Magnetic and transport studies on $R_3Pt_{23}Si_{11}$ (R=La and Ce) compounds with dilute rare earth content

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Magnetic susceptibility, electrical resistivity, and low temperature heat capacity measurements have been carried out on $R_3Pt_{23}Si_{11}$ (R=La and Ce) compounds in which the rare earth content is only ~8 mole %. The La compound is a Pauli paramagnet down to 1.8 K while the susceptibility of the Ce compound shows a Curie-Weiss behavior with $\mu_{\text{eff}}=2.48\mu_B$ and $\theta_P=-4$ K. The specific heat of the Ce compound shows a large upturn below 0.6 K, indicative of the onset of magnetic ordering in this compound. The electronic specific heat coefficient, γ, is found to be 19.2 mJ/mole K per formula unit for the La compound. The electrical resistivity of these compounds is typical of metallic systems. No Kondo-like anomaly is seen in the resistivity of $Ce_3Pt_{23}Si_{11}$. Superconductivity, most likely associated with an impurity phase, is observed in $La_3Pt_{23}Si_{11}$ at 1.7 K.

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I. INTRODUCTION

Intermetallic compounds containing cerium often show unusual behavior and a variety of ground states. These include superconducting state,[1] magnetic ordering with anomalously high ordering temperature,[2] heavy fermion ground state,[3] ferromagnetic Kondo lattice system,[4] Kondo insulating ground state,[5] etc. The ground state properties of cerium compounds depend on the hybridization of the Ce-4f electrons with those on the neighboring ions. In our laboratory, we have been carrying out a study of a variety of cerium-based compounds to look for different ground states. Recently, synthesis of the compound $Ce_3Pt_{23}Si_{11}$ has been reported[6] which is found to crystallize in a cubic structure with a unique site for Ce ions. The cerium content in this compound is only about 8 mole %. Therefore, this compound offers the opportunity to study the behavior of Ce ions in a dilute form but still in a crystalline lattice. The dilute metallic systems containing Ce often show properties associated with the Kondo effect.[7] We have carried out magnetic, heat capacity and electrical resistivity measurements on $R_3Pt_{23}Si_{11}$ (R=La and Ce) compounds and the results are presented in this communication.

II. EXPERIMENTAL DETAILS

The $R_3Pt_{23}Si_{11}$ (R=Ce and also La) samples were prepared by melting stoichiometric amounts of the constituent elements in an arc furnace on a water-cooled Cu hearth under a continuous flow of argon gas. Initially, rare earth and Pt metals were melted together. Later, Si was added to this and the alloy buttons melted several times, turning over after every melting, to ensure homogeneity. The weight loss was small in both the cases. The samples were characterized by powder x-ray diffraction (Siemens x-ray diffractometer) using Cu-K_α radiation and by EDAX (INCA200, Oxford) measurements. Magnetization measurements in the temperature range of 1.8 to 300 K and in various applied fields were carried out using a superconducting quantum interference devices magnetometer (MPMS, Quantum Design). Heat capacity measurements were carried out by the relaxation method and electrical resistivity measurements were carried out by the four-probe dc method using a standard set up (PPMS, Quantum Design). In order to search for superconductivity and/or magnetic order at very low temperatures, heat capacity, and electrical resistivity measurements were extended down to He-3 temperature range.

III. RESULTS AND DISCUSSIONS

A. Structure

Powder x-ray diffraction studies revealed that $Ce_3Pt_{23}Si_{11}$ was a single-phase compound with no detectable impurities within the x-ray detection limit. The $La_3Pt_{23}Si_{11}$ compound has been made by us for the first time, to our knowledge, and is found to show x-ray pattern identical to that of its Ce analog. This compound is nearly single phase with about 5% unknown impurity phase. An impurity phase of about 5% was also noted in $Ce_3Pt_{23}Si_{11}$ reported in Ref. 6. EDAX measurements confirmed the stoichiometry of the samples. The x-ray patterns of both the compounds could be analyzed on the basis of a face-centered cubic structure (space group $Fm3m$, No. 225) proposed in Ref. 6. The lattice parameter for the Ce compound obtained in the present work is $a=16.848(1)$ Å, which is in good agreement with the value of 16.837 Å reported for the same.[6] For the La compound of this series, the lattice parameter is $a=16.865(1)$ Å, and is consistent with the lanthanide expansion as one goes towards lighter rare earths in the same series.

There are eight formula units per unit cell in the structure of $R_3Pt_{23}Si_{11}$, but the Ce/La ions occupy a unique crystallographic site with a very rare type of tetragonal prism polyhedra surrounding them. The shortest Ce-Ce distance is about 5.95 Å, which is much too large to have any direct overlap of Ce-4f electrons on adjacent Ce ions. This coupled with the low Ce content suggests that this compound may be treated as a dilute ensemble of weakly interacting Ce ions in a metallic matrix.

B. Magnetization

Figure 1 shows a plot of magnetic susceptibility (χ) versus temperature (T) for $La_3Pt_{23}Si_{11}$ and $Ce_3Pt_{23}Si_{11}$ com-

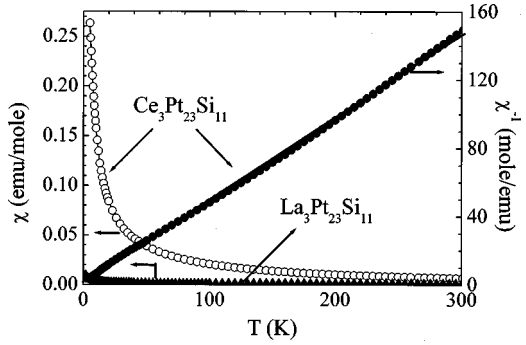

FIG. 1. Magnetic susceptibility (χ) vs temperature (T) for $La_3Pt_{23}Si_{11}$, $Ce_3Pt_{23}Si_{11}$, and χ^{-1} vs. T for $Ce_3Pt_{23}Si_{11}$. The fit to the susceptibility of $Ce_3Pt_{23}Si_{11}$ by the modified Curie-Weiss law is shown as a solid line in the χ^{-1} vs T plot.

pounds and also a plot of χ^{-1} versus T for the Ce compound in the temperature range of 300–1.8 K. The La compound is a Pauli paramagnet down to 1.8 K. The susceptibility of the Ce compound shows a Curie-Weiss behavior $[\chi=\chi_0+C/(T-\theta_P)]$ with $\chi_0\sim 0$, $\mu_{\text{eff}}=2.48\mu_B$ and $\theta_P=-4$ K. The value of μ_{eff} is close to that of the free Ce^{3+} ion ($2.54\mu_B$). The small negative value of θ_P suggests the presence of weak magnetic interactions in this compound. The magnetization-field (M-H) isotherms for the Ce compound exhibit a straight-line behavior at 10 K (Fig. 2) consistent with the paramagnetic behavior of this compound. However, the M-H isotherms below 5 K show a deviation from straight line behavior either due to the paramagnetic saturation effect or due to impending magnetic order in this compound. At 1.7 K and in a 5-T applied field, the magnetic moment per Ce ion has attained the value of $1.15\mu_B$, which may be compared with the magnetic moment of $0.714\mu_B$ expected for the Γ_7 doublet of Ce^{3+}. This suggests the possibility of a Γ_7 ground state of Ce^{3+} in this compound, with the quartet Γ_8 located at a short energy difference of few tens of K from it.

C. Heat capacity

Figure 3 shows a plot of the heat capacity (C) versus temperature (T) for $La_3Pt_{23}Si_{11}$ and $Ce_3Pt_{23}Si_{11}$. The same data are plotted in inset as C/T versus T^2 for the La compound. No anomaly is seen in the heat capacity of the La compounds in the temperature range investigated. The heat capacity of this compound has been analyzed using the expression: $C=\gamma T+\beta T^3$ where γT and βT^3, respectively, represents the contribution to the specific heat by the charge carriers and by the lattice. A fit to the data yields $\gamma=19.176$ (± 0.5656) mJ/mole K per formula unit (fu) and $\beta=3.79442(\pm 0.02)$. The Debye temperature is obtained from the classical expression $\Theta_D=(12\pi^4 nR/5\beta)^{1/3}$, where n is the number of atoms per formula unit and R is the gas constant. The value of β yields $\Theta_D=266.4(\pm 1.4)$ K.

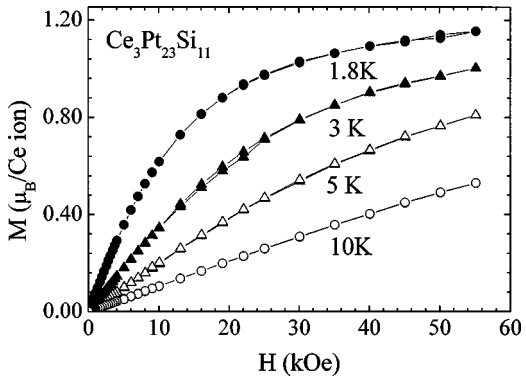

FIG. 2. Magnetization-field isotherms for $Ce_3Pt_{23}Si_{11}$ at various temperatures.

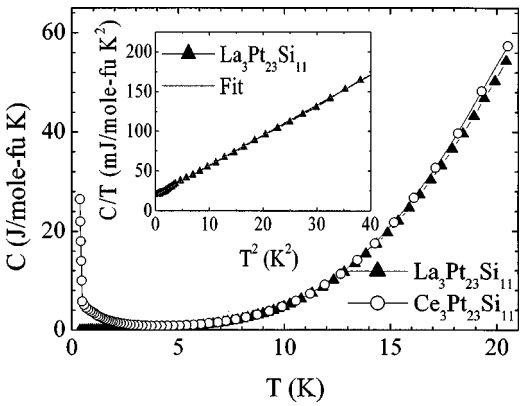

FIG. 3. Specific heat (C) vs temperature (T) for $R_3Pt_{23}Si_{11}$ (R = La and Ce) compounds. Inset shows the C/T vs T^2 for the La compound and a fit to the equation $C=\gamma T+\beta T^3$.

The heat capacity of $Ce_3Pt_{23}Si_{11}$ shows a minimum at about 4 K below which it starts increasing and reaches a value of 26.5 J/mole K per formula unit at 0.37 K—the lowest temperature attainable in our system. This large upturn in heat capacity is indicative of the impending magnetic ordering in this compound. The $4f$ contribution, C_{4f}, to the specific heat of the Ce compound is obtained by subtracting the contribution of the La compound (no $4f$ electrons) from it. Figure 4 shows a plot of C_{4f}/T vs T for $Ce_3Pt_{23}Si_{11}$. Since the heat capacity of this compound has not yet gone through the peak, it is not possible to estimate the entropy associated with the magnetic transition. However, for the sake of getting a rough estimate of the entropy, we extrapolate the heat capacity to zero at 0 K from its value reached at the lowest temperature. The entropy so calculated is plotted as a func-

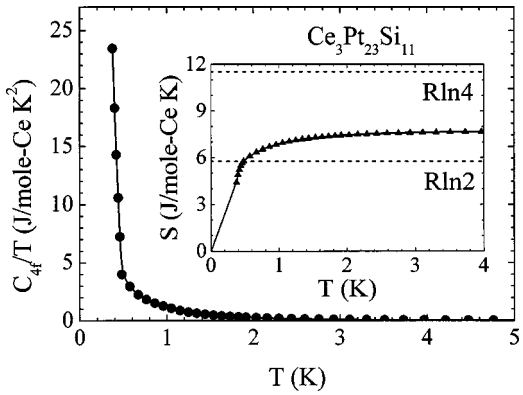

FIG. 4. Ce-$4f$ contribution, C_{4f}, to the heat capacity plotted as C_{4f}/T vs temperature (T) for $Ce_3Pt_{23}Si_{11}$. The inset shows the plot of entropy S vs temperature for the same.

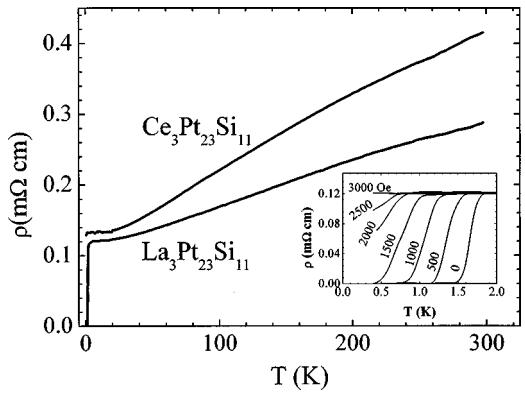

FIG. 5. Electrical resistivity vs temperature for $La_3Pt_{23}Si_{11}$ and $Ce_3Pt_{23}Si_{11}$. The inset shows the variation of resistivity vs. temperature in various applied fields for the La compound near the superconducting transition temperature.

tion of temperature in the inset of Fig. 4. For the Ce^{3+} ion, the total orbital angular momentum J has the value of $\frac{5}{2}$. Therefore, the maximum entropy per cerium ion is $R\ln(2J+1)=R\ln 6$. However, under the influence of a crystalline electric field of cubic symmetry, the degeneracy of the Ce^{3+} ion is lifted giving rise to a quartet or a doublet as the ground state. For crystalline electric fields of lower than cubic symmetry, the ground state of the Ce^{3+} ion is at least two-fold degenerate. The experimental value of the entropy per Ce ion in $Ce_3Pt_{23}Si_{11}$ has already exceeded $R\ln 2$. This is consistent with the magnetization data, which suggest a Γ_7 doublet of Ce^{3+} as the ground state with a low lying Γ_8 quartet.

D. Electrical resistivity

Figure 5 shows the behavior of electrical resistivity as a function of temperature for $La_3Pt_{23}Si_{11}$ and $Ce_3Pt_{23}Si_{11}$. Both these compounds show a metallic behavior in the temperature range investigated. However, Kondo-like minima in the resistivity, often seen in dilute Ce alloys as well as in some of the concentrated Ce compounds, is not seen in this system. In the La compound, a sharp drop in resistance is seen at about 1.7 K, indicative of a superconducting transition. This transition shifts towards lower temperatures with applied magnetic field (inset in Fig. 5). However, since no obvious jump in the specific heat is observed at this temperature, it appears that the superconductivity may be associated with a parasitic phase. Among La, Pt, and Si, and various known compounds involving them, La is superconducting at around 5 K, $LaPt_2$ at around 0.4 K,[8] $LaSi_2$ at around 2.5 K,[9] $LaPt_2Si_2$ in the 1.7—1.58-K range,[10] and LaPtSi at about 3.3 K.[11] The transition observed in the present compound could be from $LaPt_2Si_2$ or some other binary or ternary phase in this system.

IV. CONCLUSIONS

In conclusion, magnetic and transport measurements have been carried out on cubic $La_3Pt_{23}Si_{11}$ and $Ce_3Pt_{23}Si_{11}$. The rare earth content in these compounds is rather small, so that these compounds may be treated as systems with dilute rare earth impurities in a metallic matrix. The La compound has been prepared for the first time, to our knowledge, and is a Pauli paramagnet, while the Ce compound shows a Curie-Weiss behavior in susceptibility in the temperature range of 1.8–300 K with an effective magnetic moment close to that of the Ce^{3+} ion. Heat capacity measurements show the onset of magnetic ordering in the Ce compound below about 0.4 K. The electronic specific heat coefficient is determined to be 19.2 mJ/mole K per formula unit for the La compound. Both these compounds show a metallic behavior, but no Kondo-like anomaly is observed in the resistivity of $Ce_3Pt_{23}Si_{11}$.

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