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Change of the Yb valence in Yb–TM–Al compounds

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Abstract

We present an investigation of Yb–TM–Al phase diagrams with TM = Pd, Ag and Au. Several new compounds have been characterized by measurements of the magnetic susceptibility, the electrical resistivity and, in some cases, the specific heat. It seems that the crossover from the stable-trivalent to the intermediate-valent behavior occurs much more abruptly in Yb- than in Ce-based compounds on changing the composition. A comparison of the Ce–TM–Al compounds with their Yb homologs suggests that replacement of Ce by Yb in an intermediate-valent Ce compound and in a trivalent Ce compound results in an Yb^{3+} and in an Yb^{2+} state, respectively.

1. Introduction

Besides Ce, Pr, Sm, Eu and Tm, Yb is one of the rare earth (RE) elements with two almost degenerate 4f configurations. In the case of Yb, these are the configurations $4f^{13}$ and $4f^{14}$ corresponding to a Yb valence (v) of 3+ and 2+, respectively. This degeneracy leads to a number of interesting phenomena like intermediate valence (IV), the formation of Kondo lattices and heavy fermions (HF). Whereas these phenomena have been intensively discussed in Ce- (and U-) based compounds [1], much less systematic studies have been devoted to Yb-based compounds. Some results exist for IV-Yb compounds [2], *i.e.* for $2.0 < v < 2.9$. So far, there are only very few results for the regime $2.9 < v < 3.0$, where a pronounced Kondo effect and the formation of heavy fermions are expected [3]. Since this regime is still poorly understood in Yb compounds, we have started a systematic study of Yb–TM–Al (TM, transition metal) ternary phase diagrams in an extension of similar studies on the Ce homologs [4].

2. Experimental details

The Yb–TM–Al samples have been prepared by filling a Mo crucible with appropriate amounts of the pure starting elements Yb, Pd, Ag, Au and Al. To compensate for losses of Yb due to its high vapor pressure, a Yb excess of 5–10 at.% was used. After being sealed by arc melting under an argon atmosphere, the crucibles were heated in an induction furnace, again under an argon atmosphere, up to temperatures between 1000 and 1400 °C (depending on the composition) for about 10 min. The temperature was controlled by a pyrometer. Some of the as-cast samples were annealed at 800 °C for 120 h. The determination of the crystal structures has been reported elsewhere [5,6]. X-Ray (XR)powder diffraction patterns of all samples could be completely indexed using structures previously found [6]. In some cases, additional peaks with intensities lower than about 5% could be resolved in the XR patterns and identified as foreign phases of $YbAl_2$ or $YbAl_3$. The electrical resistivity $\rho(T)$, the magnetic susceptibility $\chi(T)$ and the specific heat $C(T)$ were measured utilizing standard techniques.

3. Results

We have found numerous ternary compounds in the Yb–Ag–Al phase diagram (Table 1), most of which have been investigated by means of $\chi(T)$ measurements. Some of the typical results are shown in Fig. 1. All systems show a small, almost temperature-independent susceptibility, while the upturn in $\chi(T)$ to lower temperatures is due to a small amount of paramagnetic impurities or foreign phases. Therefore, Yb has no magnetic moment in these compounds, the 4f shell is completely filled and the Yb valence is nearly 2+. A slightly different behavior is observed for $YbAg_{0.7}Al_{2.3}$, which shows a maximum in $\chi(T)$ at $T = 280$ K, indicating a tendency to IV behavior.

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TABLE 1. Crystallographic and magnetic properties of the Yb–Ag–Al compounds studied in this paper; composition, crystal structure and susceptibility χ(300 K) at room temperature

Composition			Structure	χ(300 K) (10^{-9} m^3 mol^{-1})
Yb	Ag	Al		
1	0.3	1.7	$MgCu_2$	3.4
1	1.5	0.5	$MgZn_2$	Not measured
1	0.7	2.3	$PuNi_3$	17
1	1.3	1.7	$CeNi_3$	4.8
1.8	7	10	Th_2Ni_{17}	−4.5
2	9	8	Th_2Zn_{17}	Small
1	2	3	$Sc_3Ni_{11}Si_4$	4
1	4	7	$BaHg_{11}$	3.4 (χ(50 K))
1	5.3	5.7	$BaCd_{11}$	−2.8
8	21	45	New	Not measured

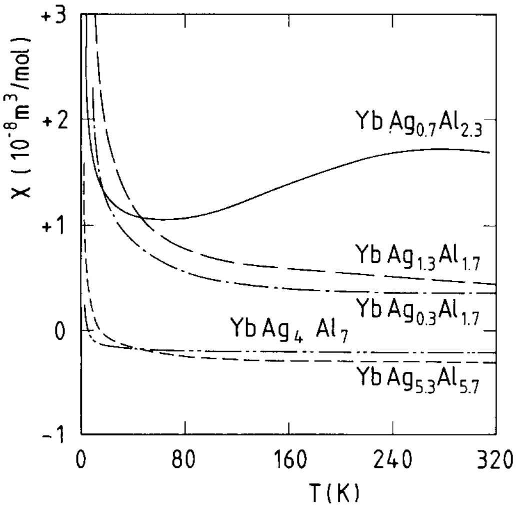

Fig. 1. Magnetic susceptibility χ vs. temperature T for Yb–Ag–Al compounds.

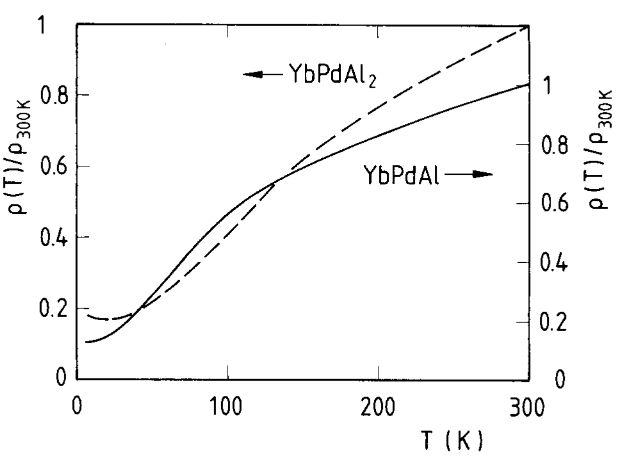

Fig. 2. Normalized electrical resistivity $\rho(T)/\rho_{300\,K}$ vs. temperature T for YbPdAl and $YbPdAl_2$.

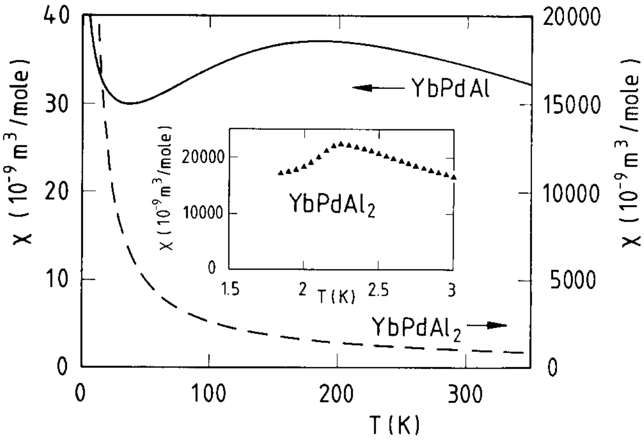

Fig. 3. χ vs. T for YbPdAl and $YbPdAl_2$. Inset shows data for $YbPdAl_2$ below $T=3$ K.

Only one composition out of the Yb–Au–Al phase diagram has been investigated in more detail: YbAuAl. It crystallizes in the orthorhombic TiNiSi-type structure with lattice parameters $a=7.198$ Å, $b=4.478$ Å and $c=7.716$ Å. The physical properties are comparable to those of the Yb–Ag–Al compounds. The electrical resistivity shows metallic behavior, the susceptibility is small and almost temperature independent, and the Yb valence is near to 2+.

In Yb–Pd–Al we have found two phases up to now: YbPdAl and $YbPdAl_2$. The former crystallizes in the orthorhombic TiNiSi-type structure with $a=6.818$ Å, $b=4.350$ Å and $c=7.795$ Å, the latter in the orthorhombic $MgCuAl_2$-type structure with $a=6.891$Å, $b=10.004$ Å and $c=4.246$Å. The temperature dependence and magnitude of the resistivity of both compounds are typical of a metal with no pronounced anomalies (Fig. 2). The 1-1-1 compound exhibits a weak "bump"in $\rho(T)$ around 100 K, whereas the 1-1-2 compound exhibits a small upturn at low temperatures, possibly indicating a weak Kondo effect. YbPdAl shows a weakly temperature-dependent susceptibility with a maximum around 180 K (Fig. 3).

The $\chi(T)$ values are three times larger compared to those of the Yb–Ag–Al compounds. The maximum in $\chi(T)$ and the change in slope of $\rho(T)$ indicate IV behavior. Applying the formula $T_{\chi,\max}=2500(3-v)$ as proposed by Klaasse *et al.* [2], which relates the temperature of the $\chi(T)$ maximum, $T_{\chi,\max}$, to the Yb valence, v, one obtains for YbPdAl an Yb valence of about 2.9+. The upturn in $\chi(T)$ as $T\to0$ is ascribed to small amounts of foreign phases. The susceptibility of the $YbPdAl_2$ compound is larger than that of the 1-1-1 compound by about two orders of magnitude and shows a Curie–Weiss behavior with an effective moment of $\mu_{Yb}=4.0\ \mu_B$. The low-temperature part of the susceptibility is shown in the inset of Fig. 3. At $T_N=2.2$ K, a kink in $\chi(T)$ is observed indicating the onset of antiferromagnetic (AF) ordering. The AF transition manifests itself also in a huge anomaly in the specific

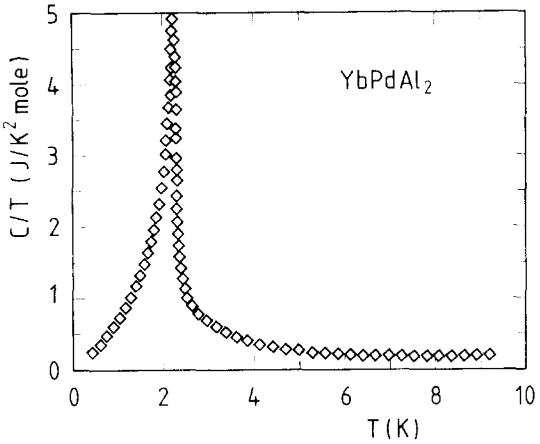

Fig. 4. Specific heat of YbPdAl$_2$ in a plot C/T vs. T.

heat at $T_N = 2.2$ K (Fig. 4). Since the contributions of both the phonons and the (spd) conduction electrons are negligible in this temperature range, the entropy related to the 4f electrons can be estimated by integrating the data of $C(T)/T$. This yields a value of $\approx 0.5R \ln 2$ at T_N, whereas the full value (for a low-lying crystal field doublet) is reached around 10 K. The reduced entropy value at T_N is probably related to short-range ordering effects, as evidenced by a large tail in $C(T)/T$ above T_N. Since C/T versus T does not obey a power law at the lowest temperatures, the residual electronic specific heat coefficient γ_0 cannot be determined in a reliable way. We estimate γ_0 to range between 50 and 200 mJ K^{-2} mol^{-1}, very similar to AF ordered Ce-based HF systems like CeAl$_2$ [7]. This comparison suggests strongly that the Yb valence must be close to 3+, and the Kondo temperature must be quite low.

4. Discussion

We focus on two problems: the first concerns the parameters determining the valence of Yb in these compounds and the second concerns the apparent weakness of the Kondo effect in the transition regime between a stable trivalency and IV.

Combining the present results with the properties of related binary and ternary compounds, previously investigated [8], we suggest the following scheme for the evolution of the Yb valence in Yb–TM–Al compounds. If TM is an element of the Ib- (Cu-) column, the Yb^{2+} state is rather stable. (Near) trivalency is observed only in the binary compounds with TM = Cu and Au at low Yb contents. The notable exception to the scheme is YbCuAl [9] with Yb being in an IV state with $v \approx +(2.9–3)$. This may be related to its Fe$_2$P-type structure, which differs from the TiNiSi type of the other 1-1-1 compounds investigated here. Upon replacing the Ib element by an element of the Ni column, the divalent Yb configuration is found to be destabilized. It seems that most of the corresponding Yb–TM binary compounds are trivalent and the valence of Yb in the Yb–Pd–Al compounds presented here is close to or equal to 3+ and is systematically larger than in the corresponding compounds with a Ib element.

It is instructive to compare this scheme with that derived for the homologous Ce compounds. There, compounds with a Ib element exhibit stable trivalent Ce, whereas in compounds with an element of the Ni column IV behavior with $v > 3$ is often encountered, especially with TM = Ni. Thus, we can state some analogy between the change of the RE valence in Ce compounds and their Yb homologs: Ib elements with their filled d shell stabilize the lower-valence state for both Ce and Yb, whereas elements with an unfilled d shell stabilize the higher-valence state. Obviously the possibility of the unfilled d shell to form hybridized states with neighboring ions renders the RE state with the larger number of valence electrons (*i.e.* lower 4f occupation number) energetically more favorable.

Apart from this similarity, an interesting difference can be noted when comparing Ce- and Yb-based compounds. In Ce compounds, the transition from trivalent to IV behavior occurs rather smoothly, when the composition is changed within a given ternary phase diagram. In the composition region, where this transition occurs, pronounced Kondo anomalies are observed for the corresponding compounds, indicating Kondo temperatures in the Kelvin (or tens of Kelvins) range. However, for the Yb–Pd–Al system, the transition from the magnetically ordered compound YbPdAl$_2$ with trivalent Yb to the adjacent IV compound YbPdAl is not accompanied by evidence for the Kondo effect in either of these compounds. The absence of a pronounced Kondo anomaly in the T dependence of the electrical resistivity has also been reported in other Yb compounds, *e.g.* YbP [10] and YbBiPt [11]. On the other hand, both systems exhibit large $C(T)/T$ values at low temperatures. Similarly, while numerous dilute Ce alloys exhibit the Kondo effect, this is very rare in the case of dilute Yb alloys. This raises the question whether the Kondo theory is an appropriate model for the description of Yb compounds with a valence close to 3+. The apparent difference between nearly trivalent Ce systems and their Yb counterparts can presumably be traced back to the different spatial extent of the 4f wave functions, being substantially smaller in Yb^{3+} than in Ce^{3+}.

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References

1 F. Steglich, U. Ahlheim, C.D. Bredl, C. Geibel, M. Lang, A. Loidl and G. Sparn, in L.C. Gupta and M.S. Multani (eds.), *Frontiers in Solid State Science*, World Scientific, Singapore, 1992.

2 J.C.P. Klaasse, F.R. de Boer and P.F. de Châtel, *Physica B, 106* (1981) 178.

3 Z. Fisk and M.B. Maple, *J. Alloys Comp., 183* (1992) 303.

4 C. Schank, F. Jährling, L. Luo, A. Grauel, C. Wassilew, R. Borth, G. Olesch, C.D. Bredl, C. Geibel and F. Steglich, *J. Alloys Comp., 207/208* (1994) 329.

5 R. Henseleit, Ph.D. Thesis, Darmstadt, 1992, unpublished.

6 G. Cordier, T. Friedrich, R. Henseleit, A. Grauel, U. Tegel, C. Schank and C. Geibel, *J. Alloys Comp., 201* (1993) 197.

7 C.D. Bredl, F. Steglich and K.D. Schotte, *Z. Phys. B, 29* (1978) 327.

8 Landolt-Börnstein, *Group III*, Vol. 19e1 and Vol. 19d2, 1990.

9 W.C.M. Mattens, R.A. Elenbaas and F.R. de Boer, *Communications on Physics, 2* (1977) 147.

10 H.R. Ott, H. Rudigier and F. Hulliger, *Solid State Commun., 55* (1985) 113.

11 J.D. Thompson, P.C. Canfield, A. Lacerda, M.F. Hundley, Z. Fisk, H-R. Ott, E. Felder, M. Chernikov, M.B. Maple, P. Visani, C.L. Seaman, M.A. Lopez de la Torre and G. Aeppli, *Physica B, 186–188* (1993) 355.