

Influence of hybridization and actinide spacing in $U_2Pt_x(Os, Ir)_{1-x}C_2$ systems

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The superconductor U_2PtC_2 has an electron effective mass midway between that of a normal metal and that of a heavy-fermion system. Via doping of Os or Ir on the Pt sites, we have discovered (a) increasingly strong magnetic correlations which correlate with $5d$ valence-electron concentration, showing a peak in the $5d$ valence-electron number between 8 and 8.3, (b) a metamagnetic transition at 3 T in $U_2Pt_{0.25}Ir_{0.75}C_2$ which has 8.6 $5d$ electrons, and (c) strong indications of non-Fermi-liquid behavior (i.e., $C/T \propto \ln T$) for $U_2Pt_{0.78}Ir_{0.22}C_2$ and $U_2Pt_{0.5}Ir_{0.5}C_2$.

INTRODUCTION

One of the interesting extant questions in the study of high-effective-electron-mass f -electron systems (known as "heavy-fermion" systems) is the relative role played by the f - f atom separation vs f -atom–ligand-atom hybridization. We report here on studies of U_2PtC_2 to help determine this question, via specific-heat and susceptibility measurements of specimens where d_{U-U} is varied via Th and La doping on the U site and where the U ligand hybridization is varied via Os or Ir doping on the Pt site. (Both U_2OsC_2 and U_2IrC_2 exist in the same structure as U_2PtC_2 .)

U_2PtC_2 is a (not quite) heavy-fermion system, with a specific heat, C , γ , proportional to the electronic effective mass m^* , ($C = \gamma T + \beta T^3$) of 75 mJ/mole K^2 , whereas a true heavy-fermion system is usually defined to have a significantly larger (> 400 mJ/mole K^2) γ . U_2PtC_2 is superconducting ($T_c = 1.4$ K), and has a $d_{U-U} = 3.52$ Å, very near to the Hill limit below which the uranium f orbitals overlap (i.e., there is no local magnetic moment) and above which magnetism occurs unless f -ligand hybridization intervenes to delocalize the f electrons. It is exactly this nearness to the Hill limit, and accompanying sensitivity to changes in d_{U-U} and hybridization, that caused us to choose U_2PtC_2 for this study.

SAMPLE PREPARATION

The samples were synthesized by a standard arc-melting technique under purified argon atmosphere. The purity of the starting elements U, Th, La, and Os was 99.9% or better (Cameco, Los Alamos National Laboratory, Ames Laboratory, Colonial Metals), Pt and Ir were

of 4N and 99.95% quality, respectively (Colonial Metals). The elements were weighed stoichiometrically and after remelting the samples three times they were checked for weight loss, which was always smaller than 0.5%. Since it is well known¹ that U_2PtC_2 is difficult to prepare as a single phase, we paid extra attention to proper annealing, annealing all samples under vacuum at 1050°C for four weeks.

The phase purity, crystal structure, and room-temperature lattice constants were determined by x-ray diffraction. It turned out that existing foreign phases could be reduced to 5–10% after annealing. This is at least as good and in some cases better than what has been described in the literature.^{1,2} It is interesting to note our discovery that doping with Os and Ir *improves* phase purity, i.e., the structure forms more easily with Os and Ir as compared to Pt.

RESULTS AND DISCUSSION

The x-ray-diffraction measurements show that the crystal structures of the terminal systems U_2XC_2 ($X = Pt, Os, Ir$) are body-centered tetragonal. In these compounds the nearest U-U spacing is equal to the lattice constant a_0 . The measured lattice constant (Table I) are consistent with previously published results.^{1,2} By doping U_2PtC_2 on the platinum sites with osmium or iridium the crystal structure was maintained over the whole doping range. For both pseudoternary systems $U_2Pt_xOs_{1-x}C_2$ and $U_2Pt_xIr_{1-x}C_2$ the concentration dependence of the lattice constant a_0 follows Vegard's law (Table I), i.e., further evidence that both Os and Ir are fully soluble in U_2PtC_2 .

The magnetization measurements were performed in a

TABLE I. Lattice parameter a_0 , susceptibility at 1.8 K $\chi(1.8 \text{ K})$, superconducting transition temperature T_c , and Sommerfeld coefficient γ of all samples investigated in this paper. Samples marked with "*" exhibit a maximum in χ vs T at around 10 K.

Sample	a_0 Å	$\chi(1.8 \text{ K})$ memu/U mole	T_c K	γ mJ/U mole K ²
U ₂ PtC ₂ ^a	3.52	1.1	1.47	75
U ₂ Pt _{0.995} Os _{0.005} C ₂	3.52	5*	1	
U ₂ Pt _{0.9} Os _{0.1} C ₂	3.52	13.5		90
U ₂ Pt _{0.78} Os _{0.22} C ₂	3.51	21		95
U ₂ Pt _{0.5} Os _{0.5} C ₂	3.49	16		65
U ₂ Pt _{0.25} Os _{0.75} C ₂	3.47	7		45
U ₂ OsC ₂	3.46	1		20
U ₂ Pt _{0.995} Ir _{0.005} C ₂	3.53		1.5	
U ₂ Pt _{0.95} Ir _{0.05} C ₂	3.52	7*	1	
U ₂ Pt _{0.78} Ir _{0.22} C ₂	3.51	26		113
U ₂ Pt _{0.5} Ir _{0.5} C ₂	3.50	64		120
U ₂ Pt _{0.25} Ir _{0.75} C ₂	3.49	17.5*		115
U ₂ IrC ₂	3.48	7.5*		110
U _{1.8} Th _{0.2} PtC ₂	3.53	9		55
U _{1.8} La _{0.2} PtC ₂	3.52	4.5		60

^aU₂PtC₂ data were taken from Ref. 2.

Quantum Design superconducting quantum interference device (SQUID) magnetometer. The temperature-dependent susceptibility was determined for a temperature range from 1.8 to 400 K in a magnetic field of 5 kG. Values of $\chi(1.8 \text{ K})$ for all the samples are given in Table I. Some typical $\chi(T)$ curves for Os- and Ir-doped samples are displayed in Fig. 1. Below about 50 K all samples, e.g., U₂Pt_{0.78}Ir_{0.22}C₂, with the exception of U₂OsC₂ show a more or less strong enhancement of the susceptibility, which leads to high values of $\chi(1.8 \text{ K})$. Some sam-

ples exhibit a maximum in $\chi(T)$ around 10 K (marked with "*" in Table I). In the high-temperature range all samples show a linear temperature dependence for $1/\chi$ vs T values which indicates a Curie-Weiss behavior with an effective magnetic moment between $2.47\mu_B$ and $2.88\mu_B$, which is close to the magnetic moment of one localized $5f$ electron ($2.54\mu_B$). As is commonly seen in heavy-fermion systems, this high-temperature evidence in the $1/\chi$ data for localized electrons does *not* result in local-moment long-range order at lower temperatures due to interactions of the f electrons with the conduction electrons.

The $\chi(1.8 \text{ K})$ values versus the platinum concentration listed in Table I show a maximum in both the Os- and Ir-doping series. First, the $\chi(1.8 \text{ K})$ values point out a strong increase with decreasing platinum concentration, reaching their largest values at 21 memu/U mole and 64 memu/U mole for U₂Pt_{0.78}Os_{0.22}C₂ and U₂Pt_{0.5}Ir_{0.5}C₂, respectively. The increase of the $\chi(1.8 \text{ K})$ values correlates with a strong magnetic saturation of the samples as was detected by $M(H)$ curves. In Fig. 2(a) the $M(H)$ curves for all U₂Pt_xIr_{1-x}C₂ samples are shown. There is no substantial deviation from initial linearity up to 5.5 T for the parent substances and the substances with low $\chi(1.8 \text{ K})$ values, whereas the other samples show a strong deviation. We believe this behavior may be due to magnetic correlations which start below about 50 K. Interestingly, the magnetization curve of U₂Pt_{0.25}Ir_{0.75}C₂ at 2 K indicates a metamagnetic transition between 3 and 4 T, similar to that observed in CeRu₂Si₂.³ As shown in Fig. 2(b) this transition is a function of temperature and vanishes above 20 K; it is not observed in any of the other dopings. This metamagnetic transition is currently under further investigation.

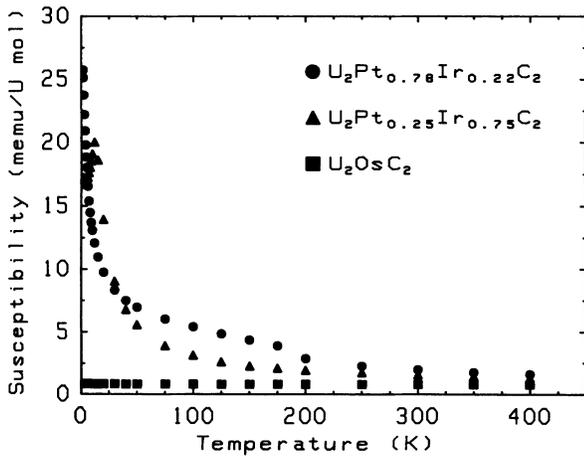


FIG. 1. Magnetic susceptibility between 1.8 and 400 K in a magnetic field of 5 kG. These three chosen samples represent typical $\chi(T)$ curves for the U₂Pt_x(Ir,Os)_{1-x}C₂ systems discussed in the text. It should be mentioned that U₂Pt_{0.78}Ir_{0.22}C₂ indicates a \sqrt{T} dependence at low temperatures which is currently under further investigation.

All samples were checked down to 150 mK for superconductivity, via ac-susceptibility measurements. A rapid reduction of T_c is observed when platinum is replaced by either osmium or iridium. In the Ir system, T_c decreases from 1.47 K (U_2PtC_2) to 1 K when 5% of the platinum is replaced by iridium. In the osmium system T_c already is depressed to 1 K for a 0.5% osmium-doped sample. We note that this decrease of T_c in both systems corresponds with the observed increase of χ (1.8 K) (see Table I) and therefore with the beginning of magnetic correlations.

Specific-heat measurements primarily in the temperature range 1.3–12 K (occasionally down to 0.33 K) and in zero field, were made on small mass (~ 10 mg) pieces of each specimen using a time-constant method technique.⁴ The specific heat divided by temperature of selected samples between 1.3 and 12 K is displayed in Fig. 3. The solid lines represent $C(T)/T = \gamma + \beta T^2$ obtained by

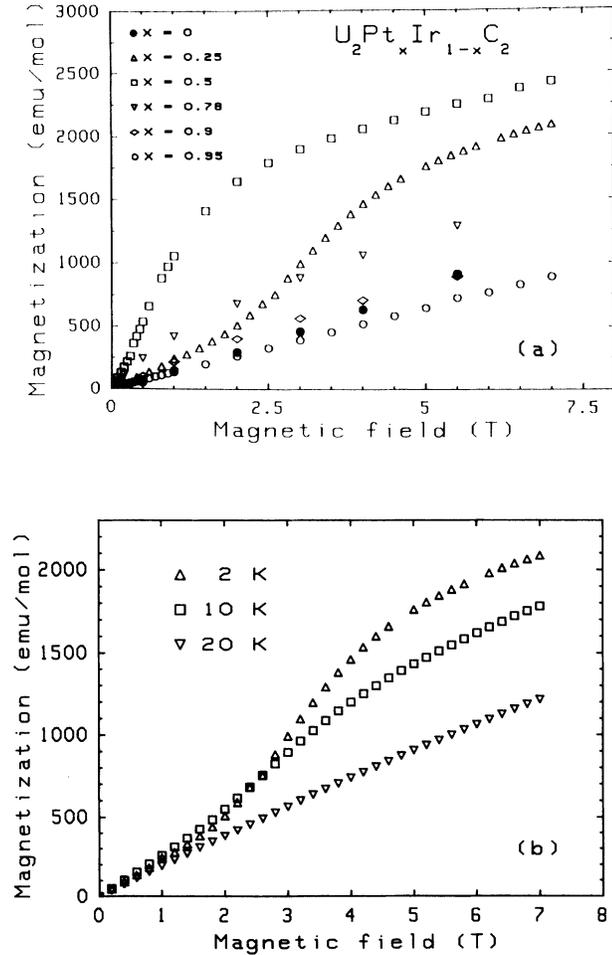


FIG. 2. (a) $M(H)$ curves for the $\text{U}_2\text{Pt}_x\text{Ir}_{1-x}\text{C}_2$ samples. The increase of the χ (1.8 K) values listed in Table I correlates with increasing magnetic saturation. This behavior may be due to magnetic correlations which start below 50 K. (b) $\text{U}_2\text{Pt}_{0.25}\text{Ir}_{0.75}\text{C}_2$ indicates a metamagnetic transition between 3 and 4 T at 2 K which vanishes above 20 K.

fitting to the linear region of $C(T)/T$ vs T^2 . The resulting γ values are listed in Table I. As may be seen in Table I, doping lanthanum and thorium onto the uranium sites, where the effective U-U distance is then increased, results in a decrease in γ .

With the exception of the parent substances U_2OsC_2 and U_2IrC_2 , all samples show a slight upturn in $C(T)/T$ at low temperatures like $\text{U}_2\text{Pt}_{0.5}\text{Os}_{0.5}\text{C}_2$ (Fig. 3). The two

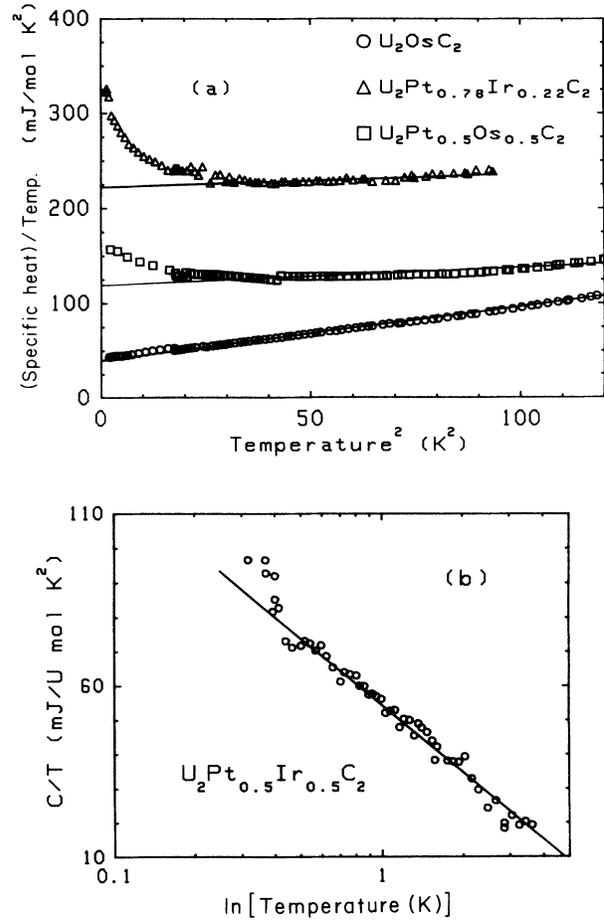


FIG. 3. (a) Specific heat divided by temperature vs temperature squared for three selected samples between 1.3 and 12 K in zero field. U_2OsC_2 shows no significant deviation from normal metallic behavior. With the exception of $\text{U}_2\text{Pt}_{0.78}\text{Ir}_{0.22}\text{C}_2$ and $\text{U}_2\text{Pt}_{0.5}\text{Ir}_{0.5}\text{C}_2$ which show a strong increase of C/T at low temperatures, all the other Os- and Ir-doped samples show only a smooth increase of C/T , e.g., $\text{U}_2\text{Pt}_{0.5}\text{Os}_{0.5}\text{C}_2$. This strong increase can be well described by a $\ln T$ dependence shown in (b). (b) The electronic part of the specific heat divided by temperature is plotted vs temperature squared for $\text{U}_2\text{Pt}_{0.5}\text{Ir}_{0.5}\text{C}_2$ between 0.33 and 4 K. A background is subtracted from the measured specific-heat data using the following formula $\Delta C/T = C/T - (229.9 + 0.3079T^2)$. The term in brackets is determined by a simple two-parameter fit to the data between 9 and 11 K. The $\ln T$ behavior displayed in this figure is not sensitive to the background fit used. Thus, $\text{U}_2\text{Pt}_{0.5}\text{Ir}_{0.5}\text{C}_2$ shows a $\ln T$ dependence for C/T over at least one decade in temperature. This may be taken as strong evidence for non-Fermi-liquid behavior.

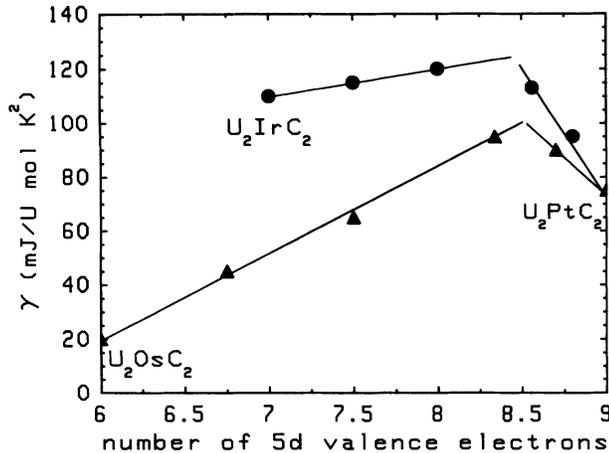


FIG. 4. For the $U_2Pt_xOs_{1-x}C_2$ and $U_2Pt_xIr_{1-x}C_2$ samples γ is plotted vs the 5d valence-electron concentration. It is shown that there is a peak in both systems between the 5d valence-electron number of 8 and 8.5. However, the actual dependence of the 5d electrons in both systems differs considerably.

parent substances yield a straight line without any upturns at the lowest temperatures. It should be mentioned that in contrast to the other samples, $U_2Pt_{0.78}Ir_{0.22}C_2$ and $U_2Pt_{0.5}Ir_{0.5}C_2$ have a *strong* pronounced upturn below 5 K. Therefore, the specific heat of these samples was measured down to 330 mK, see Fig. 3(b). It was found that these two samples show a $\ln T$ dependence of $C(T)/T$ at low temperatures. Such a temperature dependence, ranging over more than one decade in temperature, is indicative^{5,6} of non-Fermi-liquid behavior. It is no surprise to find such behavior in a system where [due to (presumably) nearness to the Hill limit] magnetic correlations are created by changing the *f*-ligand hybridization. Such "nearness" to magnetism is become accepted⁷ as a possible cause for such non-Fermi-liquid behavior.

To study whether the enhancement of γ , and thus m^* , in the systems investigated here is due primarily to *spd-f*-hybridization changes or to the change of the *f-f* atom spacing, γ was plotted against the 5d-electron number (Fig. 4). Because there is only a small change of the lattice parameter, no unambiguous correlation between γ and the *f-f* atom spacing could be found. However, it is remarkable to note that in both systems there is a maximum of the γ values between the amount of 8 and 8.5 5d electrons (although the actual γ dependence of the 5d electrons in both systems differs considerably). In the Ir system the γ values are much higher than in the Os system and are a less rapid function of the *d*-electron num-

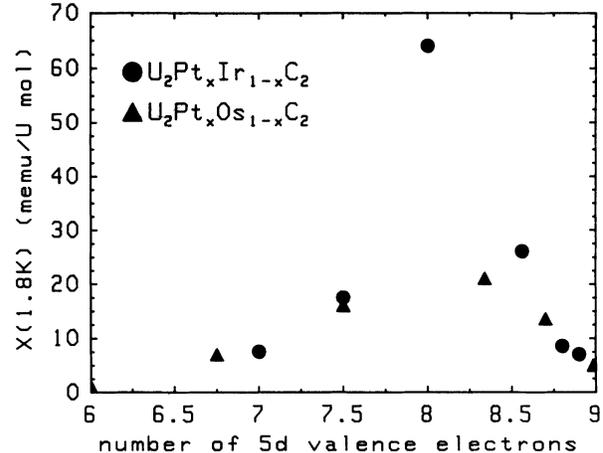


FIG. 5. For the $U_2Pt_xOs_{1-x}C_2$ and $U_2Pt_xIr_{1-x}C_2$ samples $\chi(1.8 K)$ is plotted versus the 5d-electron concentration. Compared with the γ values the $\chi(1.8 K)$ values also show a peak between the 5d-electron numbers of 8 and 8.5

ber, whereas in the Os samples γ is strong function of the 5d-electron number. Interestingly, in comparison to the γ values, the χ values for both Ir- and Os-doped systems also show a maximum at the same amount of 5d electrons, shown in Fig. 5. These strongly enhanced susceptibility values indicate magnetic correlations, with no phase transition visible in the specific-heat data. Far away from the maximum in χ in Fig. 5, at the edge of the phase diagram, the samples are paramagnetic for the pure Os and Ir compounds and superconducting for U_2PtC_2 .

CONCLUSIONS

Our doping studies on U_2PtC_2 show that Os and Ir doping causes an increase in the low-temperature magnetic susceptibility as a function of 5d-electron concentration that we ascribe to magnetic correlation effects. For the largest values of the low-temperature susceptibility, i.e., for $U_2Pt_{0.78}Ir_{0.22}C_2$ and $U_2Pt_{0.5}Ir_{0.5}C_2$, we observe a $\ln T$ dependence in the specific heat of the two samples and the beginning of a \sqrt{T} dependence of χ at low temperatures down to 1.7 K. These results indicate that both samples might be new candidates for studying the so-called non-Fermi-liquid behavior.^{5,6} For the next sample in the doping series, $U_2Pt_{0.25}Ir_{0.75}C_2$, we observe an even stronger indication of nearness to magnetism, i.e., a metamagnetic transition at 3 T, via magnetization vs field measurements.

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