specifically, the atoms were all placed in the 4c position of the space group *Cmcm* (D_{2h}^{17}) with fractional coordinates: Ce or La (0,0.107,0.25), Pt (0,0.316,0.25), Si(1) (0,0.457,0.25), and Si(2) (0,0.749,0.25). The agreement of intensities indicates that no significant antisite disorder or vacancies are present in our samples. Figure 1 displays this standard unit cell with the atoms labeled accordingly.

Figure 2 displays the temperature dependence of the resistivity of $CePtSi_2$ and $LaPtSi_2$. Two maxima in $\rho(T)$ for $CePtSi_2$ are observed, one at around 30 K, which probably is due to the crystal-field effects or anisotropy of the resistivity in the orthohombic structure of $CePtSi_2$, and another at 6.5 K. Data for $CePtSi_2$ are extended to 100 mK to reveal the continued decrease in resistivity. The magnetic contribution $\rho_{mag}(T)$ of $CePtSi_2$, which has been obtained by subtracting the resistivity of the isostructural $LaPtSi_2$ compound is shown in Fig. 3. This curve displays a logarithmic increase with decreasing temperature in the high-temperature region. This phenomenon is caused by the scattering processes of the conduction electrons with independent Kondo centers in the presence of crystal-field splitting. According to the theory of Cornut and Coqblin,[18] the ratio of the high- and low-temperature logarithmic slopes is

$$[(2J+1)^2-1]/(\lambda_0^2-1)\ ,$$

where $J = \frac{5}{2}$ and λ_0 is the degeneracy of the ground state. From the data in Fig. 2, we calculate the ratio of the logarithmic slopes to be $\tan\theta_1/\tan\theta_2 = 11.6$, a value which

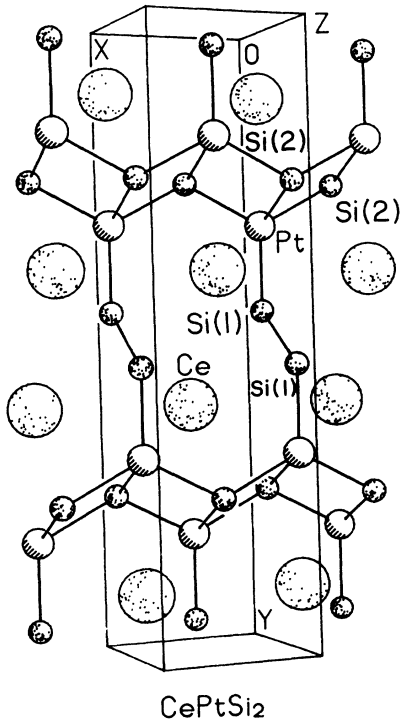

FIG. 1. Crystal structure of $CePtSi_2$, space group *Cmcm*.

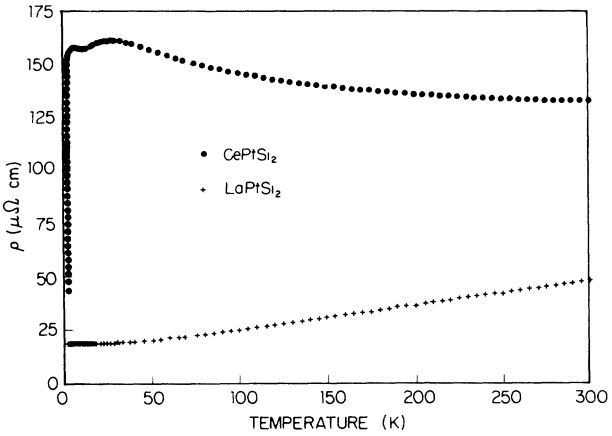

FIG. 2. Resistivity vs temperature of $CePtSi_2$ and $LaPtSi_2$.

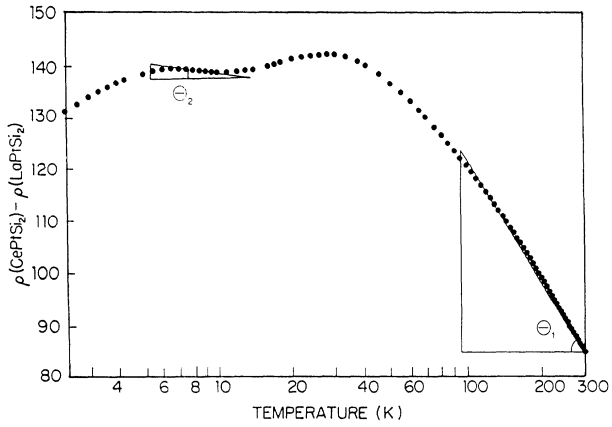

FIG. 3. The resistivity minus the phonon contribution vs $\ln T$ for $CePtSi_2$. The phonon contribution is taken to be the temperature-dependent part of the resistivity of $LaPtSi_2$.

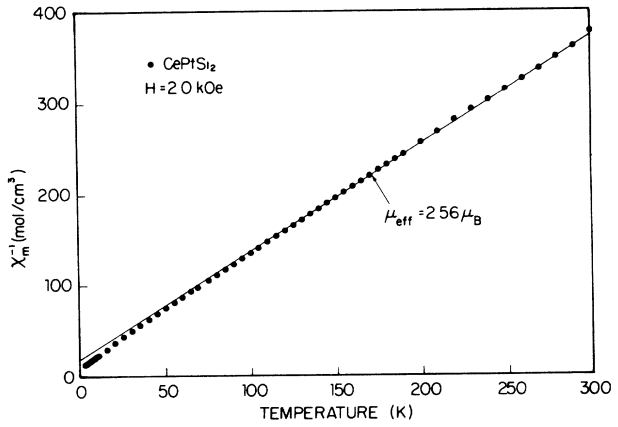

FIG. 4. Temperature dependence of the inverse molar magnetic susceptibility χ^{-1} for $CePtSi_2$ between 2.0 and 300 K.

corresponds to $\lambda_0=2$. This indicates that the decrease of ρ_{mag} just above 6.5 K may originate from the Kondo effect on a ground-state doublet, whereas the decrease at high temperature is due to the Kondo effect on the entire multiplet.

The temperature dependence of the inverse molar magnetic susceptibility χ^{-1} data for the compound $CePtSi_2$ measured in a field of 2.0 kOe between 2.0 and 300 K is presented in Fig. 4. Utilizing low-frequency ($\sim$25 Hz) ac susceptibility techniques in combination with a dilution refrigerator, we extended these measurements to 70 mK. By matching χ_{ac} data to the SQUID data in a common temperature range (2 to 10 K), we observe a smooth continuation of the χ^{-1} versus T data down to 70 mK. This behavior is evidence for an absence of long-range magnetic order or superconductivity above 70 mK. The high-temperature data ($T>100$ K) can be fitted to a linear Curie-Weiss law with an effective moment of $2.56\mu_B$ per cerium atom and a paramagnetic Curie temperature -17 K. This value of μ_{eff} is sufficiently close to the free Ce^{3+} ion value to preclude intermediate valence. Below about 100 K the magnetic susceptibility data reveal deviations from the Curie-Weiss line, a manifestation of the crystalline electric-field effects as interpreted by Bushow and Fast.[19]

Figure 5 shows the specific-heat data plotted as C/T against T^2 for $CePtSi_2$ measured in zero field between 0.66 and 30 K. The mass of the sample used was 1.078 g. The C/T data show an upturn below about 10 K, reaching a maximum close to 1700 mJ/mol K^2 around 1.25 K. Such a maximum has been observed in other nonmagnetic or nonsuperconducting Kondo lattice systems; namely, $CePt_2Si_2$ ($T_{max}=2$ K),[13] $CeAl_3$ ($T_{max}=0.5$ K), $CeCu_2Si_2$ ($T_{max}=0.5$ K) (Ref. 20) and $CeCu_6$ ($T_{max}=0.3$ K).[21] Referring to the inset of Fig. 5, we note that a small feature on the low-temperature side of the main peak occurs at a temperature of about 1 K. The size of this feature places it well within our experimental uncertainty; therefore, it probably does not reflect the presence of another phase transition. This conclusion is supported by our ac magnetic susceptibility results which are featureless in the temperature range from 2 K to 70 mK. Nevertheless, we cannot completely eliminate the possibility of spin fluctuations leading to a weak magnetic transition that would have no signature in the ac magnetic susceptibility. Experimental evidence for this type of situation has been presented for UPt_3 for example.[22–24]

Turning to a quantitative analysis of these heat-

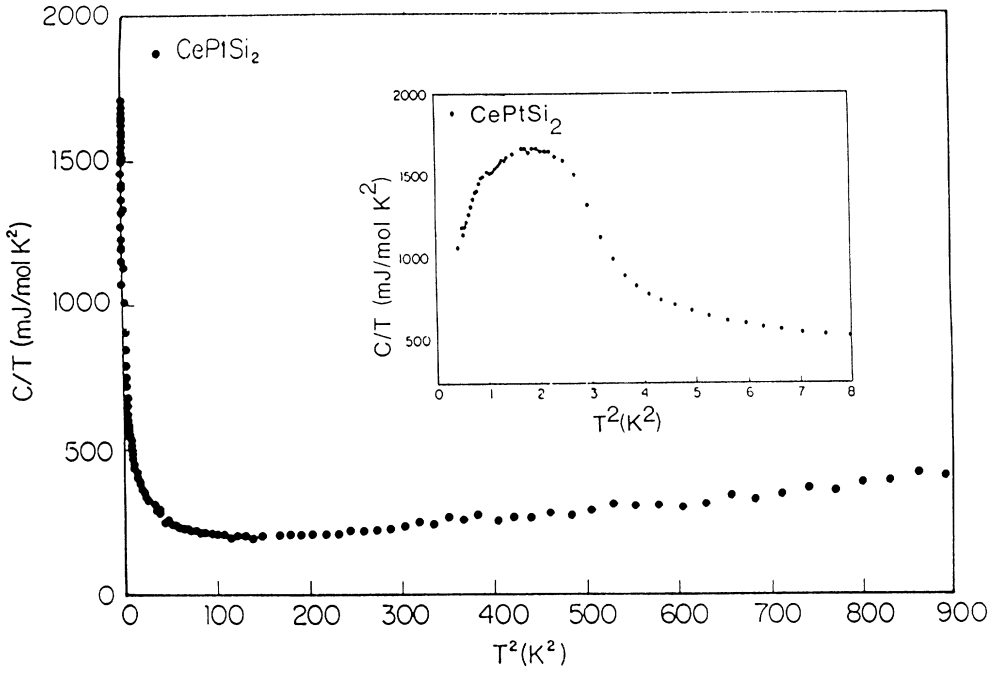

FIG. 5. Specific heat divided by temperature C/T vs T^2 of $CePtSi_2$ between 0.66 and 30 K. Inset: C/T vs T^2 between 0.66 and 2.8 K.

capacity data, we note that a high-temperature (14 K $< T <$ 30 K) extrapolation to 0 K of C/T versus T^2 yields a γ value of about 145 mJ/mol K^2 and a β value of about 0.297 mJ/mol K^4 or a Debye temperature $\theta_D = 298$ K. As was previously pointed out,[25] such high γ values, which exceed those of normal metals by nearly two orders of magnitude, are indications of Kondo interactions. Similar γ values have been observed in the Kondo lattice systems, $CeCuAl_3$,[26] $CeAl_2$,[25] $CeCu_2$,[27] and $CeCu_5$.[28] Below the maximum in C/T versus T^2, an extrapolation of the linear portion of the curve ($T < 1$ K, see inset of Fig. 5) to 0 K yields a larger value of γ of approximately 70 mJ/mol K^2, which is one of the characteristic features of heavy-fermion systems. Considering the single-ion theory of independent Kondo impurities, the coefficient of the electronic specific heat $\gamma_{\max}$ is related to the Kondo temperature by the expression $\gamma_{\max} = 0.68R/T_K$,[27] which gives $T_K = 3.3$ K in $CePtSi_2$. This Kondo temperature is very close to those found in other Ce-based heavy-fermion systems, for example, $CeAl_3$ (3 K), $CeCu_2Si_2$ (4.5 K)[29] and $CeCu_6$ (3.9 K).[30] Another estimation comes from the low-temperature susceptibility[29] i.e., $T_K = 0.15/\chi(0)$. This leads to $T_K = 1.5$ K which is consistent with the estimate based on heat-capacity data. The heat-capacity data are also consistent with the prediction of a ground-state doublet based on the transport properties presented earlier. Using numerical integration, we estimate the entropy as a function of temperature from the heat-capacity raw data. The temperature at which $S = R \ln 2$ is 9 K, in reasonable agreement with estimates of the Kondo temperature for this material.

The "Sommerfeld ratio"

$$R = \frac{\chi(0)}{\gamma(0)} \frac{\pi^2 k_B^2}{\mu_0 \mu_{\text{eff}}^2}$$

is often used for comparison purposes among heavy-fermion materials, Kondo alloys, and valence fluctuation compounds (Ref. 31 for example). Based on our experimental data, we obtain a rough estimate of $R = 2.6$. This value is comparable to other Ce-based intermetallic compounds[31] that show enhanced γ values.

In conclusion, the intermetallic compound $CePtSi_2$, which crystallizes in the $CeNiSi_2$-type structure, exhibits several interesting properties. This compound is found to be a Kondo lattice compound with $T_K \sim 3$ K from the unusual resistivity, specific heat and magnetic data.

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