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4f-conduction electron hybridization in ternary Ce–TM–Al compounds

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Abstract

We present an investigation of Ce–TM–Al phase diagrams with TM = Ru, Pd, Pt and Au. Several new compounds have been characterized by measurements of the electrical resistivity $\rho(T)$, the dc susceptibility $\chi(T)$ and, in some cases, the specific heat $C(T)$. We find that in the compounds with TM = Ru, the hybridization strength between 4f and conduction electrons is strong, leading in most compounds to an intermediate valent (IV) state. By contrast, most of the investigated compounds with TM = Pd, Pt and Au order magnetically indicating a much weaker hybridization strength. However, some of the Pt and especially Pd compounds are very near to the crossover from the magnetic to the non-magnetic regime as deduced from a Kondo-type maximum in the resistivity and a large electronic specific heat at low temperatures.

1. Introduction

Among the seven heavy-fermion (HF) superconductors known up to date, five are U-based compounds, whereas only two are Ce-based compounds [1]. Since the discovery of the last two HF superconductors UNi_2Al_3 and UPd_2Al_3 2 years ago [2] which order antiferromagnetically (AF) at 4.5 K and 14.5 K and become superconducting below 1.2 K and 2.0 K, respectively, much effort has been devoted to finding Ce homologs in which the transition metals Ni and Pd are replaced by Ru, Rh, Pt, Cu, Ag and Au, and Al is replaced by Ga. Surprisingly, only three isostructural compounds have been found, one of them being the HF compound $CePd_2Al_3$ [3] which orders antiferromagnetically at $T_N = 2.8$ K. In order to find more Ce-based HF systems with different compositions and structures, in this paper we present an investigation of the ternary phase diagrams Ce–TM–Al with TM = Pd, Pt, Au and Ru. Similar studies on Yb homologs are reported elsewhere [4].

2. Experimental details

Numerous polycrystalline samples within the ternary phase diagrams Ce–TM–Al with different compositions of the starting materials Ce, Pd, Pt, Au, Ru and Al have been prepared by a standard arc-melting technique. The as-cast samples have been characterized by X-ray (XR) powder diffraction in order to check for structure, lattice parameters and foreign phases. Most of the samples have been annealed at about 600–900 °C (depending on the composition and the constituents) for approximately 1 week. The physical properties of the samples have been investigated by measurements of the electrical resistivity $\rho(T)$ and the magnetic dc susceptibility $\chi(T)$ in the temperature range $0.4\ \text{K} < T < 300$ K. In some cases, the specific heat $C(T)$ was measured from 0.4–9 K.

3. Results

We have found a number of ternary compounds in the Ce–TM–Al phase diagrams with TM = Pd, Pt, Au and Ru. These are of similar compositions and structures in the case of TM = Pd, Pt and Au, but different for TM = Ru (Table 1).

3.1. Ce–Pd–Al

Concerning the Ce–Pd–Al ternary phase diagram, we have found three new compounds: CePdAl, $CePdAl_3$ and $CePd_2Al_2$. As-cast CePdAl samples crystallize in the hexagonal ZrNiAl structure with lattice parameters $a = 7.219$ Å and $c = 4.231$ Å. Typically they contain about

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TABLE 1. Crystallographic and magnetic properties of Ce–TM–Al compounds with TM = Pd, Pt, Au and Ru; composition, crystal structure, magnetic ordering temperature, T_N (K), and characterizing remarks

Composition	Structure	T_N (K)	Remarks[a]
CePdAl	ZrNiAl	3	AF, HF
$CePdAl_3$	$PrNiGa_3$	6	AF, HF
$CePd_2Al_2$	$CaBe_2Ge_2$	2.4	AF
CePtAl	TiNiSi	8[c]	FM
$CePtAl_2$	$MgCuAl_2$		PM, $\mu_{eff}=2.5\ \mu_B$[b]
$CePtAl_3$	$PrNiGa_3$		K
$CePt_3Al_2$	$CeCo_3B_2$		
CeAuAl	TiNiSi		
$CeAuAl_3$	$BaNiSn_3$		PM, $\mu_{eff}=2.4\ \mu_B$[b]
Ce_2RuAl_3	Sc_2RhSi_3	9[c]	FM, $\mu_{eff}=2.1\ \mu_B$
Ce_2RuAl_2	$MgZn_2$		
$Ce_4Ru_3Al_5$	$MgZn_2$		
$Ce_4Ru_3Al_4$	$MgZn_2$		
CeRuAl	$MgZn_2$		CEF
$Ce_3Ru_4Al_{12}$	$Ce_3Ru_4Al_{12}$ [8]		IV

[a] AF, antiferromagnetically ordered system; HF, heavy fermion system; K, weak Kondo effect; FM, ferromagnetically ordered system; PM, paramagnetic behavior; CEF, crystal electric field effects; IV, intermediate valent system.

[b] No magnetic ordering down to $T=2.0$ K, but large effective moment.

[c] Ferromagnetic ordering Curie temperature T_c.

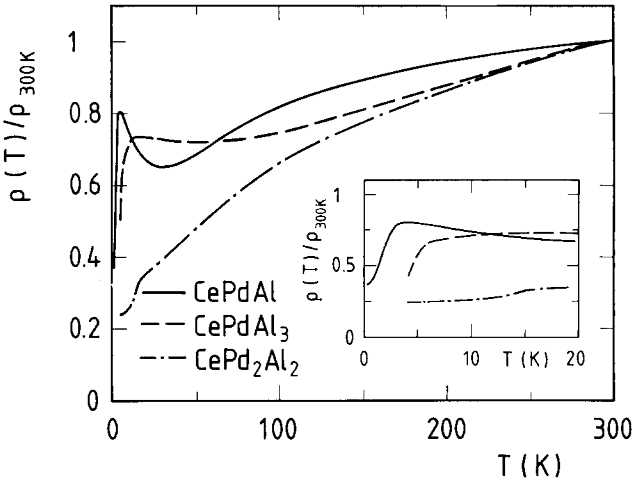

Fig. 1. Normalized electrical resistivity $\rho(T)/\rho(300\ K)$ *vs.* temperature T of CePdAl, $CePdAl_3$ and $CePd_2Al_2$. Inset shows data below $T=20$ K.

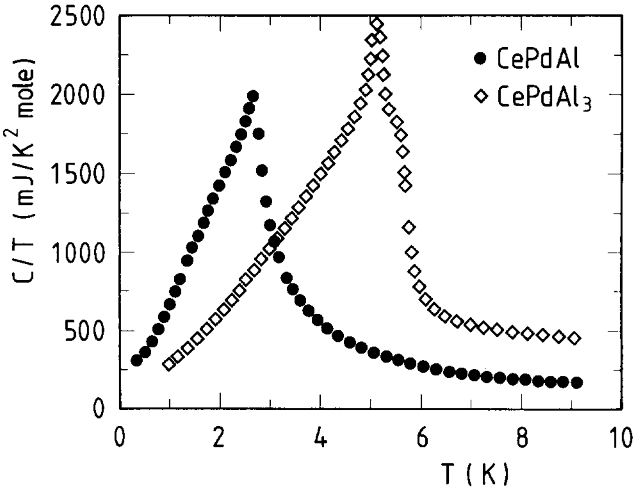

Fig. 2. Specific heat of CePdAl and $CePdAl_3$ in a plot C/T *vs.* T.

10% of a foreign phase. After an annealing process at temperatures between 700 and 900 °C the XR-diffraction patterns look totally different, indicating a structural phase transition or chemical decomposition. On the other hand, since an annealing process at 1000 °C leaves the original XR pattern almost unchanged, CePdAl with the ZrNiAl structure can be characterized as a high-temperature phase. The compound $CePdAl_3$ synthesized subsequently crystallizes in the tetragonal $PrNiGa_3$ structure with $a=4.343$ Å and $c=10.578$ Å. Here, one site is randomly occupied by Pd and Al. XR patterns of as-cast samples indicate the presence of ~20% foreign phases, mainly $CePd_2Al_3$. As in the case of CePdAl, an annealing process leads to a structural phase transition. The structure developing after annealing has not yet been determined. The third new compound $CePd_2Al_2$ crystallizes in the tetragonal $CaBe_2Ge_2$ structure with lattice parameters $a=4.416$ Å and $c=9.876$ Å. An amount of 30 at.% $CePd_2Al_3$ in the as-cast samples has been reduced to about 5 at.% by annealing them at 800 °C for 120 h. The temperature dependence of the reduced electrical resistivity, $\rho(T)/\rho(300\ K)$, of as-cast CePdAl as well as annealed $CePdAl_3$ and $CePd_2Al_2$ are shown in Fig. 1. CePdAl exhibits a pronounced Kondo effect indicated by an upturn in $\rho(T)$ to lower temperatures followed by a sharp decrease presumably due to short-range Ce—Ce correlations. In addition, the low-temperature part of $\rho(T)$ shows a change in slope at about $T_N=3$ K (see inset of Fig. 1), indicating a cooperative AF phase transition as confirmed by susceptibility measurements $\chi(T)$. (Similar results were obtained by Kitazawa *et al.* [5]). $CePdAl_3$ shows a positive temperature coefficient of $\rho(T)$ above ~50 K, but a Kondo-type of behavior at lower temperature, which is terminated by an AF transition at $T_N=6$ K. For $CePd_2Al_2$, the temperature coefficient of $\rho(T)$ is positive for all temperatures. A change in slope occurs at $T'=15$ K being associated with the formation of a helical spin structure [6]. These authors also report AF ordering at $T_N=2.4$ K for this compound. The specific heats $C(T)/T$ of CePdAl and $CePdAl_3$ are shown in Fig. 2. For both compounds, large anomalies at $T_N=3$ and 6 K, respectively, indicate the onset of AF ordering. Concerning $CePdAl_3$, we have observed a main transition at 5.7 K and a smaller transition at 5.2 K. For both

CePdAl and $CePdAl_3$, the residual Sommerfeld coefficient γ_0 of the electronic specific heat can be extrapolated from a C/T versus T^2 plot to 250 and 200 mJ mol^{-1} K^{-2}, respectively. For $CePdAl_3$, the value of the molar entropy at T_N is surprisingly high: 1.1*R*ln2 per mole. This suggests a quartet as the crystal field (CF) ground state of Ce^{3+} (or two closely spaced low-lying doublets) in $CePdAl_3$. The reduction from the theoretical entropy value of 2*R*ln2 per mole to the observed value, 1.1*R*ln2 per mole, is ascribed to the Kondo effect. Note that our conclusion of two low-lying CF doublets in $CePdAl_3$ is consistent with the results for $CePd_2Al_3$ [3], where the lowest lying and the first excited CF doublets are separated by an energy gap of only ~25 K. As far as the structure of annealed $CePdAl_3$ is not known, a true quartet, occurring only for a cubic site symmetry of Ce^{3+}, cannot be excluded. In comparison, for CePdAl, the value of the molar entropy at T_N is 0.55*R*ln2 per mole. To summarize our present results, we have discovered, besides the already known HF system $CePd_2Al_3$ [3], two new AF ordering HF systems, namely CePdAl and $CePdAl_3$ within the ternary phase diagram Ce–Pd–Al.

3.2. Ce–Pt–Al

In the Ce–Pt–Al ternary phase diagram, we have found similar compositions and structures as in the Ce–Pd–Al phase diagram: CePtAl (orthorhombic TiNiSi structure with lattice parameters $a=7.201$ Å, $b=4.482$ Å and $c=7.794$ Å), $CePtAl_2$ (orthorhombic $MgCuAl_2$ structure with $a=4.223$ Å, $b=11.141$ Å and $c=7.037$ Å), $CePtAl_3$ (tetragonal $BaAl_4$-type structure with $a=4.317$ Å and $c=10.677$ Å) and $CePt_3Al_2$ (hexagonal $CeCo_3B_2$ structure with $a=5.581$ Å and $c=3.949$ Å). CePtAl and $CePtAl_3$ are almost single phase before as well as after annealing at 800 °C for 120 h. According to the XR patterns, the latter compound shows random occupation of the 4(d) and 4(e) sites by Pt and Al. $CePtAl_2$ as well as $CePt_3Al_2$ form after the above mentioned annealing process only, with additional reflections in the XR patterns indicating ~20 at.% and 10 at.% foreign phases, respectively. It is interesting to note that in none of the ternary phase diagrams investigated so far, could a 1-3-2 composition with the corresponding $CeCo_3B_2$ structure be found, if a 1-2-3 composition with the $PrNi_2Al_3$ structure exists, and vice versa; a $CePt_2Al_3$ compound apparently does not exist. In addition to the four newly found Ce–Pt–Al compounds there is evidence for two more ternary compounds: resistivity measurements performed on two samples with the respective composition 2-3-9 and 1-2-6 cannot be explained by the $\rho(T)$ curves of the four compounds described above. Although a large number of samples with different compositions has been prepared out of the interesting region of the ternary phase diagram, the exact composition and structure of those two phases could not be determined. The resistivity $\rho(T)$ exhibits a positive temperature coefficient for all Ce–Pt–Al compounds. For $CePtAl_2$ and $CePt_3Al_2$, no pronounced anomalies are found, whereas $CePtAl_3$ shows a slight upturn in $\rho(T)$ at low temperatures probably indicating a Kondo effect (low T_K) in this 1-1-3 compound, since the amount of foreign phase is very small. CePtAl exhibits a sharp change in slope of $\rho(T)$ at $T_c=8$ K indicating a ferromagnetic phase transition [7]. Measurements of the susceptibility $\chi(T)$ on $CePtAl_2$ infer an effective Ce moment $\mu_{eff}\approx 2.5\ \mu_B$ very close to that of the free Ce^{3+} ion. Thus, we suppose that this compound, which shows paramagnetic behavior down to 1.7 K, orders magnetically below this temperature.

3.3. Ce–Au–Al

In the Ce–Au–Al ternary phase diagram, we have found two new compounds with the compositions 1-1-1 and 1-1-3. Both compounds crystallize in the same structures as their Pt homologs (CeAuAl: TiNiSi structure with $a=7.586$ Å, $b=4.590$ Å and $c=7.714$ Å, $CeAuAl_3$: $BaAl_4$ structure with $a=4.333$ Å and $c=10.843$ Å). However, $CeAuAl_3$ adopts the completely ordered $BaNiSn_3$ type. (Note that $CePtAl_3$ crystallizes in the structurally disordered $PrNiGa_3$ type of tetragonal $BaAl_4$ structure.) In the whole temperature range, both compounds show an increasing $\rho(T)$ upon warming. For $CeAuAl_3$, $\chi(T)$ measurements reveal $\mu_{eff}=2.4\ \mu_B$/Ce indicating a Ce valence of almost 3+. We thus expect magnetic ordering to occur in this compound below the temperature limit of our investigation ($T_{min}=2$ K).

3.4. Ce–Ru–Al

In Ce–Ru–Al we have found structure types and compositions that differ significantly from those of the systems described above. We have observed two different phases. The structure of the first one, $Ce_3Ru_4Al_{12}$, has already been determined by Dörsam *et al.* [8], but its physical properties have been unknown until now. The second, crystallizing in the hexagonal $MgZn_2$ structure type, has been found to occur over a very large composition range. At composition 2-1-3, XR diffraction patterns suggest a complete ordering of Al and Ru leading to the Sc_2RhSi_3 structure type. All other compositions exhibit a random occupation of the non-rare earth positions as is often observed for such Laves phases. The lattice parameters decrease with increasing Ru content from $a=5.663$ Å and $c=8.887$ Å for Ce_2RuAl_3 to $a=5.505$ Å and $c=8.070$ Å for CeRuAl. Since a linear correlation between the unit-cell volume and the Ru content is found for five new compounds, we suppose that all of them originate in the same compound with a large homogeneity range from the composition 2-1-3 to, at least, 1-1-1.

As to the physical properties of the investigated Ru-based compounds, Ce_2RuAl_3 is the only one which orders magnetically, namely ferromagnetically (FM) at $T_c = 9$ K. This ordering temperature is surprisingly high when compared to what is known for adjacent binary compounds, *e.g.* $T_N(CeAl_2) = 3.9$ K [9]. The electrical resistivity of almost all of the investigated Ru-based compounds decreases almost linearly with decreasing temperature without showing any pronounced anomalies; except for Ce_2RuAl_3, for which $\rho(T)$ exhibits a kink at $T_c = 9$ K. The $\rho(T)$ curve of CeRuAl exhibits a distinct curvature at about $T \approx 70$ K which suggests CF effects. The $\chi(T)$ curve of $Ce_3Ru_4Al_{12}$ shows only a weak temperature dependence. We propose that this compound is an intermediate valent (IV) system in which the 4f electrons are hybridized with the (spd)-conduction electrons, much stronger than in the prototypical Kondo-lattice (or HF) systems.

4. Discussion

When comparing the physical properties of the compounds described above, one concludes that the hybridization of the 4f electrons with the conduction electrons increases on going from TM = Au in the Ib column of the Periodic Table to TM = Ru; most of the compounds with TM = Pd, Pt and Au order magnetically, while those with TM = Ru exhibit a less magnetic character. The change from more to less localized behavior in Ce–TM–Al compounds can also be observed within the Ni column: While CePtAl orders antiferromagnetically, CePdAl also shows AF ordering in the presence of HF effects indicating a weak delocalization of the 4f electrons, and CeNiAl appears to be an IV compound [10]. This trend is associated with a decrease in the unit-cell volume of these 1-1-1 compounds on going from TM = Pt to TM = Ni. A possible reason for the observed differences in the physical properties of CePdAl and CePtAl can be found in the reduction of the symmetry of the crystal lattice from hexagonal (CePdAl) to orthorhombic (CePtAl). We now turn to the homologous compounds CePdAl and CeCuAl (ZrNiAl-type structure) [10], for which an interesting effect of the filling of the TM-d shell can be observed. Although both compounds have almost the same unit-cell volume, CeCuAl (with full 3d shell) shows AF ordering without HF behavior [10] indicating a weaker hybridization of the 4f electrons than in the AF ordered HF system CePdAl (with open 4d shell). A similar behavior was recently observed for Yb–TM–Al compounds [4]. There, compounds with TM out of the Ib column (Cu, Ag, Au) were found to exist in the lower valence state (2+) of Yb, while elements from the Ni column with their unfilled d shell stabilize the higher valence state (3+); in order to maximize hybridization, the unfilled d shell prefers a rare earth state whose number of valence electrons is as large as possible.

In conclusion, in the ternary Ce–Pd–Al phase diagram, we found two new AF ordered HF compounds: CePdAl and $CePdAl_3$. The 4f electrons in Ce–TM–Al compounds with TM = Pt and Au appear to be better localized since these systems show magnetic ordering between “stable 4f moments”. The systems with TM = Ru display less magnetic behavior which can be ascribed to a somewhat stronger 4f-conduction electron hybridization.

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