Magnetic and Nonmagnetic Charge States in YbPd

P. Bonville, J. Hammann, J. A. Hodges, P. Imbert, and G. J. Jéhanno
Département de Physique Générale, Service de Physique du Solide et de Résonance Magnétique, Centre d'Etudes Nucléaires de Saclay, 91191 Gif-sur-Yvette, France
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In YbPd, ^{170}Yb Mössbauer measurements show that two different Yb charge states, one magnetic and one nonmagnetic, are present in essentially equal proportions. For the magnetic fraction the saturated spontaneous magnetic moment is $1.15\mu_B$, which is lower than that in any of the Yb^{3+} cubic crystal-field levels, and there is no evidence of any anisotropy in the $4f$-shell charge distribution. These results suggest the presence of $4f$–conduction-band hybridization. Both above and below the ordering temperature of the magnetic fraction, the remaining Yb possess a negligibly small magnetic susceptibility and an isomer-shift value characteristic of a charge state close to Yb^{2+}.

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The interaction between the localized f electrons and the conduction-band electrons in metallic rare-earth and actinide compounds is responsible for a number of exotic properties (for example those linked with Kondo-lattice[1] and heavy-fermion[2] systems), and is the center of much current attention. The magnetic properties of compounds with unstable f shells are particularly interesting because of the potential competition between the hybridization of the f electron with the conduction band, which tends to dissolve the crystal electric-field–fashioned f-shell moment, and the exchange interactions, which can act to stabilize these moments. Among Ce compounds, for example, cases are known where the hybridization is strong enough to prevent the formation of an ordered moment ($CeBe_{13}$),[3] or where it is just strong enough to result in a reduced moment (CeTe).[4] The modulated nature of the size of the magnetic moment in $CeAl_2$[5] has been attributed to the presence of a site-dependent competition between the two effects.

Yb-based intermetallics have attracted less attention than those containing Ce. Because of the low de Gennes scaling factor for Yb, any magnetic ordering will generally occur at correspondingly low temperatures. In fact, for Yb intermetallics, magnetic order has only been evidenced in a relatively small number of cases. The moments observed are found to be fashioned essentially by the crystal field alone (e.g., $YbBe_{13}$[6]) and until now no case has been reported of the reduction of the Yb spontaneous magnetic moment due to hybridization.

The equiatomic compound YbPd occupies a unique position in the Yb-Pd phase diagram. For the alloys which are rich in Pd (such as $YbPd_3$), the Yb^{3+} state is stabilized, whereas for the Yb-rich alloys (such as Yb_3Pd) the Yb^{2+} state is stabilized.[7] YbPd, situated at the border between the two zones, has long been known to show anomalous properties which have been linked to $4f$-charge instabilities.[8] Recently a comprehensive experimental study was made by use of a number of different macroscopic techniques.[9] This study concluded that in YbPd, the Yb was in a homogeneous mixed-valence state with a valency ($\sim$2.8) which is slightly lower than that corresponding to Yb^{2+}-Yb^{3+} configuration crossover (2.89) and that magnetic ordering occurred at 0.5 K. Photoemission results[10] also gave a similar average valency ($\sim$2.75).

Here we show that magnetic ordering occurs, in fact, at 1.9 K and while we confirm that YbPd is mixed valent, we show that it appears to be a unique case where in a simple alloy two rare-earth charge states, one strongly magnetic, the other nonmagnetic, are present in essentially equal proportions. In cases where two or more different rare-earth charge states have been evidenced previously, the alloys were made up of three or more constituents and the different charge states were linked to local environmental effects such as chemical disorder.[11]

The sample was prepared in a sealed tantalum crucible and was annealed at 260 °C for 10 days. Higher annealing temperatures lead to the formation of some Yb_3Pd_4. YbPd is conventionally taken to have the cubic CsCl-type structure. However, a small distortion of the unit cell has recently been observed at low temperatures.[12] X-ray measurements show broad lines at all temperatures and at 4.2 K we observe a tetragonal distortion with $c/a = 1.007$. This ratio decreases as the temperature increases and it is possible that a weak residual distortion is still present at room temperature. If the results at room temperature are expressed in terms of an assumed cubic lattice, the cell parameter is 3.443 ± 0.001 Å. To within the limits set by the linewidths all the sites occupied by the Yb are crystallographically equivalent. The intensity measurements show that the Yb and Pd are well ordered on their respective sublattices.

Mössbauer absorption measurements at 4.2 K and below were made on the isotope ^{170}Yb with use of a TmB_{12} (^{170}Tm) source. For ^{170}Yb $I_{g.s.}=0$, $I_{ex}=2$, $E_\gamma=84$ keV, and a Doppler velocity of 1.0 mm/s corre-

sponds to 68 MHz.

Figure 1 shows the zero-applied-field line shapes at 0.05, 1.4, and 4.2 K. At 0.05 K, the absorption pattern is made up of two subspectra of essentially equal weights. The first consists of five equally intense lines and the second of a single line at about the same Doppler velocity as the central component of the quintet. The quintet is well fitted by an effective-field Hamiltonian which shows that the associated Yb are magnetically ordered. The hyperfine field is 1.16 ± 0.02 MOe and the component of the electric field gradient parallel to the hyperfine field direction is $e^2q_{zz}Q = -0.8 \pm 0.3$ mm/s. This is a very small value showing that in the presence of magnetic ordering, the $4f$-shell charge distribution does not show any significant anisotropy. At 1.4 K, the quintet spectrum is well fitted in terms of an effective hyperfine field of 0.88 ± 0.06 MOe. The lines are broader than at 0.05 K and this may be attributed to magnetic relaxation within the ordered state or to a distribution of hyperfine fields which becomes visible as the magnetic ordering temperature is approached. At both 0.05 and 1.4 K the overall line shapes are symmetric and can only be fitted in terms of the superposition of a single line and an effective-field line pattern. They cannot be fitted in terms of paramagnetic Yb experiencing a quadrupolar hyperfine interaction or undergoing relaxation. From the observed thermal variation of the hyperfine field (which is proportional to the $4f$-shell magnetic moment) in the range $0.05 < T < 1.7$ K, we establish that the magnetic ordering temperature is close to 1.9 K. The phase transition previously identified at this temperature is thus magnetic in origin and not quadrupolar as suggested in Ref. 9. There is no anomaly in the thermal variation of the hyperfine field at 0.5 K which was previously identified as the magnetic ordering temperature. A comparison of the intensities of the two subspectra shows that $52 \pm 5\%$ of the Yb are magnetically ordered. At 4.2 K a fairly narrow, symmetric, single line is visible and there is no evidence of magnetic or quadrupolar interactions on any of the Yb. This shows that despite the weak tetragonal lattice distortion, the Yb show essentially cubiclike behavior.

The narrow single-line nature of the second subspectrum (Fig. 1) shows that at these temperatures the associated Yb experience no hyperfine field and no electric field gradient. The absence of a hyperfine field below 1.9 K may be due to one of two possibilities. Either these Yb are intrinsically paramagnetic but they do not carry a polarized magnetic moment, or they are intrinsically nonmagnetic. To distinguish between these two possibilities, we made Mössbauer measurements in an applied magnetic field which was oriented parallel to the incident γ-ray direction. The results at 4.2 and 1.4 K in a field of 5.5 T are shown in Fig. 2. Both above and below the ordering temperature of the magnetic fraction, two subspectra, a central single line and a well split doublet, are visible. The central line in Fig. 2 at both 4.2 and 1.4 K is due to Yb experiencing a magnetic field which is only of the order of the applied field (5.5 T). These Yb thus have vanishingly small field-induced $4f$-shell moments and thus possess a vanishingly small magnetic susceptibility. The doublet is due to Yb experiencing a sizable hyperfine field, that is, to Yb carrying a sizable $4f$-shell moment, oriented parallel to the γ-ray direction. (When the hyperfine field is oriented parallel

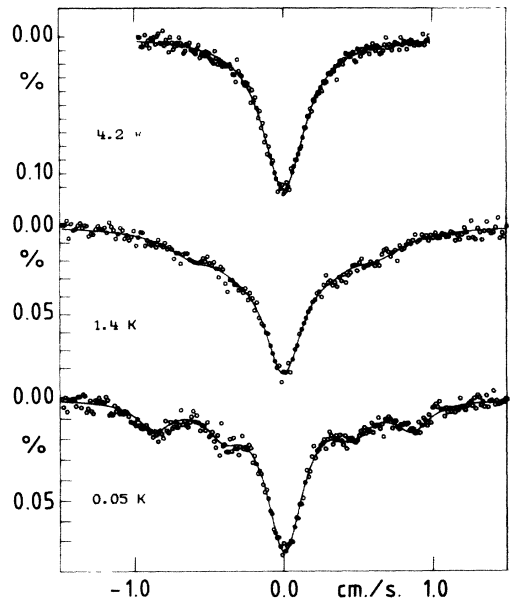

FIG. 1. ^{170}Yb Mössbauer absorption for YbPd at 4.2, 1.4, and 0.05 K. At both 1.4 and 0.05 K two subspectra of essentially equal intensities, the first a quintet pattern fitted by an effective hyperfine field, the second a single line, are present.

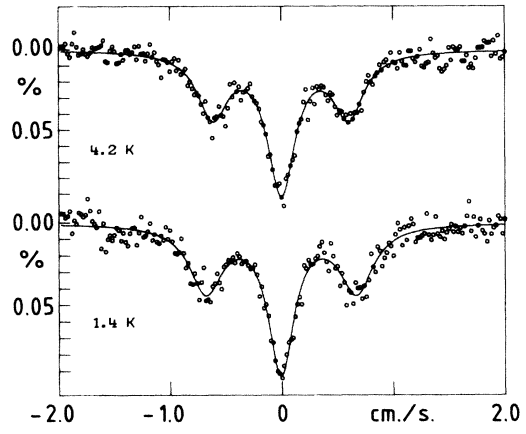

FIG. 2. ^{170}Yb Mössbauer absorption for YbPd at 1.4 and 4.2 K in a field of 5.5 T applied parallel to the γ-ray propagation direction. At both temperatures, two subspectra of essentially equal intensities, the first a split doublet, the second a single line, are present.

to the γ-ray direction, selection rules eliminate the $\Delta m_I = 0$ and ± 2 transitions leaving only the $\Delta m_I = -1$ transitions, that is, the second and fourth lines of the quintet pattern.) At 4.2 K the hyperfine field is 1.6 MOe and at 1.4 K it is 1.7 MOe. A comparison of the intensities of the two subspectra shows that at both temperatures again $52 \pm 5\%$ of the Yb belong to the magnetic fraction.

We have also measured the bulk magnetization for a sample taken from the same preparation as used for the Mössbauer study and it is interesting to compare the two sets of results. As mentioned previously the Mössbauer results show that only about half of the Yb are magnetized by a magnetic field and that at 4.2 K in a field of 5.5 T, the magnetic moments are aligned parallel to the applied field direction. The magnetization measurements at 4.2 K and 5.5 T give a sample-averaged moment of $(0.84 \pm 0.04)\mu_B$/Yb so that the magnetic moment of the [(52 ± 5)% abundant] magnetic fraction is $(1.61 \pm 0.16)\mu_B$/Yb. As the hyperfine field for these Yb at the same temperature and field is 1.60 ± 0.03 MOe, the hyperfine constant is thus near 1.0 MOe/μ_B. This is the standard Yb^{3+} value,[13] and it is also the value found for Yb in the nonordering intermediate-valence alloys $YbAl_3$[14] and YbCuAl[15] presenting $4f$–conduction-electron hybridization. The value of the hyperfine constant found here cannot, by itself, be used to obtain information concerning the presence by hybridization.

Neutron inelastic scattering measurements on YbPd have suggested that Yb has a Γ_8 ground state.[12,16] The field dependence of the magnetization and of the hyperfine field (which is linearly related to the magnetization), calculated at 4.2 K with the level scheme of Ref. 16, is in fairly good agreement with the experimental data up to about 5.0 T. However, two other low-temperature experimental results are in disagreement with the predictions of a purely cubic cystalline electric field model.

First, in the magnetically ordered state, the saturated spontaneous magnetic moment per Yb of the magnetic fraction as deduced from the hyperfine-field measurements is only $1.15\mu_B$ whereas the theoretical saturated value for the (anisotropic) Γ_8 state is at least $1.75\mu_B$. The measured saturated spontaneous moment is also smaller than those calculated for the Γ_7 ($1.7\mu_B$) and Γ_6 ($1.3\mu_B$) levels. In addition the experimental low-temperature saturated quadrupole interaction is over an order of magnitude smaller than that in any of the sublevels of the Γ_8 state.

Second, the simulations of the low-temperature Mössbauer spectra in a 5.5-T magnetic field, computed for a polycrystalline sample with the level scheme of Ref. 16, show asymmetrical line broadenings due to the combined anisotropic effects of the magnetic and quadrupolar interactions. Experimentally, no such asymmetrical broadenings are observed.

We have examined whether these two disagreements can be resolved by addition of a small tetragonal term into the cubic crystal field. As far as the properties in the magnetically saturated state are concerned, it is possible to produce a ground state with the same moment ($1.16\mu_B$) and quadrupole interaction (~ 0) as found experimentally. This can be done by our choosing a value for the tetragonal term and then applying a molecular field of reasonable strength at about 10° to the tetragonal distortion axis. The magnetic moment so produced lies approximately along the [111] direction. It is not evident why these particular directions would be favored in the YbPd lattice. However, in an external 5.5-T magnetic field, the simulations of the low-temperature Mössbauer spectra obtained with the tetragonally deformed crystal field still give rise to asymmetric line shapes in disagreement with experiment.

It thus appears that the properties of the Yb belonging to the magnetic fraction cannot be coherently interpreted in terms of a Yb^{3+} charge state experiencing only a crystal field. Both the isotropic character of these Yb and the lowering of the saturated spontaneous magnetic moment can be attributed to the perturbation of the $4f$ crystal-field properties arising from hybridization with the conduction-band states. This hybridization is, however, of relatively modest strength as it does leave a good-sized ordered magnetic moment.

For ^{170}Yb, meaningful isomer-shift measurements can generally be made only for narrow single-line spectra arising from a unique charge state. In the present case such measurements provide reasonably reliable results for the central single-line component observed in an applied magnetic field (Fig. 2). Relative to $TmAl_2$ and with the correction due to dispersion included, the isomer-shift value for this nonmagnetic charge state is -0.12 ± 0.04 mm/s. This value is the same as that observed for Yb in metallic hosts such as Yb metal (-0.10 ± 0.02 mm/s) and Ag metal (-0.12 ± 0.02 mm/s),[17] where the charge state is close to Yb^{2+}.

The two Yb charge states evidenced here are well defined on a time scale characteristic of the present Mössbauer measurements. If any fluctuations exist between the two charge states, they must occur on a time scale much longer than 10^{-10} s. A shorter fluctuation time would, for example, have begun to smear out the line shapes shown on Fig. 2. This time scale is a few orders of magnitude longer than that characteristic of single-atom interconfiguration charge fluctuations.

We have presented evidence showing that in YbPd at low temperature, two different charge states are present in essentially equal proportions. It is known that YbPd shows a small range of solid solution[8] and it would be interesting to examine whether the relative proportions of the two charge states vary across this range. Our x-ray measurements have not provided any evidence showing that there are two crystallographically different Yb sites.

The presence of two different charge states (having two different atomic volumes), however, would mandate the presence of two inequivalent sites however subtle the difference between them. We do not know whether the two charge states form an ordered array. Neutron-diffraction measurements at, say, 4.2 K in a sufficiently high external field would provide enough information to answer this point. It would also be interesting to examine the spontaneously magnetized structure (collinear or spin-glass arrangements?) both below the magnetic ordering temperature of 1.9 K and below the susceptibility anomaly observed near 0.5 K.

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