ON THE MIXED VALENCE BEHAVIOUR OF YTTERBIUM IN THE COMPOUND YbPd*

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Summary

The expansion coefficient and the magnetic susceptibility in the compound YbPd were measured at various temperatures. The data obtained were compared with those for TmPd, LuPd and CaPd. From these measurements it is possible to state that the compound YbPd contains ytterbium in a mixed valence state. The quantity of trivalent ytterbium increases slowly with temperature from 67% to 89% in the range 100 - 1000 K.

1. Introduction

Some years ago we studied the phase diagram of the binary system Yb-Pd [1]. Similar to other binary systems of ytterbium [2], the ytterbiumrich compounds Yb₃Pd and Yb₅Pd₂ contain ytterbium in the divalent state while the more palladium-rich phases are formed from ytterbium(III).

This behaviour, which has similarities to and differences from the phase diagrams of the trivalent rare earth-Pd alloys [3], can be deduced from magnetic measurements and structural data.

The compound YbPd appears to have ytterbium atoms in a mixed valence state, since the value of the lattice constant is not intermediate between but is higher than those of TmPd and LuPd; also the melting point of YbPd is much lower than the melting points of TmPd and LuPd. From the lattice constant values and from the melting points it can be inferred [4] that there is approximately 80% ytterbium(III) in YbPd. The magnetic susceptibility of the compound has been determined by Klaasse [5], who has found a Curie-Weiss behaviour with a magnetic moment a little lower than that of the free ytterbium(III) ion.

^{*}Dedicated to Professor Wilhelm Klemm on the occasion of his 85th birthday.

Since YbPd could be an example of a mixed or fluctuating valence compound, we carried out a reinvestigation and we present in this work the results obtained from measurements of the lattice constant and of the magnetic susceptibility.

2. Experimental

According to the phase diagram, YbPd melts congruently at 1460 °C. Below 1435 °C it crystallizes with the CsCl ordered structure type. Although another modification, an FeB type, has been reported [6], neither we nor other investigators have observed it. A limited solid solution is possible at high temperature, but it has a very small range below 1000 °C.

We examined many samples prepared by direct synthesis from the two elements. Ytterbium metal was a product of Koch-Light Laboratories, England, (nominal purity 99.9%) and was purified with respect to hydrogen content following the method described in ref. 7. The melting point and the transformation temperature were found to be 817 °C and 765 °C respectively. Palladium was a commercial powder of 99.9% purity which was heated *in vacuo* at 700 °C.

Fresh turnings of ytterbium and palladium powder were mixed together and were pressed in a tantalum crucible, which was soldered under very pure argon and was heated at 1500 - 1550 °C in an induction oven. All the samples obtained were examined micrographically and only those which appeared to be homogeneous were used in the analyses.

Something must be said about the preparation of these samples and about the products obtained. With ytterbium and palladium of the same batches as starting materials it is possible to obtain samples which are magnetically and micrographically different, depending on the reaction of the liquid alloy with the container. The best method for obtaining homogeneous samples with reproducible properties is to use tantalum and to avoid contact of the liquid alloy with the crucible for more than 5 min. The use of molybdenum as the container leads to unsatisfactory results, as will be shown in the following discussion on the magnetic properties.

The lattice constants of YbPd and of the isostructural compounds TmPd, LuPd and CaPd, prepared in a manner analogous to that for YbPd, were obtained at various temperatures.

Magnetic susceptibility measurements were carried out using the Foex-Forrer method in the range 100 - 600 K, while for higher temperatures a Faraday method with a Cahn-100 microbalance was employed. The measurements were made on samples soldered *in vacuo* in Pyrex or silica tubes up to 600 K. Since these materials react with the YbPd alloy, for higher temperatures we used small cylindrical containers of molybdenum which were then closed *in vacuo* in silica tubes and suspended on the balance.



Fig. 1. The variation of the lattice constants of RPd (R = Ca, Yb, Tm, Lu) CsCl-type compounds with temperature. The experimental points were fitted with the full curves according to the following expressions: CaPd, $a = 3.501 + 4.25 \times 10^{-5}T + 2.5 \times 10^{-8}T^2$; YbPd, $a = 3.439 + 0.49 \times 10^{-5}T + 2.5 \times 10^{-8}T^2$; TmPd, $a = 3.427 + 3.29 \times 10^{-5}T + 1.3 \times 10^{-8}T^2$; LuPd, $a = 3.403 + 3.79 \times 10^{-5}T + 0.6 \times 10^{-8}T^2$.

3. Results

Lattice constants of YbPd were measured for samples with compositions of 47.5, 48.7 and 55.0 at.% Pd, and on many samples with the stoichiometric composition which were prepared under various conditions and then quenched or slowly cooled. The filings of the alloys had to be annealed for some days at about 300 °C *in vacuo* to obtain sharp powder photographs. The lattice constants obtained from homogeneous or heterogeneous samples varied between 3.447 and 3.442 Å, indicating some solid solution.

The lattice constants were measured in a temperature range from about 100 K to the highest temperatures compatible with the reactivity of the silica capillaries with the alloy: for CaPd, up to 755 K; for TmPd, 900 K; for LuPd, 910 K; for YbPd, 960 K. The results are reported in Fig. 1.

Magnetic susceptibility measurements were made in the range 100 -1300 K on many samples of YbPd. The less homogeneous samples gave susceptibility values which were higher than those of the homogeneous samples.



Fig. 2. The variation of the magnetic susceptibility with temperature for two samples of YbPd.



Fig. 3. The variation of the reciprocal magnetic susceptibility with temperature for the two samples of Fig. 2.

The results for two "good" samples of different preparation are reported in Fig. 2 (χ is given in electromagnetic units per mole); Fig. 3 shows the behaviour of $1/\chi$ as a function of temperature. The reciprocal susceptibility increases linearly with temperature according to a Curie–Weiss law with C = 1.82 and $\theta = -92$ K.

4. Discussion

The determination of the percentages of the two types of atom with different valence seems to be important for intermediate valence compounds; these percentages correspond to the fractional occupation of the states with higher and lower energy (in the case of ytterbium compounds those corresponding to ytterbium(III) and ytterbium(II) respectively).

Of the various methods used to study fluctuating valence compounds, the determination of the structural cell parameter data and of their variations with temperature and pressure appears to be the most simple. These data, obtained from bulk samples, are not sensitive to the surface state and are also not very dependent on the purity and the homogeneity of the samples. However, they are dependent on the different dimensions of the two types of atom.

The lattice constants of RPd ($R \equiv$ rare earth) CsCl-type compounds decrease regularly from DyPd to LuPd [4] with the exception of that of YbPd; this compound has a lattice constant which is higher than that of TmPd, indicating the presence of some quantity of ytterbium(II) in the compound since the metallic radius of divalent ytterbium (1.939 Å) is higher than that of trivalent ytterbium (1.741 Å).

It can be seen from Fig. 1 that, while the lattice constants of TmPd and LuPd show identical increases with temperature, that of YbPd increases more slowly and only becomes lower than the lattice constant of TmPd at about 600 K; however, the value is still higher than that expected. Therefore YbPd should always contain, in the range of temperatures examined, ytterbium(II) in an amount which decreases with increasing temperature.

We can attempt to use the values of the lattice constants given in Fig. 1 to evaluate the percentages of ytterbium(II) and ytterbium(III) at the various temperatures. Those of YbPd with all the ytterbium atoms in the trivalent state can be determined easily at any temperature by taking the mean value between the data for TmPd and LuPd.

The temperature dependence of the lattice constant of YbPd with ytterbium atoms in the divalent state can be assumed to be the same as that for CaPd; however, the lattice constant value at room temperature must be determined. This can be obtained in the following ways.

(1) In the intermetallic isostructural compounds MCd, MHg, MTl (CsCl type) and MPb (AuCu type) ($M \equiv Ca, Yb(II)$), the lattice constants of the calcium compounds are always higher than those of the ytterbium compounds by about 0.75 - 0.80%, corresponding to the larger metallic

radius of calcium compared with that of ytterbium. From the lattice constant of CaPd (a = 3.516 Å) we obtain a = 3.490 Å for Yb(II)Pd.

(2) Different values are found by considering the volume contraction in the formation of the given MX compounds of calcium and ytterbium(II) from the elements; the contraction $\Delta V\%$ is always higher for the calcium compounds. The molar volume of Yb(II)Pd may be obtained from that of CaPd using the same difference in $\Delta V\%$; the corresponding *a* value varies between 3.487 and 3.501 Å, with a mean value of 3.494 Å.

(3) Since palladium shows a considerable electronegativity, YbPd may have a slight ionic character. Ca²⁺ is a little larger than Yb²⁺ in ionic compounds (ionic radii of 0.99_7 Å and 0.99_3 Å respectively); using the corresponding difference in the distances we would obtain an *a* value of 3.511 Å for YbPd ($a_{CaPd} = 3.516$ Å).

From all these considerations we can assume that $a = 3.495 \pm 0.005$ Å for YbPd at 298 K with all the ytterbium atoms in the divalent state; this seems to be a reasonable intermediate value between the two extremes of a = 3.487Å and a = 3.511 Å. The lattice constants calculated for Yb(II)Pd and Yb(III)Pd using this value and the measured constants are reported in Fig. 4 for different temperatures.



Fig. 4. The variation of the lattice constant with temperature: Yb(II)Pd, calculated; Yb(III)Pd, calculated; YbPd, measured.

The percentages of ytterbium in the two valence states can be determined by assuming a linear dependence of the lattice constant on the composition in the hypothetical system Yb(II)Pd-Yb(III)Pd. This linear behaviour was checked in many systems of isostructural intermetallic compounds of various trivalent rare earths, and also in the system $EuAl_2-LaAl_2$ [8] in which europium and lanthanum are respectively divalent and trivalent.

The percentage of ytterbium(III) is given in Fig. 5. It can be seen that it changes slowly from about 70% at low temperatures to about 88.6% at 1000 K. Strangely, if the formulae reported for the dependence of the lattice constants on temperature could be used, the same limiting constant value of about 89% Yb³⁺ would be obtained by extrapolating the values up to 1400 K.



Fig. 5. The variation of the percentage of Yb^{3+} in YbPd (evaluated from the lattice constants) with temperature.

We have already observed that the magnetic susceptibility is markedly influenced by the homogeneity and the purity of the samples, the less homogeneous samples giving higher susceptibilities. To examine the effect of impurities we prepared a sample of YbPd by melting the metals in a molybdenum crucible at 1650 °C and then maintaining the sample in the fused state at 1500 °C for 15 min. Chemical analysis showed that the sample contained nearly 2% Mo. The lattice constant at room temperature is only a little lower than that of the molybdenum-free sample; however, from the magnetic susceptibility (which followed a Curie–Weiss law) a higher value of the Curie constant was obtained (C = 2.23 which corresponds to $\mu = 4.22\mu_{\rm B}$, $\theta = -185$ K). These values are close to those found by Klaasse [5]. Therefore we believe that our values are correct.

As the measured susceptibility seems to follow a Curie–Weiss law, we cannot hope to obtain the thermal trend of the percentage of ytterbium-(III) in YbPd from these data; however, we can compare the value of the Curie constant (1.82) with the normal value for Yb^{3^+} (2.579) (or the square of the corresponding magnetic moments). The ratio of the two values is 0.71 and confirms that ytterbium is in a mixed valence state in YbPd. This value is in reasonable agreement with the values of 67 - 88% found from the analysis of the crystallographic data.

Finally, we can attempt to use the formula of Sales and Wohlleben [9] to determine the fractional occupation of the states corresponding to ytterbium(II) and ytterbium(III), and to compare these data with the percentages of ytterbium(III) found in YbPd. A satisfactory fit to the curve of Fig. 4 is obtained by assuming $T_{sf} = 92$ K and $E_{ex}/k = 300$ K. The low value of the interconfigurational excitation energy E_{ex} could explain the high percentage of Yb³⁺ in the compound YbPd under normal thermodynamic conditions.

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