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The effect of Th substitution for U in the heavy fermion U_2Pt_2In

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Abstract

Polycrystalline $(U_{1-x}Th_x)_2Pt_2In$ solid solutions with $x=0.03$, 0.05, 0.08 and 0.10 were synthesized by arc melting the constituents under a purified Ar atmosphere. All the compounds crystallize in a tetragonal U_3Si_2-type structure, with the space-group *P4/mbm*, ($Z=2$). The effects of Th substitution for U on the magnetic properties suggest pronounced electron correlations as in the heavy fermion U_2Pt_2In. However, no clear indication of magnetic ordering in all the compounds was found. The magnetic phase transitions around 3 and 19 K, found by means of ac-susceptibility and magnetization measurements are most likely due to the presence of minority phases.

Keywords: U_2Pt_2In; Intermetallics; Non-Fermi liquid behaviour; Structure determination; Magnetic characterization

1. Introduction

During the past few years, intensive studies devoted to the magnetic and electrical properties of the isostructural family of ternary intermetallics, An_2T_2X (An=actinide element, T=transition element, X=p-element) [1–3] have been performed in order to clarify hybridization phenomena in the 5f electron compounds. Within the series of U_2T_2X intermetallics, the Pauli-paramagnet U_2Pt_2In attracts special attention because of its strongly enhanced electronic specific heat at low-temperatures with C/T ($T=1.5$ K)$\approx$850 mJ/mol K^2 [4]. Experiments carried out on a polycrystalline sample in the temperature range 1.3–300 K [4] also revealed the presence of an enhanced low temperature magnetic susceptibility and a broad maximum in the resistivity around 80 K, characteristic of heavy-fermion compounds and Kondo systems. Electrical and magnetic resistivity measurements down to 1.4 K on polycrystalline U_2Pt_2In [5,6] indicated a linear temperature dependence of the electrical resistivity below 15 K suggesting a non-Fermi liquid (NFL) behaviour in this compound. More recently, specific heat data on U_2Pt_2In single crystals [7] below 6 K, together with electrical resistivity and magnetic susceptibility data on these single crystals [8,9] provided evidence for NFL behaviour and pronounced spin-fluctuation (SF) phenomena.

Previous results observed for $(U_{1-x}Th_x)_2Pt_2In$ ($0\leq x\leq 1$) compositions where U atoms are randomly replaced by Th [5,6] have shown for the $x=0.10$ compound a knee at $T=19$ K on the electrical resistivity vs. T curve suggesting magnetic order below this temperature. This transition is followed upon cooling by a quadratic decrease of $\rho(T)$ suggesting that the NFL behaviour on U_2Pt_2In is replaced by a Kondo lattice behaviour on $(U_{0.9}Th_{0.10})_2Pt_2In$. The presence of the UPt impurity phase was however reported [5]. UPt shows two magnetic phase transitions at 27 and 19 K [13,15]. In order to check the influence of impurity phases on the measured properties and to further investigate the effects of the Fermi level changes on the physical properties of U_2Pt_2In we have also undertaken the substitution of small amounts of U by Th. Besides careful structural characterization, magnetization measurements and specific heat data on the $(U_{1-x}Th_x)_2Pt_2In$ samples ($0\leq x\leq 1$) are presented here for the first time.

2. Experimental

Polycrystalline $(U_{1-x}Th_x)_2Pt_2In$ solid solutions with $x=0.03$, 0.05, 0.08 and 0.10, in a total weight of 4 g each, were prepared by arc melting the stoichiometric amounts of the constituent elements under a purified Ar atmosphere. The starting materials were used with purity higher than

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99.9%. A small excess of In was added in order to compensate for evaporation losses. To ensure the homogeneity the obtained buttons were turned around and melted at least four times. The mass loss after arc melting was less than 1%. The phase analysis was checked by scanning electron microscopy (SEM) and powder X-ray diffraction (XRD) carried out on a Philips automated diffractometer system PW1710 using CuKα_1 radiation. To collect the diffracted X-ray intensities, finely ground powder of each sample was prepared and back pressed into standard aluminium holders.

Part of the as-cast samples was annealed in vacuum at 1123 K for 4 weeks. The characterization of these samples by powder XRD revealed a higher percentage of impurity phases than on the as-cast samples that were used for further characterization work.

Bulk magnetization ($T = 1.7$–300 K, $B = 0$–12 T), ac-susceptibility (1000 Hz with $B_{ac} = 0.1$ mT, in zero DC external field) and specific heat ($T = 1.7$–300 K, $B = 0$–12 T) measurements were performed in fragments of the samples using a multipurpose characterization system MAGLAB 2000 (Oxford Instruments).

3. Results and discussion

SEM micrographs and powder XRD revealed the presence of small amounts of impurity phases in all the as-cast samples. In the $x = 0.03$ sample the impurity phase UPt already found in U_2Pt_2In sample prepared in a similar way [10] was detected. In the $x \geq 0.05$ samples UPtIn was found to be the main impurity phase. The relative intensities of the impurity diffraction peaks increased in the samples annealed at 1123 K indicating that at this temperature the $(U_{1-x}Th_x)_2Pt_2In$ intermetallics are not stable.

The Rietveld refinement [11] of the diffracted intensities of the main phases was performed and showed that they crystallized in the U_3Si_2-type structure and not in the Zr_3Al_2-type structure usually found for U_2Pt_2In grown as single-crystals [8].

In agreement with the relative values of the Th and U metallic radii [12] the estimated unit-cell parameters show a tendency to increase with the Th content of the sample (Table 1). This increase is not monotonic with x. Particularly the unit-cell parameters of the 2:2:1 phase in the $x = 0.10$ sample are smaller than in the $x = 0.08$ sample. This may be explained by different contents of impurity phases on each sample, also incorporating small amounts of Th. In this way the Th incorporated in the 2:2:1 phase might not increase proportionally with the total amount of Th in the samples. Due to the similarity of the X-ray scattering factors of U and Th, the refinement of the diffracted intensities cannot be used to estimate the Th content.

The temperature dependence of the ac-susceptibility, $\chi_{ac}(T)$, for the $(U_{1-x}Th_x)_2Pt_2In$ samples with $x = 0.03$, 0.05, 0.08 and 0.10 (Fig. 1) shows a susceptibility increase with decreasing temperature in agreement with the temperature variation of the magnetization curves. Several transitions were found for each sample, respectively at 3.6, 10 and 16.5 K for $x = 0.10$, at 3.6, 10 and 20 K for $x = 0.08$ and 0.05, and at 3.6, 14 and 20 K for $x = 0.03$. A temperature dependence of the imaginary part of some of the $\chi_{ac}(T)$ curves supports the presence of a ferromagnetic behaviour. These anomalies already detected at similar temperatures in the magnetic study of the polycrystalline U_2Pt_2In compound previously synthesized [10] may be attributed to secondary phases as In, UPt and UPtIn. The latter two phases, UPt and UPtIn, were also observed in the powder XRD. The ferromagnet UPt has been a subject of intensive studies for 3 decades and some controversy about its magnetic properties still persists due to the presence either of one magnetic transition at 27 K [13,14] or two magnetic phase transition temperatures, at 27 and 19 K [13,15]. The latter was recently attributed to a minority phase of UPt with a different crystal structure [16]. Another phase impurity is UPtIn which is an antiferromagnet with $T_N = 15$ K showing the maximum in $\chi_{ac}(T)$ at 18 K [17]. The transition at 3.6 K can be attributed to the presence of metallic In which has a

Table 1
Estimated unit-cell parameters of the U_3Si_2-type phase and impurity phases detected in the X-ray diffractograms of the $(U_{1-x}Th_x)_2Pt_2In$ as-cast samples

x	Impurity phase	a (Å)	c (Å)	V (Å^3)
0[a]	UPt	7.689(1)	3.699(1)	218.7
0.03	UPt	7.713(1)	3.694(1)	219.8
0.05	UPtIn	7.704(1)	3.711(1)	220.2
0.08	UPtIn	7.741(1)	3.722(1)	223.0
0.10	UPtIn	7.727(1)	3.714(1)	221.7

[a] From [10].

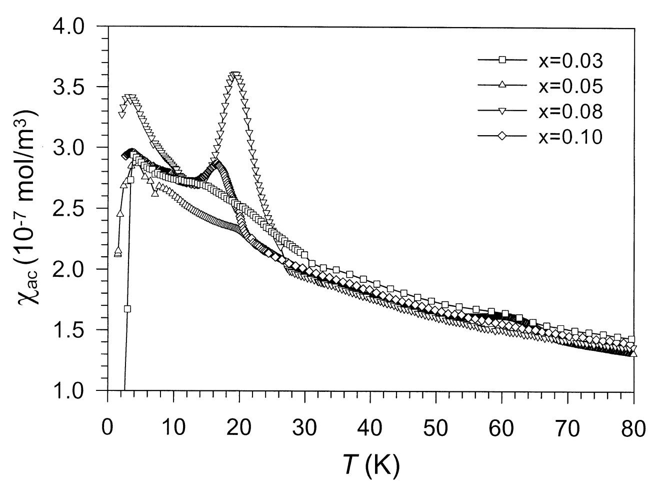

Fig. 1. Temperature dependence of the ac-susceptibility, $\chi_{ac}(T)$, of $(U_{1-x}Th_x)_2Pt_2In$ ($x = 0.03$, 0.05, 0.08 and 0.10).

superconducting (SC) transition at 3.4 K. During the arc melting synthesis it is possible that In precipitates at the grain boundaries and form a thin SC layer around the grains of the main phase. This transition is denoted by the negative χ_{ac} below 3 K during the remanent field compensated $\chi_{ac}(T)$ measurements. Another type of anomaly of not so clear origin is shown around 60 K in $x=0.05$ and $x=0.03$ samples.

The temperature variation of the magnetization M performed on the four different samples (Fig. 2) corroborated the enhanced Pauli paramagnetism behaviour previously observed on U_2Pt_2In, strongly suggesting the presence of spin fluctuations. However, none of these Th compositions show any signs of a maximum in $M(T)$ data down to 2 K as it was detected on U_2Pt_2In single crystals around 8 K (for $B//c$) [8,9]. Due to the contribution of the impurity phases at low temperatures, these curves were analysed only for $T>30$ K. No indication of a magnetic transition is found. Above 60 K, all the curves can be fitted rather well to a modified Curie–Weiss law, $\chi=\chi_0+C/(T-\Theta)$ with the parameters given in Table 2. Since these results compare quite well to the parameters previously found in the polycrystalline [4,10] and single crystals [9] U_2Pt_2In the influence of the impurity phases seems to be negligible. The disappearance of the anomalies due to the impurity phases for $B\geq 0.5$ T also confirms their low percentage in the samples. In all compounds the Θ values are negative indicating the existence of antiferromagnetic interactions. The effective magnetic moments, μ_{eff}, are considerably reduced from the free-ion values for U^{3+} and U^{4+} configurations, suggesting a strong hybridization between the f electrons and the conduction band. The magnetic field dependence of the magnetization, $M(B)$, up to 12 T shows a linear behaviour at temperatures above 20 K with no saturation. At temperatures below 20 K a small non-linearity at low magnetic fields is noticed probably due to the saturation of magnetic impurities. At 2 K, the magnetization reach values around 0.25 $\mu_B fu^{-1}$ for a magnetic field of 5.5 T (Fig. 3), rather close to the obtained for U_2Pt_2In single crystals ($B//c$) [8].

Table 2
Fitting parameters of the modified Curie–Weiss law $\chi=\chi_0+C/(T-\Theta)$ applied to the paramagnetic susceptibilities ($B=1$ T and 60 K$<T<$300 K) of U_2Pt_2In single crystals with B along the a and c axis [9] and $(U_{1-x}Th_x)_2Pt_2In$ with $x=0.03$, 0.05, 0.08 and 0.10

Compound	χ_0 ($\times 10^8$ m^3/mol)	Θ (K)	μ_{eff} (μ_B/U)
U_2Pt_2In $B//c$	2.2	−62	2.6
U_2Pt_2In $B//a$	2.2	−63	2.2
$(U_{0.97}Th_{0\ 03})_2Pt_2In$	1.2	−89	2.7
$(U_{0.95}Th_{0.05})_2Pt_2In$	1.8	−73	2.5
$(U_{0.92}Th_{0.05})_2Pt_2In$	1.5	−63	2.4
$(U_{0.90}Th_{0.10})_2Pt_2In$	1.6	−70	2.5

Specific heat measurements performed for all the x compositions show no anomaly between 2 and 30 K confirming that the magnetic transitions detected by χ_{ac} or M are due to impurity phases present in minor percentage (Fig. 4). The absence of any magnetic transition up to 10%Th ($x=0.10$) also contrasts with the suggestions made on the basis of the electrical resistivity data of $(U_{0.90}Th_{0.10})_2Pt_2In$ [5,6]. Below 10 K, the $C(T)$ curves taken at different magnetic fields are fitted rather well by a $C=T\ln T+T^3$ law and are field independent, indicating that the NFL behaviour noticed on U_2Pt_2In is still present up to $x=0.10$ [18]. For $x<0.1$, this C/T behaviour was also found to be rather insensitive to the Th composition x, as already observed in the $CeCu_{6-x}Au_x$ system [19].

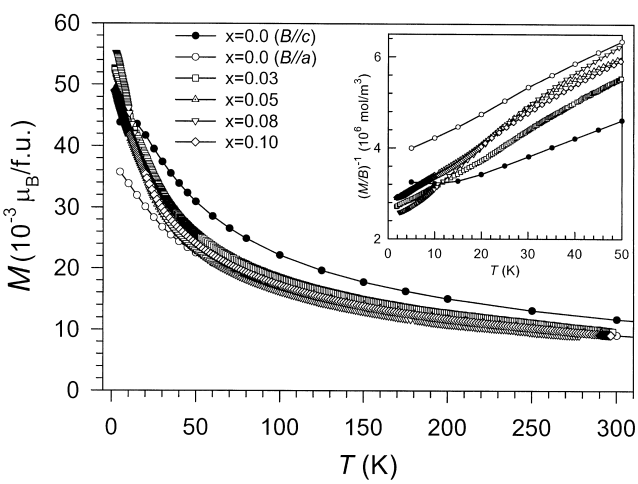

Fig. 2. Temperature dependence of the magnetization, $M(T)$, of $(U_{1-x}Th_x)_2Pt_2In$ ($x=0.03$, 0.05, 0.08 and 0.10) measured at 1 T. The insets show in detail the inverse, $(M/B)^{-1}(T)$ at low temperature. For comparison, the results of U_2Pt_2In single crystal for $B//c$ and $B//a$ ($x=0.0$) also have been included [9].

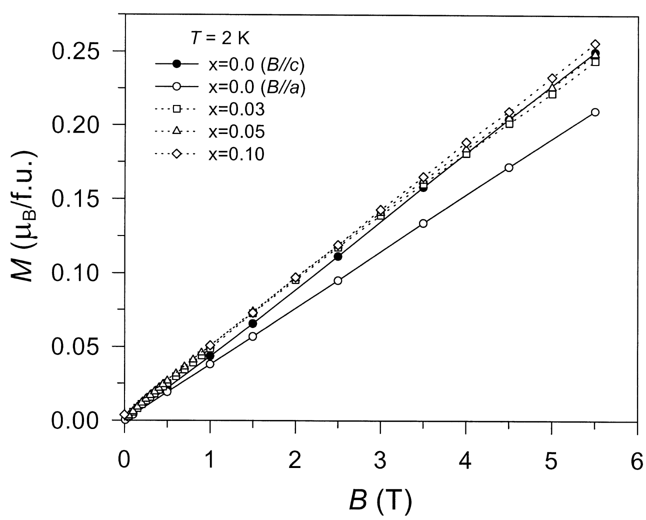

Fig. 3. Field dependence of the magnetization, $M(B)$, of $(U_{1-x}Th_x)_2Pt_2In$ ($x=0.03$, 0.05, and 0.10) measured at 2 K. For comparison, the results of U_2Pt_2In single crystal for $B//c$ and $B//a$ ($x=0.0$) also have been included [8].

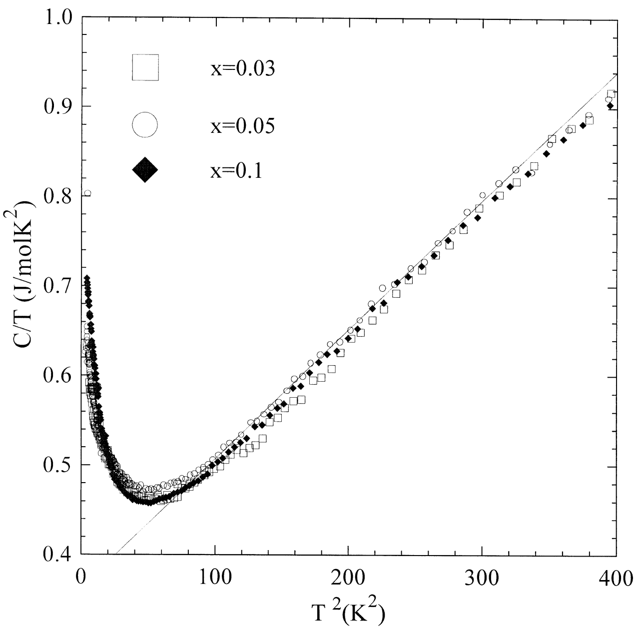

Fig. 4. Specific heat divided by temperature, C/T, versus T^2 of $(U_{1-x}Th_x)_2Pt_2In$ ($x=0.03$, 0.05, and 0.10).

4. Conclusion

$(U_{1-x}Th_x)_2Pt_2In$ intermetallics with different Th contents ($0 \leq x \leq 0.10$) were prepared and characterized. As these phases seem to be unstable at 1123 K it was not possible to prepare single-phase samples by annealing at this temperature. An increase of the unit-cell volume with Th content is confirmed from our study. However, due to the similarity of the X-ray scattering factors of Th and U and the presence of some amounts of impurity phases, no precise determination of the Th content on each sample could be performed. No structural comparison is possible with previous work since no unit-cell parameters were reported [5,6].

All the magnetic transitions observed in the $M(T)$ curves in low magnetic fields obtained for these samples are explained by the presence of the minority phases UPt, UPtIn and In. Heat capacity measurements are also consistent with this conclusion [18]. Particularly, the ferromagnetic transition observed at 19 K in all cases (including U_2Pt_2In polycrystals prepared in the same way [10]) is most probably due to UPt rather than to the magnetic ordering transition which was suggested from the electrical resistivity data of $(U_{0.90}Th_{0.10})_2Pt_2In$ [5,6].

Except for a small increase of the magnetic susceptibility at low temperature, no significant differences on the magnetic behaviour of the Th containing samples relative to U_2Pt_2In could be detected. Similarly, the NFL specific heat behaviour detected in U_2Pt_2In is also observed in all the substituted samples and remains up to 10% Th for $T > 1.7$ K [18].

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