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HEAT CAPACITIES FROM 400 TO 1200 K OF $CaAl_2$, $EuAl_2$, $ErAl_2$ AND OF THE INTERMEDIATE VALENCE COMPOUND $YbAl_2$

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ABSTRACT

Heat contents of the intermediate valence compound $YbAl_2$ and of the isotypic phases $CaAl_2$, $EuAl_2$ and $ErAl_2$ were measured in a drop calorimeter over the temperature range 400–1200 K. Whilst the heat capacity of the compounds of Ca, Eu and Er increases linearly with temperature, an anomalous trend is observed for $YbAl_2$. The excess heat capacity displayed by $YbAl_2$ 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 continuous increase of the trivalent ytterbium percentage in the temperature range examined. The problems of the evaluation of the degree of advancement of the electronic process, and the correct choice of a proper reference system, are discussed. The promotion molar enthalpy has been approximately evaluated, providing a value of 8 kJ $mole^{-1}$.

INTRODUCTION

It is known that some rare earth elements can display fractional values of the valence in many intermetallic compounds; moreover, this intermediate valence state can change depending on different thermodynamic conditions. So, the experimental results of magnetic and structural measurements carried out on the $YbAl_2$ compound were interpreted on the basis of variable percentages of trivalent and divalent ytterbium [1], the percentage of Yb (III) appearing to increase with the temperature in the whole range examined (70–850 K).

In the present work, heat content measurements of $YbAl_2$ have been carried out in the temperature range 400–1200 K; the isotypic compounds $CaAl_2$, $EuAl_2$ and $ErAl_2$ have been analogously measured as possible reference systems, in order to compare single valence (valence 2 for $CaAl_2$ and $EuAl_2$; valence 3 for $ErAl_2$) and intermediate valence ($YbAl_2$) compounds, and to evaluate the promotion enthalpy of the process $Yb(II)Al_2 \rightarrow Yb(III)Al_2$.

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TABLE 1

Experimental enthalpy data for $CaAl_2$, $EuAl_2$, $ErAl_2$ and $YbAl_2$

$CaAl_2$		$EuAl_2$		$ErAl_2$		$YbAl_2$	
T (K)	$H_T^0 - H_{273}^0$ (kJ mole^{-1})	T (K)	$H_T^0 - H_{273}^0$ (kJ mole^{-1})	T (K)	$H_T^0 - H_{273}^0$ (kJ mole^{-1})	T (K)	$H_T^0 - H_{273}^0$ (kJ mole^{-1})
376.0	7.38	361.9	6.45	371.7	7.25	355.7	6.31
376.2	7.34	389.5	8.64	406.3	10.12	399.4	9.67
426.8	11.32	426.0	11.28	406.5	9.81	427.9	11.90
427.0	11.06	476.3	15.36	451.0	13.38	440.3	12.94
479.4	15.34	510.2	17.95	452.5	13.47	464.2	15.09
479.7	15.23	515.3	18.37	505.0	17.42	475.9	16.10
526.8	18.75	566.3	22.63	508.5	17.82	522.1	19.90
536.1	19.43	566.6	22.69	591.1	23.93	524.0	20.21
539.7	19.98	592.8	24.21	593.3	23.99	553.1	22.39
573.6	22.46	595.8	24.21	665.6	30.20	554.9	22.60
586.4	23.41	618.0	26.96	666.4	29.76	595.9	26.01
628.4	26.79	650.4	28.98	690.8	32.28	606.5	26.53
629.1	26.66	693.9	32.53	692.9	32.29	648.7	30.07
668.7	29.70	699.2	32.55	730.0	35.09	657.9	30.97
690.5	31.61	734.2	36.15	730.7	35.25	691.7	34.02
725.6	34.34	734.2	35.74	768.8	37.58	694.4	34.37

734.2	35.20	784.7	[illegible]	[illegible]	[illegible]		
775.1	38.71	846.3	44.52	829.3	43.00	740.3	38.43
780.2	39.32	851.1	45.08	833.7	43.41	767.9	40.67
828.9	43.28	851.2	45.38	878.1	47.12	786.7	42.10
829.5	43.50	867.5	47.00	882.5	47.58	802.6	43.45
843.0	44.66	903.5	49.87	918.5	51.01	828.6	45.81
860.4	45.66	910.1	50.69	919.3	50.99	829.6	46.12
885.2	48.32	940.9	52.99	936.9	52.08	832.0	45.80
887.2	48.74	945.3	52.93	937.6	52.01	844.2	47.17
916.6	51.26	994.6	56.98	997.3	56.57	886.9	50.91
935.7	52.33	997.1	57.10	1021.4	59.05	920.7	53.65
971.9	55.50	1037.7	60.79	1069.0	62.59	923.8	53.88
975.4	56.26	1077.4	64.21	1071.6	63.19	954.4	56.40
1022.6	60.11	1126.8	68.99	1099.9	65.24	973.8	58.54
1027.1	60.31	1151.2	70.39	1105.4	66.21	1004.6	61.20
1079.2	65.46	1171.0	72.16	1133.7	68.74	1013.1	61.82
1087.0	65.67	1181.8	73.40	1173.4	72.47	1021.9	62.64
1116.9	68.97					1041.7	64.48
1125.7	69.77					1042.9	64.66
1190.5	75.78					1062.5	66.50
						1075.9	67.42
						1086.9	68.86
						1099.9	69.72
						1121.4	71.42
						1139.7	73.29
						1144.2	73.49

EXPERIMENTAL AND RESULTS

The metals used in the preparation of the compounds were Ca of 99.9 wt. % purity (Fluka, Switzerland), Eu, Er and Yb of 99.5, 99.8 and 99.5 wt % purity, respectively (Koch–Light, Gt. Britain), and Al of 99.999 wt. % purity (Koch–Light, Gt. Britain). Hydrogen was removed from the ytterbium by diffusion through the tantalum container, whilst heating under a dynamic vacuum at 1173 K [2].

The samples were obtained by melting, in an induction furnace, stoichiometric amounts of the two elements in tantalum containers, sealed by arc-welding under an argon atmosphere. The monophasic structure of the alloys was checked by micrographic examination. X-Ray analysis, carried out by the powder method, confirmed for each compound the already known crystal structure, $MgCu_2$ type, with cell constant values in good agreement with the literature data.

Heat contents were measured in a drop calorimeter over the temperature range 400–1200 K. The design of the furnace and the Bunsen ice calorimeter was similar to that described by Ginnings and co-workers [3,4]. The furnace was divided into three sections, each heated independently; three copper cylinders occupied the inside of the furnace, in positions corresponding to the three heaters. The sample was suspended at the center of the middle cylinder. The temperature was measured by a Pt/Pt–10% Rh thermocouple, located within the middle copper cylinder, and previously calibrated in situ by means of a calibrated thermocouple which occupied the usual position of the sample. The apparatus was kept under vacuum during the sample heating and equilibrated at the desired temperature (for 1–2 h); some time after the drop, argon was injected into the calorimeter to facilitate the thermal exchange. The volume variation produced by the ice melting was measured by weighing the corresponding mercury amount drawn into the calorimeter. The value of the calibration factor obtained at the National Bureau of Standards [3–5] was used in the heat calculation, namely 270.48 ± 0.03 J g^{-1} Hg. Both precision and accuracy, as tested in the whole temperature range by a series of repeated heat content measurements on a high purity copper sample, were found to range over 1–2%.

The samples were enclosed in cylindrical tantalum containers, sealed by arc-welding under argon. A series of measurements on the empty container provided the heat contribution of tantalum. The quantities of the alloys were 6.0218, 14.1574, 15.3045 and 13.6686 g for the Ca, Eu, Er and Yb compounds, respectively.

Table 1 reports the experimental enthalpy results, referred to one mole of substance. For the compounds of Ca, Eu and Er, the enthalpy values can be represented as a function of the temperature by a parabolic equation, least-squares fitted to the experimental data

$$\left(H_T^0 - H_{273}^0\right) = a_1(T - 273) + a_2(T - 273)^2$$

TABLE 2

Least-squares calculated values of the constants in the two enthalpy–temperature equations used for $CaAl_2$, $ErAl_2$, $EuAl_2$ and $YbAl_2$, corresponding standard deviations (in parentheses) and mean deviations, $\bar{d}$, of the experimental points from the fitted curves

Compound	a_1 (J $mole^{-1}$ K^{-1})	a_2 (J $mole^{-1}$ K^{-2})	a_3 (J $mole^{-1}$ $K^{-0.5}$)	A (K)	$\bar{d}$ (%)
$CaAl_2$	70.75 (0.24)	12.85 (0.35)$\times 10^{-3}$			0.49
$EuAl_2$	74.31 (0.33)	6.99 (0.47)$\times 10^{-3}$			0.73
$ErAl_2$	73.59 (0.35)	7.11 (0.50)$\times 10^{-3}$			0.58
$YbAl_2$	75.70 (0.69)	6.90 (0.34)$\times 10^{-3}$	122 (35)	−327 (20)	0.39

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

$$C_p = a_1 + 2a_2(T - 273)$$

The thermal trend of the heat content of $YbAl_2$ is more complex, and this analytical representation requires a higher number of parameters. A positive difference, regularly increasing with temperature, between the enthalpy of $YbAl_2$ and that of $EuAl_2$ or $ErAl_2$ is observed. Some equations were tested,

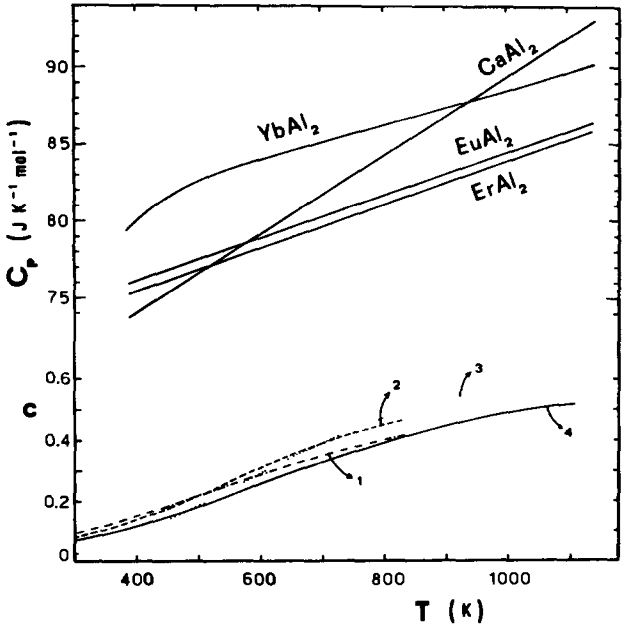

Fig. 1. Variation of the molar heat capacity of $CaAl_2$, $EuAl_2$, $ErAl_2$ and $YbAl_2$ with temperature. Some different temperature dependences of c, the fraction of Yb(III) ions, are also indicated, as proposed on the basis of magnetic susceptibility data (curve 1, ref. 1; curve 3, ref. 4; curve 4, ref. 3), or of lattice constants (curve 2, ref. 1).

simply by adding to a parabolic function a third term, which should describe the excess enthalpy of $YbAl_2$ as regards a "normal" trend. After some trials, the following function was selected

$$\left(H_T^0 - H_{273}^0\right) = a_1(T-273) + a_2(T-273)^2 + a_3(T-273)^{0.5}\exp\frac{A}{(T-273)}$$

The heat capacity of $YbAl_2$ becomes

$$C_p = a_1 + 2a_2(T-273) + a_3\exp\frac{A}{(T-273)}\left[\frac{1}{2(T-273)^{0.5}} - \frac{A}{(T-273)^{1.5}}\right]$$

The values of the constants in the enthalpy–temperature equations, their corresponding standard deviations and the mean deviations of the experimental values from the fitted equations are reported in Table 2 for the four compounds examined. Figure 1 shows the corresponding C_p trends in the temperature range considered.

DISCUSSION

As can be seen in Fig. 1, the thermal behaviour of $YbAl_2$ appears anomalous as regards the other compounds studied. On the other hand, in spite of the different metallic radius, atomic weight and valence state of Eu and Er, the difference between the heat contents of $EuAl_2$ and $ErAl_2$, less than 1%, lies within the experimental accuracy limits. So, neglecting other lattice effects, the higher C_p values of $YbAl_2$ appear mostly connected to the valence change occurring in the temperature range considered, namely to a gradual increase of the trivalent ytterbium percentage.

The evaluation of the molar energy, E_p, of this electronic promotion process should be possible by using the C_v values, both of the mixed-valence system and of a proper reference system. Lacking compressibility and thermal expansion data of these compounds, the C_p values obtained in the present work may be used to evaluate the molar promotion enthalpy, H_p.

When the system, containing one mole of $YbAl_2$, changes from the temperature T_1 [corresponding to a certain value, $c(T_1)$, of the percentage of Yb^{III}] to the temperature T_2 [corresponding to a different value $c(T_2)$], the mean value of H_p in the temperature range considered can be given by

$$H_p = \frac{\left(H_{T_2}^0 - H_{T_1}^0\right)_{YbAl_2} - \left(H_{T_2}^0 - H_{T_1}^0\right)_{ref.}}{c(T_2) - c(T_1)}$$

where $(H_{T_2}^0 - H_{T_1}^0)_{ref.}$ is the enthalpic change of a proper reference system.

Questions arise concerning the valuation of $c(T)$ and of the choice of reference system. Concerning $c(T)$, this quantity has been obtained in the literature by means of both magnetic and lattice constants measurements

[1,6,7]. Figure 1 also reports these data, which show a similar trend, with a total quantitative disagreement of about 10%; this can be ascribed to different handling of the experimental results. On the basis of the $c(T)$ values proposed by Klaasse et al. [6], which cover the whole temperature range examined in the present work, the increase of the trivalent ytterbium percentage, going from 400 to 1100 K, is evaluated to be 41%.

The unusual type of transformation which occurs in $YbAl_2$ makes difficult the choice of the reference system. Actually, the process of valence change continues during the whole of the temperature range examined, as seen in Fig. 1, and it does not seem completely correct to select a part of the observed C_p curve of $YbAl_2$ as the reference line to evaluate the excess heat capacity. The compounds $CaAl_2$, $EuAl_2$ and $ErAl_2$, which are all isotypic with $YbAl_2$, were initially selected as possible reference systems. Nevertheless, the temperature dependence of the heat capacity of $CaAl_2$ clearly appears too different from the other compounds; this behaviour can be due to a probably lower value of the Debye temperature, and to the higher coefficient of volume expansion (see the comparison between $CaAl_2$ and $LuAl_2$ reported in ref. 1).

$EuAl_2$ and $ErAl_2$ were therefore taken as reference RAl_2 systems, containing a rare earth element with stable and not fractional valence. Using a mean value of the enthalpic data of $EuAl_2$ and $ErAl_2$, the molar promotion enthalpy, H_p, of $YbAl_2$ is 8 ± 1.5 kJ mole^{-1}. Also, within the large limits of accuracy, this value appears considerably lower than the value of 38 kJ mole^{-1}, calculated by Gschneidner [8] for the process Yb(II) $\rightarrow$ Yb(III). Nevertheless, a comparison cannot be made, because this last value was obtained on the basis of thermodynamic cycles involving substantially ionic compounds of Yb (oxides and halides).

On the other hand, the promotion enthalpy obtained in the present work can be directly compared with the excitation energy of about 15 kJ mole^{-1}, estimated [5,6] for the ytterbium atoms on the basis of magnetic data; in that case, high temperature data of magnetic susceptibility for $YbAl_2$ were discussed with a two levels model. The observed difference between the two values can be ascribed to electron–phonon interactions, caused by the large cell volume change occurring in the valence change [9]. Lattice vibrations and valence fluctuations show a reciprocal influence, and this coupling can make uncertain the evaluation of the intermediate valence value at the different temperatures, and consequently the calculation of the excitation energy.

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