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Superconductivity and spin fluctuations in doped CeIr$_5$

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Abstract

We report a detailed investigation of the binary compound CeIr$_5$. Owing to difficulty in being able to prepare single-phase CeIr$_5$, we studied the low-temperature properties of CeIr$_5$ by investigating the doping-stabilized CeIr$_5$ systems (Th$_{1-x}$Ce$_x$)Ir$_5$, $x \leq 0.7$, and Ce(Pt$_{1-x}$Ir$_x$)$_5$, $x \leq 0.85$. Via measurements of the specific heat and magnetic susceptibility, we observed spin fluctuations in the Ce(Pt$_{1-x}$Ir$_x$)$_5$ system, arising from a Pauli paramagnetic state, and superconductivity in (Th$_{1-x}$Ce$_x$)Ir$_5$.

Keywords: Heavy fermion; Low temperature; Spin fluctuations

1. Introduction

In the past a number of heavy or nearly-heavy fermion systems have been found based on compounds with AB$_5$ stoichiometry. Some of them, like UCu$_5$ [1] or UPt$_4$Au [2], crystallize in the cubic AuBe$_5$(cF24) structure while other alloys have the hexagonal CaCu$_5$(hP6) structure, for example CeCu$_4$Al or CeCu$_4$Ga [3]. The occurrence of AuBe$_5$ or CaCu$_5$ phases is ruled by the Goldschmidt radii ratios of the A and B elements [4]. The CaCu$_5$-type compounds exist in the relative clear-cut radius range above $r_A/r_B = 1.30$, and the AuBe$_5$-type compounds below.

At the present time, most binary alloys with a rare earth or actinide element have been well investigated for heavy fermion behavior. Although literature exists on CeIr$_5$ [5,6], it has not yet been systematically investigated, probably owing to preparation difficulties resulting in an ambiguousness in the crystal structure. Vorobev and Melnikova [5] report on CeIr$_5$ in the AuBe$_5$ structure whereas Blazina et al. [6] found a CaCu$_5$ structure. Moreover, at least the former sample contained second phases of Ce$_2$Ir$_7$ and pure Ir. On the other hand, superconductivity at $T_C = 1.8$ K was reported by Geballe et al. [7] in an unknown structure of CeIr$_5$.

The aim of this work is to clarify this situation and establish CeIr$_5$ as a starting point for the search for possible heavy fermion behavior, as has been done for UPt$_5$ and its heavy derivative UPt$_4$Au in the AuBe$_5$ structure.

2. Experimental and results

From the radius ratio of 1.34 of Ce and Ir, which lies clearly above the aforementioned limit of 1.30, we expected the samples to have the CaCu$_5$ structure. Owing to our failure in preparing single-phase CeIr$_5$ (which presumably is responsible for the above-mentioned controversy [5,6]), we tried to approach this composition as closely as possible by doping ThIr$_5$ (CaCu$_5$, $a = 5.315$ Å, $c = 4.288$ Å) [8] with Ce. Similarly we doped the well-characterized compound CePt$_5$ (CaCu$_5$, $a = 5.367$ Å, $c = 4.385$ Å) [9] with Ir, approaching CeIr$_5$ from a second direction.

Polycrystalline samples of (Th$_{1-x}$Ce$_x$)Ir$_5$ and Ce(Pt$_{1-x}$Ir$_x$)$_5$ were prepared by arcmelting in a purified argon atmosphere and remelted three times. Starting components were Ce (Ames), Ir (3N5), Pt (4N) and Th (4N). The X-ray powder diffraction was performed using a Siemens D5000 diffractometer in Bragg–Brentano geometry with Cu radiation. In the case of (Th$_{1-x}$Ce$_x$)Ir$_5$, we achieved doping concentrations up to 70% Ce, obtaining single-phase samples for $x \leq 0.7$ and multiphased material for higher concentrations. Annealing of the samples did not improve the maximum attainable Ce concentration. The Ce(Pt$_{1-x}$Ir$_x$)$_5$ samples were single-phased for $x \leq 0.85$. In both cases the samples always yielded the hexagon-

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al $CaCu_5$ structure, the cubic $AuBe_5$ phase was never observed.

Concerning the lattice parameters observed, with increasing Ce concentration in $(Th_{1-x}Ce_x)Ir_5$ a weak linear reduction of the a axis and a corresponding enhancement of the c axis occurred, whereas in $Ce(Pt_{1-x}Ir_x)_5$ both axes were diminishing. Extrapolating to the limiting case of $x = 1$ the values for $CeIr_5$ of Ref. [6] are approximately obtained ($a = 5.282$ Å, $c = 4.328$ Å).

The specific heat of the specimen was measured with a relaxation method, details of which are given in Refs. [10,11]. The absolute accuracy is ±4%. The susceptibility $\chi(T)$ was obtained using a Quantum Design SQUID susceptometer in a magnetic field of 0.5 T for $1.65\ \mathrm{K} \leqslant T \leqslant 400$ K.

2.1. $(Th_{1-x}Ce_x)Ir_5$

Fig. 1 shows the specific heat C of the measured samples with the results summarized in Table 1. As is clearly visible, the superconducting transition of $ThIr_5$ at 3.9 K, previously reported by Geballe et al. [7], is suppressed with increasing Ce concentration to lower temperatures. In a T_C vs. x plot, the reduction of T_C with doping concentration reveals a straight line for $x \geqslant 0.2$. By extrapolating to $x = 1$ we would obtain $T_C(CeIr_5) = 1.9$ K. This corresponds well with the value reported by Geballe et al. [7]. Unfortunately, the authors of Ref. [7] gave no comment on the crystal structure of $CeIr_5$. From our results we suggest that superconductivity in $CeIr_5$ (if it was single-phased) is most likely occurring in the $CaCu_5$ structure. The Sommerfeld parameter γ was calculated from the linear dependence (for $T > T_c$) of the specific heat in a C/T vs. T^2 plot (not shown). This linear behavior holds up to at least 10 K. As Table 1 shows, $CeIr_5$ in the $CaCu_5$ structure with $d_{Ce-Ce} = 4.3$ Å does not show an enhanced γ value.

Fig. 2 shows the magnetic susceptibility $\chi(T)$ normalized to one Ce mole. We observe a constant value in a wide temperature range from 400 K down to 30 K with a small upturn below approximately 30 K. Such behavior is obviously indicating Pauli paramagnetism

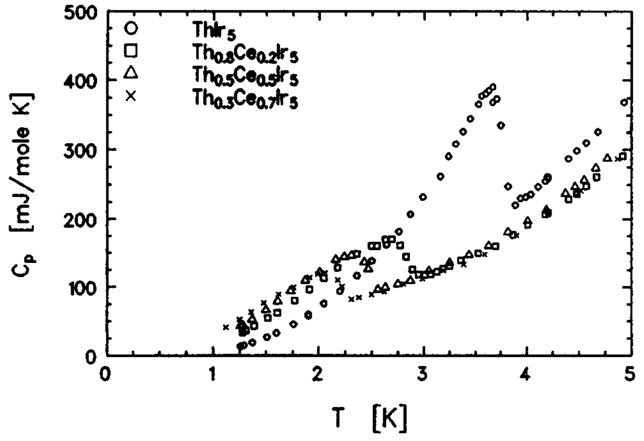

Fig. 1. Specific heat measurements on $(Th_{1-x}Ce_x)Ir_5$.

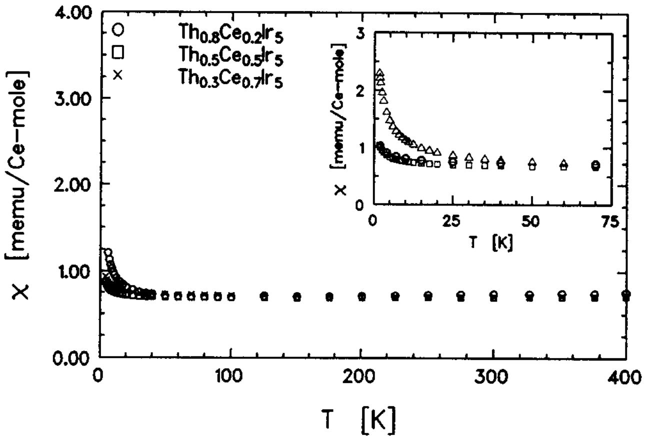

Fig. 2. Magnetic susceptibility normalized per Ce mole versus temperature of $(Th_{1-x}Ce_x)Ir_5$. Data of the superconducting state are excluded. The inset shows the same quantity for $CeIr_{4.25}Pt_{0.75}$ (○), $CeIr_4Pt$ (□) and $CeIr_3Pt_2$ (△).

Table 1
Results of measurements on $(Th_{1-x}Ce_x)Ir_5$ and $Ce(Pt_{1-x}Ir_x)_5$

	γ(mJ mol^{-1} K^{-2})	T_c(K)	$\Delta C/\gamma T_c$	Θ_D	Ref.
$ThIr_5$	25	3.80	2.40	180	
$ThIr_5$	–	3.93^a	–	–	[7]
$Th_{0.8}Ce_{0.2}Ir_5$	21	2.75	1.65	185	
$Th_{0.5}Ce_{0.5}Ir_5$	20	2.40	1.65	190	
$Th_{0.3}Ce_{0.7}Ir_5$	20	2.20	1.60	195	
$CeIr_5$	–	(1.82)^a	–	–	[7]
	γ(mJ mol^{-1} K^{-2})	β(mJ mol^{-1} K^{-4})	δ(mJ mol^{-1} K^{-4})	T_{SF}	Ref.
$CeIr_{4.25}Pt_{0.75}$	27	−0.2	0.36	6	
$CeIr_4Pt$	32	−0.8	0.50	13	
$CeIr_3Pt_2$	44	−2.58	0.94	40	
$CePt_5$	30	–	–	1.0^b	[9]

[a] Obtained by a resonant shift frequency technique.

[b] In this case denoting the antiferromagnetic Néel temperature T_N.

with $\chi \approx 0.75$ memu mole^{-1}. This implies that the f-electrons are completely hybridized in the conduction band showing, therefore, no magnetic dipole moment. Similar spd–f hybridizations have been found, for example, in UIr$_3$ and some other isostructural UX$_3$ compounds [12].

2.2. $Ce(Pt_{1-x}Ir_x)_5$

While the above results for (Th$_{1-x}$Ce$_x$)Ir$_5$, including the occurrence of superconductivity, were not too surprising, the results of Ce(Pt$_{1-x}$Ir$_x$)$_5$ are somehow more striking. The superconductivity is destroyed (at least above 1.2 K) and no linear dependence (in C/T vs. T^2) of the specific heat is observed in any temperature interval from 1.2 to 20 K. Instead, the specific heat could excellently be fitted using an additional $T^3 \ln T$ term, commonly interpreted as a sign of spin fluctuations [13].

Fig. 3 shows the low-temperature specific heat of CeIr$_{4.25}$Pt$_{0.75}$, CeIr$_4$Pt and CeIr$_3$Pt$_2$. The lines represent a least-squares fit of $C/T = \gamma + \beta T^2 + \delta T \ln T$ (after Ref. [14]). The first terms represent the electronic and lattice contributions, the latter part coming from the spin fluctuations. To fit the whole temperature range there has to be taken into account an additional μT^4 term (see inset of Fig. 3). The γ values (see Table 1) tend, in the limit of CeIr$_5$, to $\gamma \approx 20$ mJ mole^{-1} K^{-2}, which is consistent with the observations of the (Th$_{1-x}$Ce$_x$)Ir$_5$ series. In the other direction, the spin fluctuations pass over with increasing Pt content into antiferromagnetism with CePt$_5$ being an antiferromagnet at 1.0 K [8], which has a corresponding γ of about 30 mJ mole^{-1} K^{-2}.

The development of spin fluctuations observed here may be interpreted in terms of lattice parameter and hybridization. As previously mentioned, increasing Pt concentration leads to an enlargement of the unit cell. Thus, the hybridization of the f-electrons with the conduction electrons is weakening. This tends in the direction of increasing localization of the f-moments, which we observe in the increasing spin fluctuation term. Further lattice expansion results in magnetism in the case of CePt$_5$.

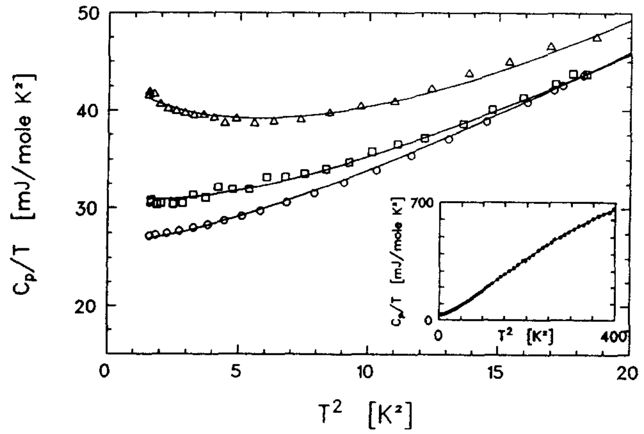

Fig. 3. Specific heat of CeIr$_{4.25}$Pt$_{0.75}$ (○), CeIr$_4$Pt (□) and CeIr$_3$Pt$_2$ (△) in a C/T versus T^2 plot. The lines are representing a least-squares fit of $C/T = \gamma + \beta T^2 + \delta T^2 \ln T$. The inset shows the data for CeIr$_4$Pt over a wider temperature range. An additional unharmonic lattice term (μT^4) was necessary to obtain a good fit over the whole temperature range.

Although the specific heat data strongly indicate spin fluctuations, we observe a similar Pauli state in χ as for (Th$_{1-x}$Ce$_x$)Ir$_5$, with greater deviations at low temperatures only for CeIr$_3$Pt$_2$ (see inset of Fig. 2), which shows the strongest spin fluctuations.

3. Conclusions

If CeIr$_5$ could be produced in the hexagonal CaCu$_5$ structure we predict it to be superconducting with a transition temperature T_C of approximately 1.8–1.9 K and an only moderately enhanced γ of about 20 mJ mole^{-1} K^{-2}. Additionally we have discovered spin fluctuations in the crossover between a non-magnetic, superconducting regime (CeIr$_5$) and magnetism (CePt$_5$). Moreover, the spin fluctuations at low temperatures arise from a Pauli paramagnetic state.

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