Thermochimica Acta, 99 (1986) 187–191
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

HIGH TEMPERATURE HEAT CAPACITY OF ErPd AND TmPd AND THE INTERMEDIATE VALENCE COMPOUND YbPd

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(Received 6 September 1985)

ABSTRACT

Heat contents of the intermediate valence compound YbPd and the isotypic phases ErPd and TmPd were measured in a drop calorimeter over the temperature range 400–1200 K. The anomalous trend in heat capacity observed for YbPd as regards the other rare earth single valence phases can be ascribed to the promotion enthalpy associated with the electronic process occurring in this compound, namely the increase in percentage of trivalent ytterbium in the temperature range considered. The total energy required for this process has been evaluated as 0.13 eV.

INTRODUCTION

The purpose of this work is to compare the high temperature heat contents of pure trivalent rare earth compounds, ErPd and TmPd, and the mixed valence compound YbPd.

It is well known that YbPd is a mixed valence compound [1–4]. Its intermediate valence state can change depending on different thermodynamic conditions. Experimental results of magnetic and structural measurements carried out on this compound [3] were interpreted on the basis of variable percentages of trivalent and divalent ytterbium, the percentage of Yb^{3+} appearing to increase with temperature over the whole range examined. Knowledge of the heat content over a wide temperature range, when compared with that of a pure trivalent isostructural compound, can lead to the evaluation of the heat of promotion in the electronic process $Yb^{2+} \rightarrow Yb^{3+} + e^-$, if the valency change in the same temperature range is known. In the present work the results obtained for the intermediate valence compound YbPd and for ErPd and TmPd, which have been chosen as possible fixed valence, reference phases, are reported.

According to the corresponding phase diagram, YbPd melts congruently at 1733 K and below 1708 K it crystallizes with the cubic CsCl structure type [1]. ErPd melts congruently at 1813 K and undergoes a structural transfor-

0040-6031/86/$03.50

mation at about 820 K between orthorhombic FeB and cubic CsCl types [5]. TmPd probably melts congruently at about 1850 K (extrapolated value [2]) and crystallizes only with the CsCl structure type [6].

EXPERIMENTAL AND RESULTS

The R metals and palladium used in this research were commercial products with a nominal purity of 99.5 and 99.9%, respectively. The alloys, about 15 g each, were prepared by fusion in an induction furnace of weighed amounts of pure elements, sealed in tantalum crucibles under pure argon. No annealing treatment was carried out in the samples. X-ray and metallographic analyses were carried out in order to ascertain the homogeneity of the alloy, after and before repeated thermal cycles in the drop calorimeter. DTA curves were made to confirm the thermal data already known. Calorimetric measurements were made by means of a conventional Bunsen ice drop calorimeter over the temperature range 400–1200 K, according to a previously described method [7]. The samples were enclosed in cylindrical tantalum containers sealed by arc-welding under pure argon. Table 1 reports the experimental enthalpic results, for one mole of each intermetallic compound.

In the case of TmPd, the enthalpy values can be represented as a function of temperature by a parabolic equation, least-squares fitted to the experimental data

$$(H_T^0 - H_{273}^0) = A(T-273) + B(T-273)^2 \quad (\mathrm{J\ mol^{-1}})$$

Direct differentiation of this equation gives the thermal dependence of the heat capacity

$$C_P = A + 2B(T-273)^2 \quad (\mathrm{J\ mol^{-1}K^{-1}})$$

Any attempt to fit, by least-squares, the experimental enthalpic values of YbPd with a polynomial function of temperature like that of TmPd gave unacceptable results. Some equations were tested, simply by adding a third term to a parabolic function, which should describe the excess enthalpy of YbPd compared to a normal trend. Finally the following was selected

$$(H_T^0 - H_{273}^0) = A(T-273) + B(T-273)^2 + C(T-273)^{1/2} \quad (\mathrm{J\ mol^{-1}})$$

The heat capacity of YbPd becomes

$$C_P = A + 2B(T-273) + C/2(T-273)^{-1/2} \quad (\mathrm{J\ mol^{-1}\ K^{-1}})$$

In the case of ErPd, the experimental data cannot be fitted with only a single function of temperature, owing to a discontinuity in the 820–870 K temperature range: the enthalpic contributions above this temperature are higher than those below it. As previously found, by differential thermal and X-ray

TABLE 1

Experimental enthalpy data for ErPd, TmPd and YbPd

ErPd		TmPd		YbPd	
T (K)	$H_T^0 - H_{273}^0$ (kJ mol^{-1})	T (K)	$H_T^0 - H_{273}^0$ (kJ mol^{-1})	T (K)	$H_T^0 - H_{273}^0$ (kJ mol^{-1})
390.2	6.07	379.2	5.97	365.7	5.12
390.9	6.16	444.8	9.40	366.6	5.07
442.3	8.87	447.0	9.46	430.7	8.45
489.0	11.56	503.2	12.94	469.7	10.76
489.4	11.68	505.7	12.58	469.7	10.62
505.4	12.19	552.5	15.07	524.5	13.76
588.2	17.11	603.7	18.30	526.2	13.63
589.0	17.23	638.2	20.37	527.7	13.88
589.2	17.48	698.2	24.07	584.7	16.67
629.1	19.40	698.7	24.02	585.2	16.93
679.3	22.31	751.7	26.92	586.5	16.71
684.0	22.57	754.2	27.26	587.2	16.86
684.0	22.81	783.2	29.40	630.7	19.14
725.4	24.95	821.2	30.92	631.2	19.40
756.2	26.84	880.0	34.69	675.2	21.81
760.6	26.99	945.2	38.01	674.6	22.10
795.2	29.26	947.0	38.35	678.2	22.14
804.0	29.52	1019.2	42.06	723.2	24.81
843.3	33.03	1024.2	42.81	766.0	26.94
848.6	33.08	1065.2	45.15	766.7	26.42
888.9	35.51	1090.2	46.95	767.0	26.92
888.9	35.64	1241.2	55.45	818.2	30.32
924.3	37.64			819.2	29.69
926.9	37.88			872.4	33.27
959.3	40.03			880.4	33.56
988.9	41.57			885.8	33.86
989.2	41.62			930.4	36.16
990.9	41.91			931.9	36.20
1041.2	44.68			970.8	38.50
1077.5	46.87			972.2	38.44
1119.0	49.38			1036.2	42.33
1119.2	49.62			1081.7	45.34
1181.0	53.20			1083.2	45.28
1182.9	53.29			1145.2	49.01
				1146.7	49.08
				1175.7	50.87
				1180.4	52.51

analyses, this temperature has been recognized as the transformation temperature between FeB and CsCl structure types. Handled separately, the two series of values in the high and low temperature ranges can easily be described with linear functions of temperature, like a parabola as in the case of TmPd. The first derivatives of these functions directly give the depen-

TABLE 2

Least-squares calculated values of the constants in the enthalpy–temperature equations used for ErPd, TmPd and YbPd, corresponding standard deviations (in parentheses) and mean deviations, $\bar{d}$, of the experimental points from the fitted curves

Compound	a_0 (J mol^{-1})	a_1 (J mol^{-1} K^{-1})	a_2 (J mol^{-1} K^{-2})	a_3 (J mol^{-1} K$^{-0.5}$)	$\bar{d}$ (%)
ErPd (LT)		51.98(0.21)	$7.38(0.29)\times10^{-3}$		0.21
ErPd (HT)	−1312.85(81)	59.83(0.19)	$0.23(0.07)\times10^{-3}$		0.70
TmPd		55.24(0.34)	$2.30(0.22)\times10^{-3}$		1.00
YbPd		47.66(0.23)	$7.28(0.31)\times10^{-3}$	71.94(0.30)	0.80

LT = low temperature; HT = high temperature.

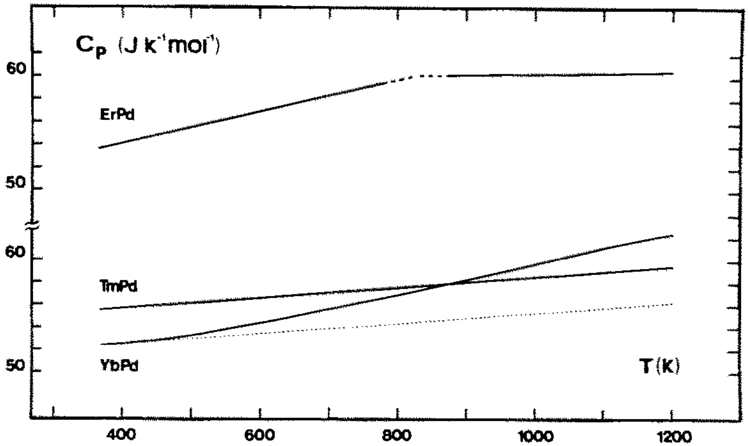

Fig. 1. Variation of the molar heat capacities of ErPd, TmPd and YbPd. For the meaning of the dotted line, see text.

dence of the specific heats of the two forms of ErPd on temperature. Values of the constants in enthalpy–temperature equations, the corresponding standard deviations and the mean deviations of the experimental values from the fitted equation, are reported in Table 2. Figure 1 shows the corresponding C_p trends in the temperature range considered.

DISCUSSION

To evaluate, on the basis of heat capacity measurements, the energy required for the electronic process $Yb^{2+} \rightarrow Yb^{3+} + e^-$, it is necessary that in the reference compounds the rare earths are present in a fixed valence state and no reaction of transformation must occur. Owing to the discontinuity found in the heat content of the ErPd compound, due to structural transformation, this compound cannot be used as a proper reference material. It is of interest to note that its behaviour at high temperature (Fig. 1), when the compound has a CsCl structure type, is very similar to that of the isostructural compound TmPd, which has a CsCl type structure over the whole temperature range. For this reason, it seems pertinent take as reference for the hypothetical $Yb^{3+}Pd$ compound an analogous trend in the specific heat, with identical slope to that of TmPd. This is represented in Fig. 1 by the dotted line. Following this graph and assuming that the ytterbium valency varies by about 6% between 500 and 1000 K, as derived from magnetic and crystallographic data [3], the energy involved in this electronic transition is calculated by integration of ΔC_p over the same temperature range. The total energy required is then about 0.13 eV, consistent with values obtained for other intermediate valence ytterbium compounds [7,8].

As regards the discontinuity found in the ErPd compound, as stated above the high temperature phase crystallizes with a CsCl type structure, while the low temperature one is of FeB type. It is possible to evaluate the difference in stability of the two crystallographic configurations. In fact the difference between the enthalpic content of the two forms, at the transition temperature, is a measurement of the heat involved in this transition. The value obtained, 0.84 kJ mol^{-1} at 820 K, agrees with that found by direct measurement in the DTA apparatus [2] and indicates a pretty good agreement between these two methods.

The knowledge of the heat capacity and heat of transformation for these compounds allows calculation of the heat of formation at room temperature ($\Delta H^0_{f,298}$), which is already known at the reaction temperature [2]. The results obtained are 67.7, 65.9 and 54.0 kJ mol^{-1} for ErPd, TmPd and YbPd, respectively.

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