Thermochimica Acta, 6 (1973) 455–460

DYNAMIC DIFFERENTIAL CALORIMETRY OF INTERMETALLIC COMPOUNDS

II. HEATS OF FORMATION, HEATS AND ENTROPIES OF FUSION OF RARE EARTHS-LEAD ($REPb_3$) COMPOUNDS

A. PALENZONA AND S. CIRAFICI
Istituto di Chimica Fisica, University of Genoa (Italy)
(Received 19 December 1972)

ABSTRACT

Dynamic differential calorimetry has been employed to evaluate the heats of formation, heats and entropies of fusion of $REPb_3$ compounds, where RE = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm and Yb. The results obtained have been estimated to be correct to within ±5–6%. The general trend is a decrease in the heat of formation from La to Tm, which is correlated with the magnitude of the lanthanide contraction in these compounds.

INTRODUCTION

In previous work[1] we have described the use of the dynamic differential calorimetric method (DDC) in the evaluation of the heats of formation, heats and entropies of fusion of the $RESn_3$ compounds. This method is based on the direct measurement of the heat evolved during the reaction of formation of the compound from the elements, while the heats and hence the entropies of fusion were measured as in the case of a pure element.

The theoretical treatment of the method has been given by Faktor and Hanks[2]; we have tested such a theory in the temperature range of 200–1100°C and have applied the DDC method to the $REPb_3$ compounds. These compounds have been chosen because lead easily reacts at low temperature with the RE's and the reaction is highly exothermic. The heat evolved is sufficient to melt the sample. Moreover, the obtainable data could be compared with those obtained for $RESn_3$ compounds, which crystallize with the same structure type, and could provide a measure of the relative stability of these phases.

EXPERIMENTAL

The apparatus, standards, and procedure to obtain the calibration curves, the sources of errors and the other operational details are described elsewhere for $RESn_3$ phases[1]; no significant changes have been made using this method for $REPb_3$ compounds.

$REPb_3$ compounds are well known structurally and recently have been revised together with all other RE–Pb compounds by Gschneidner and McMasters[3].

At the present time, the heats of formation for the $REPb_3$ phases are known for only three members of the series: Ce, Pr and Nd[4]. These values were obtained by vapour pressure measurements of lead between 993–1073 K and are, respectively: 41.60, 34.80, 39.20 kcal mole^{-1}, but the error in their determination, as quoted by the same authors, was ±20%.

RE metals and lead used in this investigation were obtained from Koch–Light Laboratories, England, and had a claimed purity of 99.9 and 99.999%, respectively. Samples ranging from 1.00 to 2.50 g each were prepared from stoichiometric quantities of chips of the two metals; they were well mixed and pressed directly into the Mo containers (1.5 kbar).

The reaction between RE and lead starts at a low temperature, practically at the melting point of lead. It is very fast for all RE's and the thermal effect due to the melting of lead must always be considered in the evaluation of the heat of formation of the corresponding compound. Typical examples of the curve obtained are reported in Fig. 1 for Eu and Gd. To ensure reproducibility of the results, several samples for each heating rate (10 and 20 deg. min^{-1}) were prepared and at least two or three "good" samples were considered in the evaluation of the results; these are reported in Table 1. After the reaction ceased, the samples were examined micrographically. Only alloys which contained a single phase were considered. X-ray examination confirmed the presence of $REPb_3$ compounds with no extra lines due to other phases or to

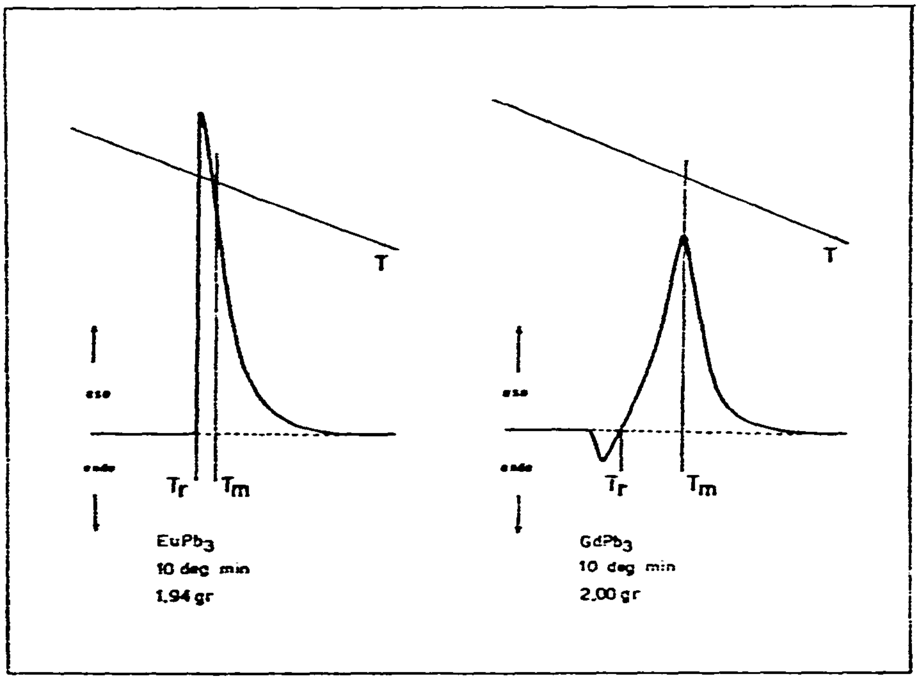

Fig. 1. Examples of curves obtained for the reaction between rare earths and lead.

unreacted metals. The values of the lattice constants are in good agreement with those in the literature[3].

TABLE 1

HEATS OF FORMATION FOR $REPb_3$ COMPOUNDS AT 298 K

Compound	n[a]	T_r (K)[b]	ΔH_f(kcal mole^{-1})
$LaPb_3$	3	590	−49.18
$CePb_3$	2	585	−46.89
$PrPb_3$	3	585	−50.31
$NdPb_3$	3	595	−49.81
$SmPb_3$	4	600	−47.28
$EuPb_3$	2	595	−41.94
$GdPb_3$	4	600	−42.88
$TbPb_3$	2	595	−41.90
$DyPb_3$	2	610	−40.88
$HoPb_3$	2	600	−39.14
$ErPb_3$	3	610	−35.73
$TmPb_3$	2	600	−33.85
$YbPb_3$	2	590	−35.37

[a] n = number of determinations used to evaluate the ΔH_f values. [b] T_r = temperature at which the reaction starts.

As the heats of formation are obtained at different temperatures, they should be reported by means of Kirchoff's relation at 298 K, corresponding to the reaction:

$$RE(s)+3Pb(s) \rightleftharpoons REPb_3(s)+\Delta H_f$$

Assuming the validity of the Neumann and Kopp's rule, as in the case of the $RESn_3$ compounds, the results were corrected only for the heat of fusion of lead. The total error in their determination is evaluated to be of the order of ±5–6%.

TABLE 2

HEATS AND ENTROPIES OF FUSION FOR $REPb_3$ COMPOUNDS

Compound	T_m (°C)[a]	ΔH_f (kcal mole^{-1})	ΔS_f (cal deg^{-1} mole^{-1})
$LaPb_3$	1145	20.26	14.28
$CePb_3$	1130	14.68	10.46
$PrPb_3$	1120	20.05	14.34
$NdPb_3$	1105	20.81	15.10
$SmPb_3$	970	19.78	15.91
$EuPb_3$	790	12.25	11.54
$YbPb_3$	740	13.08	12.91

[a] T_m = melting point.

Heats and entropies of fusion were determined by preparing a new series of samples, two gram each, and sealing them by arc welding under argon atmosphere in the Mo crucibles. This procedure is necessary in order to avoid losses of metals with high vapour pressures such as Sm, Eu and Yb at high temperatures. At the melting point of the alloys, which are in good agreement with those in the literature, the heat of fusion and hence the entropy was determined by means of the calibration curves. The values obtained for the compounds which have congruent melting points are reported in Table 2.

DISCUSSION

Rare earths, from La to Yb, form $REPb_3$ phases with lead which crystallize with the cubic $AuCu_3$ type of structure. The compound, $LuPb_3$, does not exist[5]. Europium and Yb in these compounds behave like alkaline-earth elements containing Eu^{2+} and Yb^{2+} in accordance with the existence of $CaPb_3$ which is isomorphous with them.

The general trend in the heats of formation for $REPb_3$ compounds is a decrease from La to Tm and this behaviour can be correlated with the lanthanide contraction in the compounds and compared to the contraction observed in the pure metals, as given by Gschneidner[6]. The unit cell volumes of the $REPb_3$ phases were divided by the atomic volume of the pure metal (RE) and these volume ratios were then divided by the volume ratio relative to the lanthanum compound giving a scale relative to lanthanum (1.000). The resultant values (Fig. 2) increase with RE atomic number, *i.e.*, the lanthanide contraction in the compounds is less than in the pure metals and a decrease in the heats of formation can be expected in going from La to Tm.

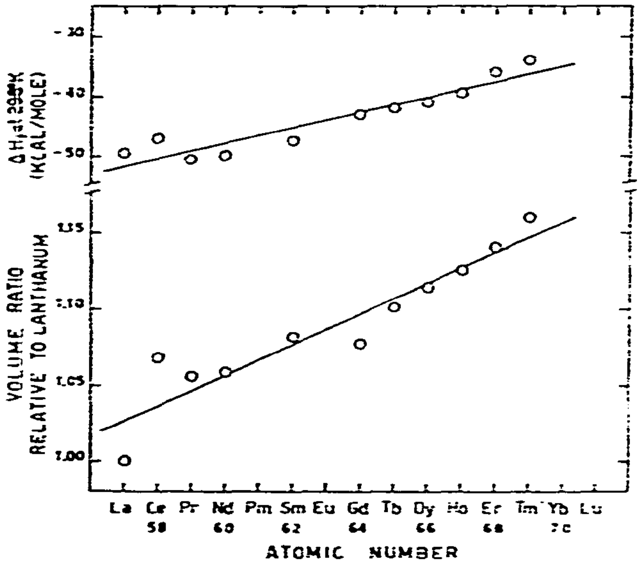

Fig. 2. Heats of formation and volume ratios for $REPb_3$ compounds *vs.* atomic number.

The same considerations are valid if we consider Ba, Eu and Yb as members of a "baride" series of divalent elements. Again the volume ratio, relative to barium, and the heats of formation *vs.* atomic number show the same trend as for trivalent RE (Fig. 3). The scatter in the value of the heat of formation for $BaPb_3$[7] could be due to the different crystal structure adopted by this compound[8].

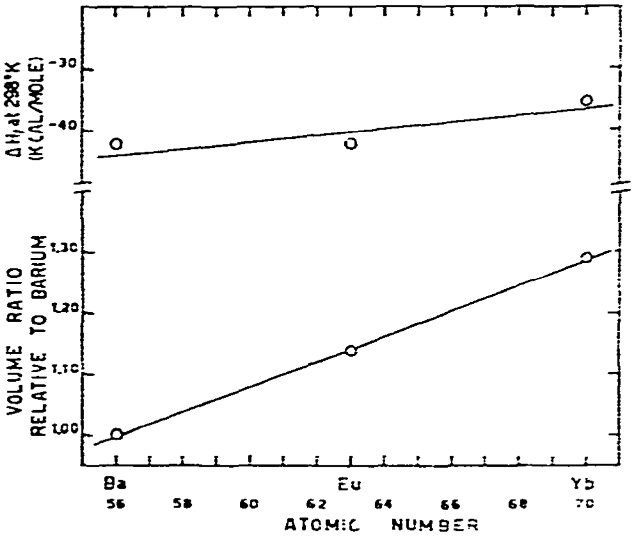

Fig. 3. Heats of formation and volume ratios for $BaPb_3$, $EuPb_3$ and $YbPb_3$ *vs.* atomic number ($BaPb_3$, rhombohedral, $R\bar{3}m$; $a = 9.565$, $\beta = 44°47'$, $Z = 3$)[8].

If compared with the values obtained for $RESn_3$ phases, the heats of formation of the $REPb_3$ compounds are systematically lower (less negative) by about 5 kcal $mole^{-1}$. This would indicate a higher stability for the $RESn_3$ phase but from Tb to Lu, the $RESn_3$ compounds do not exist, at least with the $AuCu_3$ type of structure. The difference in the heats of formation can perhaps be related to the higher change in the coordination number of tin (from 6 for white tin to 12 in $RESn_3$ phases) in alloying with the RE with respect to lead which maintains the same coordination number in the metal as in the compound.

Recently, Robinson and Bever[9] have examined all existent thermodynamic data for intermetallic compounds and have shown that some indications concerning the type of bonding could be obtained simply by considering the magnitude of these data. In our case, the heats of formation, ranging from -8.5 to -12.5 kcal g. at^{-1}, the heats of fusion, from 3.0 to 5.0 kcal g. at^{-1}, and the entropies of fusion, from 2.5 to 4.0 kcal g at^{-1} deg^{-1}, suggest that the chemical bond is predominantly of the metallic type while ionic or covalent contributions are absent or very small.

ACKNOWLEDGMENT

The authors wish to thank Prof. A. Iandelli for his aid and helpful criticism given during the present research.

REFERENCES

1 A. Palenzona, *Thermochim. Acta*, 5 (1973) 473.
2 M. M. Faktor and R. Hanks, *Trans. Faraday Soc.*, 63 (1967) 1122.
3 K. A. Gschneidner and O. D. McMasters, *Mh. Chem.*, 101 (1971) 1499.
4 P. P. Otopkov, I. Gerasimov and A. M. Evseev, *Dokl. Akad. Nauk SSSR*, 139 (1961) 616.
5 O. D. McMasters and K. A. Gschneidner, *J. Less-Common Metals*, 19 (1969) 337.
6 K. A. Gschneidner, *J. Less-Common Metals*, 17 (1969) 1.
7 O. Kubaschewski, E. Evans and C. Alcock, *Metallurgical Thermochemistry*, 4th ed., Pergamon Press, Oxford, 1967.
8 D. E. Sands, D. H. Wood and W. J. Ramsay, *Acta Crystallogr.*, 17 (1964) 986.
9 P. M. Robinson and M. B. Bever, in J. H. Westbrook (ed.), *Intermetallic Compounds*, Wiley, New York, 1967, p. 38.