Heavy-fermion behavior in CeInPt$_4$

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Results of magnetic-susceptibility, electrical-resistivity, and low-temperature specific-heat measurements on a new ternary cubic compound, CeInPt$_4$, are reported. The magnetic susceptibility follows Curie-Weiss behavior between 100 and 300 K with an effective magnetic moment of 2.54μ_B and a rather large paramagnetic Curie temperature of -225 K. Considerable deviation from Curie-Weiss behavior is observed in the susceptibility below 100 K. The specific heat (C) shows an upturn in C/T vs T^2 plot below 2 K. The γ value increases with decreasing temperatures attaining a value of 1750 mJ mole^{-1}K^{-2} at 0.1 K. As $T \rightarrow 0$, γ approaches a value of 2500 mJ mole^{-1}K^{-2} which is one of the highest in heavy-fermion compounds. The electrical resistivity is almost temperature independent between 300 and 100 K and drops linearly with temperature below 100 K, followed by T^2 dependence at still lower temperatures. The susceptibility results are analyzed using a valence-fluctuation model incorporating the effects due to crystalline electric fields.

Several intermetallic compounds containing rare earths and actinides exhibit interesting physical phenomena, such as valence fluctuation, superconductivity, spin fluctuation, Kondo effect, heavy-fermion behavior, etc.[1-13] Most of these properties are attributed to the hybridization between the conduction electron states and the localized 4f electron states. In recent years there has been a great deal of interest in the study of the heavy-fermion phenomena to understand the role of f electrons in the transport and magnetic properties. In these compounds the f electrons participate in the conduction processes with very large effective masses. In most heavy-fermion systems, it has been observed that the very large linear electronic specific-heat coefficient (γ) is accompanied by a large Pauli-type temperature-independent susceptibility $\chi(0)$, which is clearly a characteristic of a nonmagnetic many-body state which forms at low temperatures. The low-temperature resistivity of these compounds exhibits a T^2 behavior with very high resistivity values at room temperature. The resistivity of some of these compounds increases as the temperature is lowered, passing through a broad maximum (Kondo-type behavior), and eventually shows a sharp drop at very low temperatures. The rapid decrease of the resistivity at low temperature is caused by a transition from an incoherent to a coherent scattering of conduction electrons by the localized moments. The mechanisms responsible for the coherent scattering remain still unclear, although both Ruderman-Kittel-Kasuya-Yosida and quadrupolar exchange interactions have been suggested as the possible source.[14] Other interesting properties of these compounds are the coexistence of the heavy-fermion state and superconductivity and also the heavy-fermion state and antiferromagnetic

ground state.[15,16]

The compounds RPt$_5$ ($R =$ La–Nd and Eu) are known to crystallize in hexagonal CaCu$_5$-type structure with space group $P6/mmm$. The presence of two distinct Pt sites in this structure suggests that it may be possible to obtain stoichiometric ternary compounds by replacing the requisite number of Pt atoms in the unit cell by other transition metal or metalloid atoms. These compounds offer a very interesting possibility, namely, the effect of ordered or disordered substitution at a Pt site on the transport and magnetic properties of the rare-earth ions. Low-temperature measurements on CePt$_5$ indicate that this compound exhibits an antiferromagnetic ground state below 1 K with an electronic specific-heat coefficient $\gamma = 30$ mJ/mole K^2 at 0.2 K.[17] The entropy value obtained from the heat capacity is $\Delta S = 4.9$ J/mole K^2 which is 85% of $S = R$ ln2, the total value expected from a crystal-field ground-state doublet. In order to investigate the variation of the physical properties based on the above-mentioned substitutions, we have studied the crystal structure, magnetic susceptibility, electric resistivity, and specific heat of CeInPt$_4$ compound prepared for the first time in our laboratory and have observed crossover from the hexagonal magnetic compound CePt$_5$ to the cubic nonmagnetic heavy-fermion CeInPt$_4$ compound.

The polycrystalline sample of CeInPt$_4$ was prepared by arc melting of the constituent elements on a water-cooled copper hearth under Ar atmosphere. The weight losses during melting were negligible. To estimate the phonon contribution to the resistivity of CeInPt$_4$, we also prepared LaInPt$_4$, which is the nonmagnetic analog of the CeInPt$_4$ compound. Powder-x-ray-diffraction patterns were obtained on a Siemens diffractometer using Cu $K\alpha$ radia-

tion. The unit-cell parameters were determined by a least-squares fit of the observed d values. Magnetic susceptibility was measured in the temperature range of 4.2–300 K in an applied field of 6 kOe using the Faraday method. Electrical-resistivity measurements were made on rectangular samples of uniform thickness using a standard four-probe dc technique. Current and voltage contact to the samples were made using a conducting silver paint. Data were taken with current applied in both directions to eliminate possible thermal effects. The temperatures were measured using a carbon glass thermometer below 20 K and a platinum resistance thermometer above 20 K. Heat capacity was measured in an isothermal calorimeter connected to the mixing chamber of a dilution refrigerator by a mechanical heat switch. The temperatures were measured with a calibrated germanium resistance thermometer.

Powder-diffraction studies revealed that CeInPt$_4$ is a single-phase material. In contrast to CePt$_5$, which has the hexagonal CaCu$_5$-type structure (space group $P6/mmm$), CeInPt$_4$ crystallizes in the cubic structure. The structure of CeInPt$_4$ can be thought to be derived either from that of CePt$_2$ (cubic MgCu$_2$, Laves phase) by a partial substitution of the Ce atoms by the In atoms or from the cubic AuBe$_5$-type structures by a replacement of the Au by Ce and selective substitution of the two Be sites by In and Pt. The latter gives rise to an ordered MgSnCu$_4$-type structure for the ternary CeInPt$_4$. However, if a Laves phase (cubic MgCu$_2$)-type structure is assumed, then Ce and In atoms will be randomly distributed at crystallographic (8a) sites and the formula of the compound may be best represented as Ce$_{0.5}$In$_{0.5}$Pt$_2$. Detailed x-ray and/or neutron-diffraction work is necessary to determine atomic ordering in this system. In the absence of this information and in analogy with other hexagonal CeTPt$_4$ (T = Cu, Ga, Rh, and Pd) compounds[18] derived from CePt$_5$, we will write the nominal composition of this compound as CeInPt$_4$. From the plot (not shown) of unit-cell volume of cubic RInPt$_4$ (R = La to Dy) compounds as a function of the rare earths, it is noted that the unit-cell volume of CeInPt$_4$ does not deviate significantly from the

Lanthanide contraction. From this it is inferred that Ce ions in CeInPt$_4$ are in the trivalent or nearly trivalent state at room temperature.

Figure 1 shows the inverse magnetic susceptibility $\chi(T)^{-1}$ of CeInPt$_4$ as a function of temperature between 4.2 and 300 K. The $\chi(T)^{-1}$ vs T plot is linear between 100 to 300 K, i.e., $\chi(T)$ shows a Curie-Weiss behavior. However, a very large deviation from linearity is observed below 100 K. The overall behavior of magnetic susceptibility is similar to that observed in the case of heavy-fermion compounds CeAl$_3$ and CeCu$_2$Si$_2$.[19,20] In fact, the rather rapid increase in $\chi(T)$ as T approaches 0 K is a general feature of heavy-fermion systems. The values of effective magnetic moment (μ_{eff}) and paramagnetic Curie temperature (θ_p) obtained from the Curie-Weiss fit between 100 and 300 K are $\mu_{\text{eff}} = 2.54\mu_B$ and $\theta_p = -225$ K. The observed value of μ_{eff} is equal to the expected moment of a free Ce^{3+} ion with one electron occupying the $4f$ shell. The paramagnetic Curie temperature of -225 K for CeInPt$_4$ is very high compared to that in other trivalent Ce compounds and this indicates the presence of Kondo-type interactions in this compound.

The results of specific-heat (C) measurements down to 0.1 K are shown in Fig. 2 where C/T is plotted as a function of T^2. No magnetic ordering is observed in the temperature range investigated. The C/T increase continuously below 2 K, which is a characteristic property usually seen in the heavy-fermion compounds, indicating enhancement of the quasiparticle effective mass. From this behavior at low temperatures as well as the magnitude of C/T, the formation of a strong many-body temperature-dependent resonance [Abrikosov-Suhl resonance (ASR)] near the Fermi level is inferred.[4] This resonance starts to increase below a characteristic temperature known as the Kondo temperature (T_K). The rise of ASR causes the increase in the conduction-electron density of states near the Fermi level and, therefore, the increase in the electronic contribution to the heat capacity. The electronic specific-heat coefficient (γ) attains a value of 1750 mJ/mole K^2 at 0.1 K. For $T \rightarrow 0$ K, γ approaches a value of 2500 mJ/mole K^2, which is among the highest values of γ reported to data in any system. The absence of a drop in the C/T curve down to 0.1 K indicates that the coherence
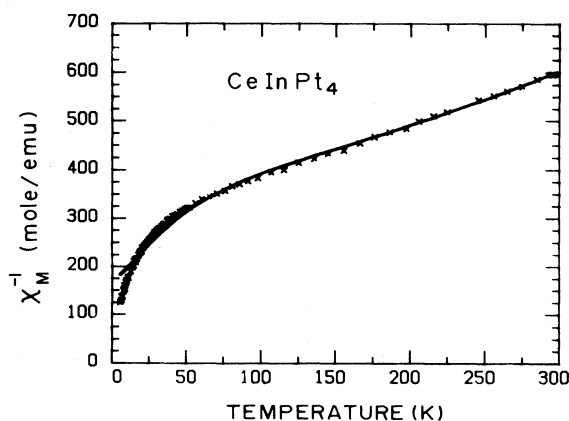

FIG. 1. Inverse magnetic susceptibility of CeInPt$_4$ as a function of temperature [solid line represents typical fit to the data based on valence fluctuation plus crystal-field model (see text)].
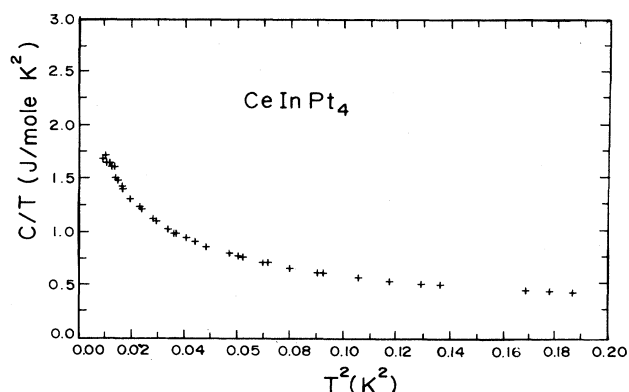

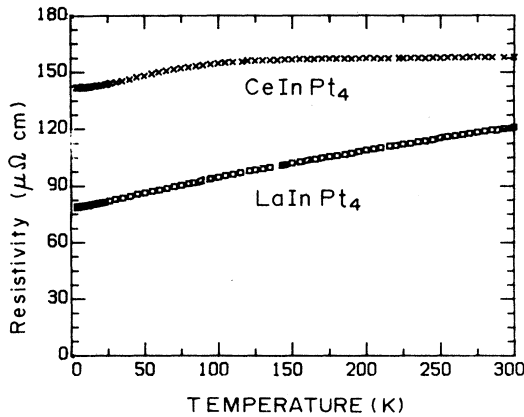FIG. 2. Specific heat divided by temperature (C/T) of CeInPt$_4$ as a function of T^2.

FIG. 3. Electrical resistivity of CeInPt$_4$ and LaInPt$_4$ as a function of temperature.

FIG. 4. Magnetic scattering resistivity (ρ_m) of CeInPt$_4$ as a function of temperature.

temperature (T^*) is below 0.1 K. The systematic studies on the Ce-based heavy-fermion system shows that the magnitude of T^* limits the maximum values of $\gamma(T)$. According to single-ion Kondo theory,[21] Kondo temperature (T_K) is related to the maximum values of $\gamma(T)$ (at $T = 0$ K) by $\gamma_{max} = 0.68R/T_K$, where R is the gas constant. The value of T_K obtained by using $\gamma = 2500$ mJ/mole K^2 is 2.2 K for CeInPt$_4$.

The electrical resistivity of CeInPt$_4$ between 4.2 and 300 K is shown in Fig. 3. To estimate the phonon contribution to the resistivity we have measured the resistivity of the anisostructural nonmagnetic compound LaInPt$_4$, results of which are also shown in Fig. 3. The resistivity of CeInPt$_4$ at 300 K is 155 $\mu\Omega$ cm, which is typically the same as observed in most of the Ce-based heavy-fermion compounds,[22,23] and is almost temperature independent between 300 and 100 K. Below 100 K the resistivity decreases with decreasing temperature and exhibits a linear temperature dependence between 80 and 20 K. At low temperatures, resistivity shows well-defined T^2 dependence. The origin of T^2 dependence of resistivity is believed to be due to the spin-fluctuation phenomena.[24] The magnetic scattering resistivity ρ_m of CeInPt$_4$ obtained by subtracting the resistivity of LaInPt$_4$, with the assumption that the residual resistivity is approximately the same in CeInPt$_4$ and LaInPt$_4$, is shown in Fig. 4. The magnetic contribution to the resistivity increases, as temperature is lowered from room temperature, and reaches a maximum value at about 70 K. The most prominent feature of ρ_m is the presence of a broad maxima at 70 K followed by the minima at 20 K. Below 20 K ρ_m increases with decreasing temperature down to 4.2 K. This type of anomaly in ρ_m has been observed in many Ce-based heavy-fermion and mixed-valence compounds and may be explained by the dynamic alloy model proposed by Wohlleben and Wittershagen.[25]

The deviation of the susceptibility of CeInPt$_4$ from Curie-Weiss behavior below 100 K may be due to the effects of crystalline electric fields (CEF). However, our effort to fit the susceptibility with pure CEF did not succeed. Therefore, we have analyzed the susceptibility data by using the valence fluctuation model in which
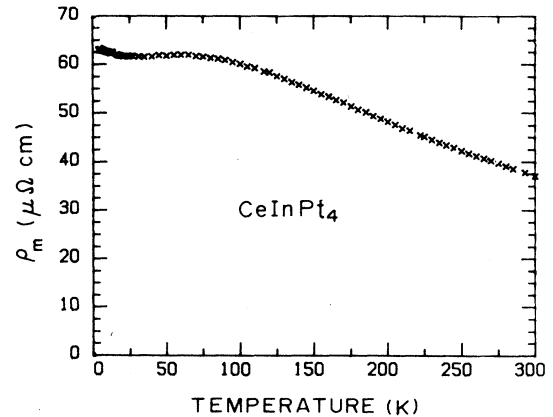
effects due to crystal field are incorporated.[19] An expression for susceptibility in this model may be written as follows:

$$\chi = \chi_4(1-p_3)+\chi_3 p_3+\chi_0, \tag{1}$$

where χ_4 is the susceptibility of Ce^{4+} ions, and χ_3 is the susceptibility of Ce^{3+} ions (in the presence of crystalline electric field), p_3 is the fractional occupancy of the Ce^{3+} state, and χ_0 is the temperature independent contribution to the susceptibility. In the presence of cubic CEF, the $J = \frac{5}{2}$ level of the Ce^{3+} ion will split into a doublet (Γ_7) and a quartet (Γ_8) and the susceptibility χ_3 is given by

$$\chi_3 = \frac{2C_7\exp(-E_{7/kT^*})+4C_8\exp(-E_{8/kT^*})}{Z_3(T^*)(T^*+\Theta)}. \tag{2}$$

Here C_7 and C_8 are the Curie constants corresponding to the Γ_7 and Γ_8 state of the Ce^{3+} ion having energies E_7 and E_8, respectively, $Z_3(T^*)$ is the partition function of the Ce^{3+} ion, Θ is the paramagnetic Curie temperature. In calculation of χ, the level width is taken into account by introducing an effective temperature T^* that is different from the lattice temperature T and is given by $T^* = (T^2+T_{sf}^2)^{1/2}$, where T_{sf} is the valence fluctuation temperature (or width of the level in units of temperature). For simplicity, widths of all the sublevels belonging to the two configurations $4f^0$ and $4f^1$ are assumed to be the same. The probability p_3 is given by

$$p_3 = \frac{Z_3(T^*)\exp(-E_{exc}/T^*)}{1+Z_3(T^*)\exp(-E_{exc}/T^*)}, \tag{3}$$

where E_{exc} is the excitation energy given by the difference between energy E_n of the $4f^n$ state and E_{n-1} of the $4f^{n-1}$ state, i.e., $E_{exc} = E_n - E_{n-1}$.

For analysis of the susceptibility, Eq. (1) for χ with Eqs. (2) and (3) has been used. A least-squares-fit procedure yields the following parameters: $B_4^0 = 1.35$ K, $T_{sf} = 1-8$ K, $\Theta \approx 15$ K, $E_{ex} = 325$ K, and $\chi_0 \approx 0$. This value of B_4^0 gives the crystal-field splitting of 480 K between doublet and quartet. The fit is somewhat insensitive to the T_{sf} parameter; values of which range from 1 to 8 K. The calculated susceptibility with above parameters is

shown as a solid line in Fig. 1. The crystal-field-split doublet level of Ce^{3+} is only few degrees above (almost degenerate) to the ground state (Ce^{4+}) and this contributes to the temperature dependence of susceptibility even at low temperature. Similar behavior has been encountered in $CeCu_2Si_2$.[19]

In conclusion a new Ce-based ternary compound $CeInPt_4$ has been synthesized for the first time, which is found to be crystallized in the cubic-type structure. Measurement of magnetic susceptibility, electrical resistivity, and specific heat indicate the anomalous nature of the Ce ions in this compound. The specific heat shows upturn in the C/T vs T^2 plot below 2 K, and the electronic specific-heat coefficient γ reaches a value of 1700 $mJ/mole\,K^2$ at 0.1 K. Thus, confirming that $CeInPt_4$ is a heavy-fermion system with one of the largest effective masses observed to date.

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