

Magnetic Order and Other Phase Transitions in Mixed-Valent YbPd

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Specific heat, thermal expansion, and electrical resistivity show that YbPd undergoes four phase transitions at 0.5, 1.9, 105, and 125 K. From magnetic-susceptibility measurements the transition at 0.5 K is found to be magnetic. The quasielastic magnetic linewidth is large as usual for mixed valence, but decreases with temperature and is smaller than $k_B T$ everywhere. The magnetic order of YbPd occurs at a fractional Yb valence of $\nu = 2.8$ (measured by L_{III} absorption), i.e., near configurational crossover of $4f^{13}$ and $4f^{14}$.

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Magnetic order of Yb in metals is rare. To our knowledge the only certain case was YbBe_{13} ^{1,2} ($T_{\text{Neel}} = 1.28$ K, $\mu_{\text{eff}} = 4.54\mu_B$) until recently. This rarity of magnetic order may be blamed on the tendency of Yb to go into a mixed-valent state. However, on the other end of the lanthanide series Ce has the same tendency and yet shows magnetic order quite frequently. Since compounds with Ce have been studied much more frequently than compounds with Yb, the rarity of magnetic order in Yb compounds may simply be a matter of insufficient statistics. Indeed, three new cases of magnetically ordering Yb compounds have recently been found: YbPd, Yb_3Pd_4 ,³ and YbIr_2 .⁴

In this paper we report a thorough study of YbPd. This compound turns out to be a very interesting system, because the magnetic order occurs clearly at fractional valence, near configurational crossover of $4f^{13}$ and $4f^{14}$.

The major problem in the initial stages of this work was the preparation of single phase YbPd. The ingots were heated in a welded Ta crucible by induction. Only minor deficiency of Yb leads to the formation of

Yb_3Pd_4 , which we also found to order magnetically.³ According to our experience a 3% surplus of Yb is the proper procedure to obtain stoichiometric YbPd. All samples (including the isostructural reference compounds LuPd and CaPd) were characterized by Debye-Scherrer patterns and microsections and showed the cubic CsCl structure.⁵

We have measured specific heat, thermal expansion, thermopower, and neutron inelastic magnetic scattering between $T \approx 1.5$ and 350 K and electrical resistivity and magnetic susceptibility between 40 mK and 300 K (Figs. 1-5).

The lattice-constant anomaly of YbPd observed between 77 and 1000 K (as compared with CaPd and LuPd) was used by Iandelli and Palenzona⁵ to classify YbPd as clearly mixed valent.

Our low-temperature specific heat of YbPd is much larger than that of the reference compounds LuPd and CaPd (inset of Fig. 1). The difference ΔC of the specific heats of YbPd and LuPd shows four anomalies at 1.9, ≈ 17 , 105, and 125 K (Fig. 1), which all can be found again in the difference of the thermal expansion coefficients $\Delta\alpha$ (Fig. 2) and in the resistivity ρ (Fig. 3).

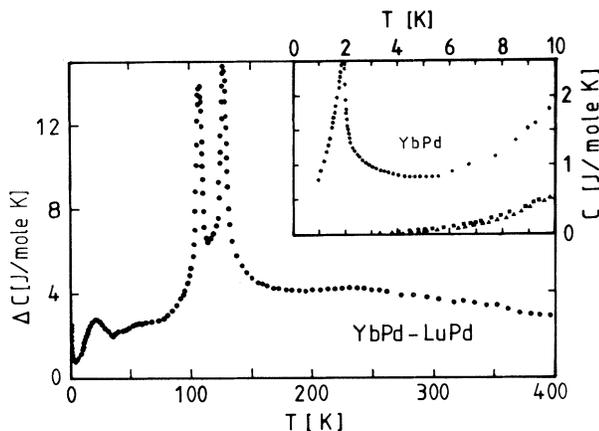


FIG. 1. Difference ΔC of the specific heats of YbPd and LuPd vs temperature. Inset: Specific heats of YbPd (circles), LuPd (squares), and CaPd (triangles) at low temperatures.

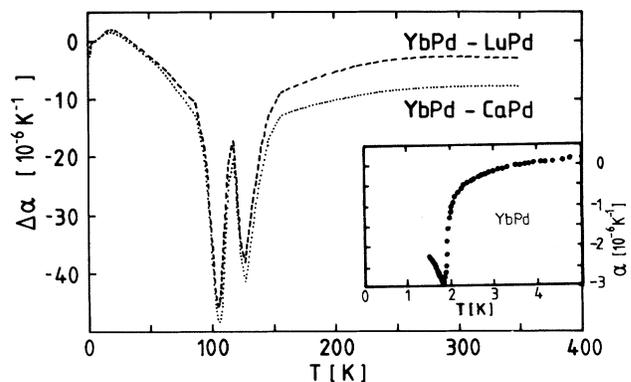


FIG. 2. Difference $\Delta\alpha$ of the thermal expansion coefficients of YbPd and LuPd/CaPd vs temperature. Inset: α at low temperatures.

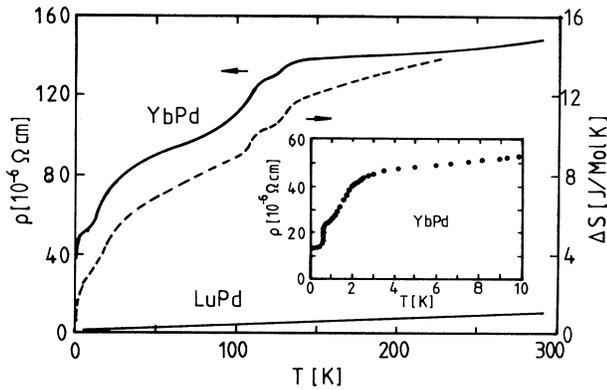


FIG. 3. Resistivity ρ of YbPd and LuPd vs temperature and difference of entropies ΔS of YbPd and LuPd vs temperature. Inset: ρ at low temperatures.

$\Delta\alpha$ is negative between 1.5 and 400 K. This is typical for an intermediate-valence (IV) Yb compound, where with increasing temperature the valence is usually shifting towards the trivalent state ($4f^{13}$) with the smaller volume. The unusual sharp spikes of $\Delta\alpha$ at 105 and 125 K could indicate a structural phase transition, but careful temperature-dependent x-ray measurements did not give any hint in this direction. However, the lines are all quite broad.

With a room-temperature valence of 2.83 or 2.79 [calculated from lattice parameters with Vegard's law (curve *b*) and with the "sagging curve" model (curve *c*)⁶] we have tried to extract the valence and its temperature dependence from the lattice constant and the thermal expansion anomaly (Fig. 6). Below about 110 K the values differ substantially from those obtained from L_{III} absorption edges (curve *a*) (Fig. 6). We interpret this discrepancy as another indication for structural phase transitions at 105 and 125 K, which seem to cause a considerable volume change without valence change, thus falsifying the valence determination

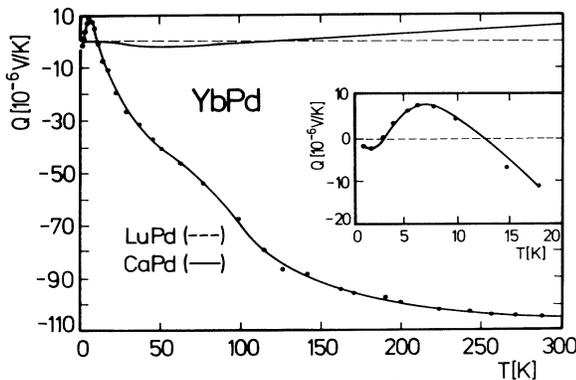


FIG. 4. Thermopowers Q vs temperature for YbPd, LuPd, and CaPd. Inset: Q at low temperatures.

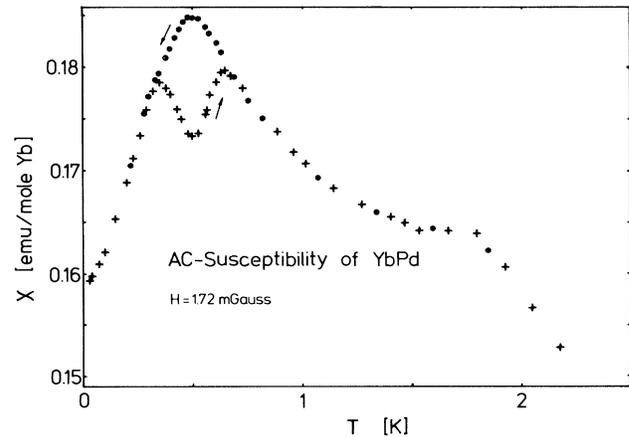


FIG. 5. Susceptibility χ vs temperature for YbPd at low temperatures (arrows indicate cooling and heating curves).

via the volume anomaly by δv_s of order 10% (Fig. 6). Another falsification of the valence determination via the volume anomaly is due to the strong temperature dependence of the fluctuation temperature (see below), which causes the finite slope of $v(T)$ above about 130 K.⁷ Both valence measurements show that YbPd is clearly mixed valent, which is confirmed by all other measurements carried through at our institute (magnetic susceptibility, neutron inelastic scattering, magnetostriction, thermal conductivity, and point-contact spectroscopy).

The thermopower of YbPd is uncommonly large and negative over a wide temperature range (Fig. 4). Note the unusual behavior at low temperatures, i.e., the two sign reversals at 3 and 12 K (inset in Fig. 4). The negative thermopower and also the resistivity are quite similar to the entropy difference ΔS . In the latter case the similarity is particularly striking over the entire temperature range of the measurement.

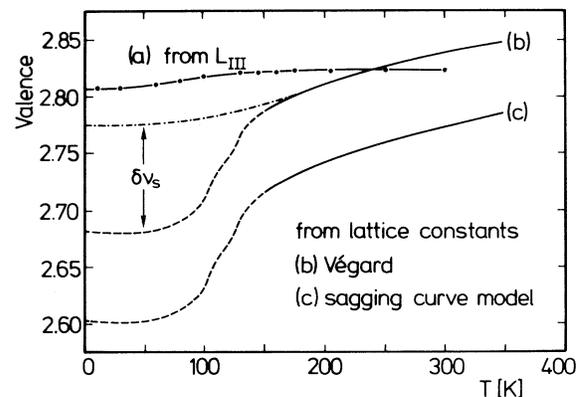


FIG. 6. Valence ν vs temperature as derived from L_{III} absorption (curve *a*), Vegard's rule (curve *b*), and "sagging curve" model (curve *c*) (see text).

The low-temperature resistivity shows two distinct anomalies at 1.9 and 0.5 K (inset in Fig. 3). The sharp decrease (together with the behavior of specific heat and thermal expansion at 1.9 K) indicates that both anomalies are caused by electronic phase transition.

In order to characterize these low-temperature phase transitions better we measured the magnetic susceptibility (inductively) down to 40 mK in a weak magnetic field of $H = 1.72$ mG (Fig. 5). The distinct anomaly of χ at 0.5 K shows that we have magnetic ordering at this temperature (probably antiferromagnetic). This result is confirmed by a rough estimate of the ordering temperature, which can be obtained by de Gennes scaling from the ordering temperature of Gd^{3+} in GdPd ($T_N = 38.6$ K). This yields $T_N = 0.8$ K for 100% Yb^{3+} and $T_N = 0.64$ K for 80% Yb^{3+} . The large specific heat near the phase transition makes it difficult to measure the actual temperature of the sample near the ordering point during the cooling and heating cycles in our cryostat. This may be the reason for the unusual hysteresis loop in the magnetic susceptibility between 0.3 and 0.7 K.

At this point one should ask: How can magnetic ordering appear in such a strongly mixed-valent compound? (At configurational crossover, i.e., at energetic degeneracy of Yb^{2+} and Yb^{3+} , the valence is 2.89). This question was answered in part by measurements of the quasielastic linewidth of the neutron spectra down to 1.4 K that show that the fluctuation temperature T_f is everywhere smaller than $k_B T$ (Fig. 7). (At 300 K the quasielastic linewidth is between 5 and 15 meV.) At low temperatures there also appear inelastic transitions between 5 and 15 meV as one would expect, for instance, when the quasielastic linewidth becomes smaller than the usual crystal-field splittings of Yb^{3+} .⁸ $T_f < T$ implies that at the ordering temperature predicted by de Gennes scaling the magnetic ordering energy $k_B T_N$ is larger than the valence fluctuation energy $k_B T_f$. The more pertinent question then is: Why does T_f drop so dramatically with temperature in YbPd , while in other mixed-valence compounds with nearly the same fractional valence T_f is fairly temperature independent and large compared to T_N extrapolated from de Gennes scaling? ($T_f \approx 40$ K in YbCu_2Si_2 ⁹; $T_f \approx 50$ K in YbCuAl ¹⁰).

The anomaly of χ at 1.9 K is not as pronounced as the one at 0.5 K. One may doubt whether the phase transition at this temperature is due to magnetic order. Rather we might observe quadrupolar ordering, as was reported for TmZn ¹¹ and UPd_3 .¹²

YbPd is a mixed-valence compound with a valence changing from $\nu = 2.82_2$ at 300 K to $\nu = 2.80_5$ near $T = 0$. We have detected four phase transitions, two of which, at 105 and 125 K, should be structural, although this could not be confirmed, while two others at 1.9 and 0.5 K are electronic. The transition at 1.9 K

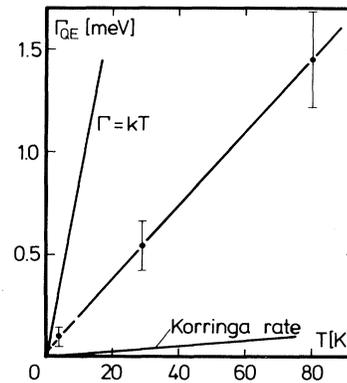


FIG. 7. Temperature dependence of the quasielastic magnetic linewidth Γ (half width at half maximum) of YbPd below 80 K. Γ is much larger than that due to the usual electronic Korringa exchange mechanism but remains smaller than $k_B T$.

may be due to quadrupolar ordering; the one at 0.5 K is due to magnetic order.

While all these phase transitions are very unusual, the magnetic one is of the greatest interest in principle, because it occurs in a clearly mixed-valent state. Up to now the absence of magnetic order in mixed valence compounds with Ce, Eu, Sm, and Yb and its existence in strongly mixed valent TmSe ¹³ has been rationalized¹⁴ by the observation that Tm has magnetic moments in the Hund's-rule ground states of both adjacent valence states ($4f^{12}$ and $4f^{13}$), while in all the other cases one of the Hund's-rule ground states is a nonmagnetic singlet. One might argue that this rule has been violated already several times in the past [e.g., in CeAl_2 and $\text{Eu}(\text{Pd}_{1-x}\text{Au}_x)\text{Si}_2$ ¹⁵], were it not for the fact that the magnetic order of these compounds is not usually associated with mixed valence, because the deviation from integral valence seems to be very small in these compounds. Thus the magnetic order of YbPd is of very special importance in this context. It confirms a different rule: Whenever the fluctuation temperature, for whatever reason, is smaller than the magnetic ordering temperature expected on the basis of de Gennes scaling from stable valent reference compounds and of the dilution effect implied in fractional valence, magnetic ordering occurs and vice versa.

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