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Thermodynamics of rare earth alloys: systematics and experimental

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Abstract

Some general remarks on rare earths' alloying behaviour and their thermodynamics are reviewed and discussed. The role of systematics is underlined and its usefulness in the prediction and assessment procedures is highlighted. Certain aspects peculiar to rare earth (R) alloy thermodynamics with particular attention to the experimental side are presented and discussed. A short summary is given of the work in progress in this field in the authors' laboratory. New enthalpy data obtained in the investigation of some rare earth alloy systems ((La,Ce)–Ag, (Gd,Tb,Dy)–Au, Y–Al, Nd–Sn, Gd–Sb) are reported and compared with the values relevant to the other rare earths. © 1998 Elsevier Science B.V.

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1. Introduction: general remarks on alloy thermodynamics

Alloy thermodynamics has a long and sound tradition (see for instance [1–3]). It is, however, a flourishing field revealing new theoretical and experimental aspects of increasing interest and application. Possibly of great significance is the attention dedicated to the equilibria computation and prediction based on computer coupling phase diagram and thermodynamic data.

It is well known that these techniques, the so-called CALPHAD (Calculation of Phase Diagrams) methods described and presented by [4,5] and successfully applied in various computer programs implemented by different authors (among whom Lukas [6] and Sundman et al. [7] may be mentioned) are aimed at:

(a) giving a more complete and consistent description of the phases existing in a certain alloy system and of their stability;
(b) providing more reliable, assessed versions of the different phase diagrams available;
(c) preparing reference data (simple phase diagrams, thermodynamics, etc.) and using them in the prediction of phase equilibria in complex, multicomponent systems and for providing and checking strategies for an optimal planning of their experimental investigation;
(d) producing a reference framework of information which should be considered in the evaluation and discussion of phase transformations and their kinetics and in the description of processes such as diffusion, preparation of metastable and amorphous alloys, mechanical alloying, etc.;
(e) giving a set of data and parameters necessary for the description and understanding of mechan-

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ical characteristics of the different alloys and, more generally, for the presentation of their functional properties as materials of technological interest [8].

Among experimental topics we may mention the increasing interest dedicated, within alloy thermodynamics, to investigations such as that of heat evolution during a reaction or transformation advancement and, consequently, of processes such as the combustion synthesis (and of its possible applications in energy-saving in melting processes, in special in situ alloy-forming procedures, etc. [9]).

As a further comment we should note that, in the general field of alloy thermodynamics within the variety of metals and alloys, different groups of alloys could be conveniently considered, and separately discussed on the basis of different properties and characteristics: for instance, those containing low melting or low boiling metals, refractory metals or noble metals, etc. Every group could receive particular consideration and special description. A particular and very important subdivision of the different metals (and of their alloys) will be the one based on their position (and grouping) in the Periodic Table. The descriptions of the alloys of, for example, the alkali earth metals or of the actinides could be alternative useful examples and highlight the role that systematics may play in alloy chemistry.

In this paper special attention will be dedicated to the alloy thermochemistry of the rare earth metals.

2. Rare earth alloys and the role of systematics

Sc, Y, La and the lanthanides are collectively known as the rare earth metals. For this group of elements it is well known that systematic rules and considerations may be successfully applied to their compounds and, specifically, to their alloys. This point has been discussed in a series of papers by Gschneidner. In a paper entitled ‘Systematics in lanthanide and actinide solids’ [10], for instance, he evidenced the possibility of rational presentation of the all intra-lanthanide and intra-actinide state diagrams, by using a kind of ‘generalized’ phase diagram.

In the specific case, moreover, of the combinations of the rare earths with other elements, several criteria have been adopted for a systematic description of selected properties of these compounds and of their formation.

Systematics of the thermochemistry of rare earth compounds and alloys has been summarized by Brewer [11], Gschneidner [12,13], Ferro et al. [14], Colinet and Pasturel [15] and Ferro and Borzone [16]. Comments have been reported by Meschel and Kleppa [17,18] and by Hennemann and Schaller [19].

The following relations have been considered and their trends as a function of the rare earth atomic number examined.

Volume contraction in a compound series [12,20]. A quantity, called the relative volume ratio, has been defined for a series of compounds having the same general formula $R_{1-x}M_x$ as:

$$r_{\mathrm{vol}} = \frac{V_{(\mathrm{R}_{1-x}\mathrm{M}_x)}}{V_{\mathrm{R}}} \Big/ \frac{V_{(\mathrm{La}_{1-x}\mathrm{M}_x)}}{V_{\mathrm{La}}} \qquad (1)$$

where V is the molar volume of stated compound or rare earth element. This ratio gives an indication, in comparison with the data concerning La or another reference element R, of the relative volume contraction in the compounds and in the elements (lanthanide contraction). If this ratio is less than 1, that is, if the contraction is more severe in the compounds, we may assume that the bond strength will increase from La to the heavy R and we may expect that the values of $\Delta_f G$ and $\Delta_f H$ will become more negative along the series. If, on the contrary, this ratio increases along the series, we may expect a decreasing exothermicity of the compound formation.

This correlation has been tested and verified for several series of compounds (see for instance [12,14,18]). In a paper by Jacob and Pandit [21] it has been observed, however, that this correlation may not hold for intermetallics rich in the non-lanthanide element, and it may be more useful for compounds closer to equiatomic composition.

Trend of melting temperature in a compound series. It has been observed that a correlation may exist between the stability trend and the ‘relative’ melting behaviour [20,22]. To this end, the slope of the ‘reduced melting temperature’ curve vs. atomic number R has to be compared with a reference slope. The reduced temperature, T_{red}, is obtained as the ratio between melting temperatures (in Kelvin) of the compound and R involved. The reference curve is obtained from the trend of the reciprocal melting temperature of R and is represented by the values 'constant/$Tm_{(R)}$' where, for convenience, the constant is assumed as equal to the melting point of one (for instance La) of the $R_{1-x}M_x$ compounds considered. This reference curve corresponds, therefore, to a hypothetical series of compounds having a constant melting point (isomelting).

$$T_{\mathrm{red}} = \frac{Tm_{(R_{1-x}M_x)}}{Tm_{(R)}} \tag{2}$$

$$T_{\mathrm{iso}} = \frac{Tm_{(La_{1-x}M_x)}}{Tm_{(R)}} \tag{3}$$

The slope of the difference $[T_{\mathrm{red}} - T_{\mathrm{iso}}]$ is considered to give an indication of the variation of the compound stability along the series.

Another simple parameter related to the melting (or transformation) temperature of the phase can be obtained by the use, according to Raynor [23,24] of the so-called stability index.

This index, which can be defined for all the intermetallic phases, is computed, in the specific case of the rare earth compounds, by:

$$I_{\mathrm{s}} = \frac{Tm_{(R_{1-x}M_x)}}{(1-x)Tm_{(R)} + x\,Tm_{(M)}} \tag{4}$$

with all the melting temperatures in Kelvin.

As mentioned before, these parameters and indexes have been discussed as a function of the atomic number of the rare earth involved and the smooth trends often observed have been used for an overall check of the different data and/or for their optimization and prediction. Fig. 1 shows an example of such relations. A similar good agreement between the different indexes has been observed for several series of phases such as, for instance, RPd, RAl_2, RTl_3, RSn_3, etc. In some cases (for instance RPd_3), however, some discrepancies have been noticed, especially in the trend of the volume ratio.

In a number of cases, for the description of specific properties, instead of the atomic number, different coordinates were used. The melting temperature of the rare earth was for instance used by Buyanov et al. [47] in graphs such as that reported in Fig. 2 based on Eremenko's suggestions.

Crystal structure data, and compound formation, have often been discussed by comparing the data observed with the atomic dimensions of the R involved. This point has been discussed for instance by [48]: The alternative use of different radii and their possible advantages has been considered.

It has been shown that, on the basis of the metallic radius (defined for instance for a coordination number of 12) some anomalies and uncertainties due to the valency presented in a given alloy may be observed for a number of rare earth elements (Eu and Yb and also Ce, Gd, etc). Another dimensional parameter which appears to change with a more regular trend, is the ionic radius. As a function of this parameter, moreover, a more regular trend has generally been observed for several properties (see some examples in Fig. 3). Another advantage of these graphs is related to the fact that they generally give a good representation of the behaviour of Y, too. The Y radius is indeed very close to that of Ho; between these elements and those next to them there is, generally, a noteworthy similarity in the alloying behaviour.

An interesting extension of these concepts may be found in the definition of the so-called 'pseudolanthanides' and its application to the prediction of the constitutional properties of certain groups of rare earth alloys [49]. It has been observed in fact that, if certain properties of the rare earth or its alloys are dependent on its atomic dimension (for instance r^{3+}), a mixture of two rare earths, R' and R'', will act as a 'pseudolanthanide', that is, will simulate the behaviour of a third intermediate rare earth, the dimensions of which are equal to the averaged values of R' and R''. For a number of properties which are not strictly related to the electron configuration and number, and for the so-called 'normal trivalent rare earths' (that is excluding Eu and Yb), a confirmation of this hypothesis has often been obtained. On this basis, Gschneidner [49] constructed a kind of 'generalised' intra-rare earth phase diagram, summarizing all the phase diagrams given by two 'trivalent' lanthanides (to which Y may be added). It has been observed [50], moreover, that isothermal sections of certain ternary systems R'–R''–M of alloys formed by two rare earth metals with a third element may be simulated by the sequence of the corresponding sections of the binary R–M systems (formed by all the trivalent R intermediate between R' and R'') placed in sequence one after the other. Phase formation and

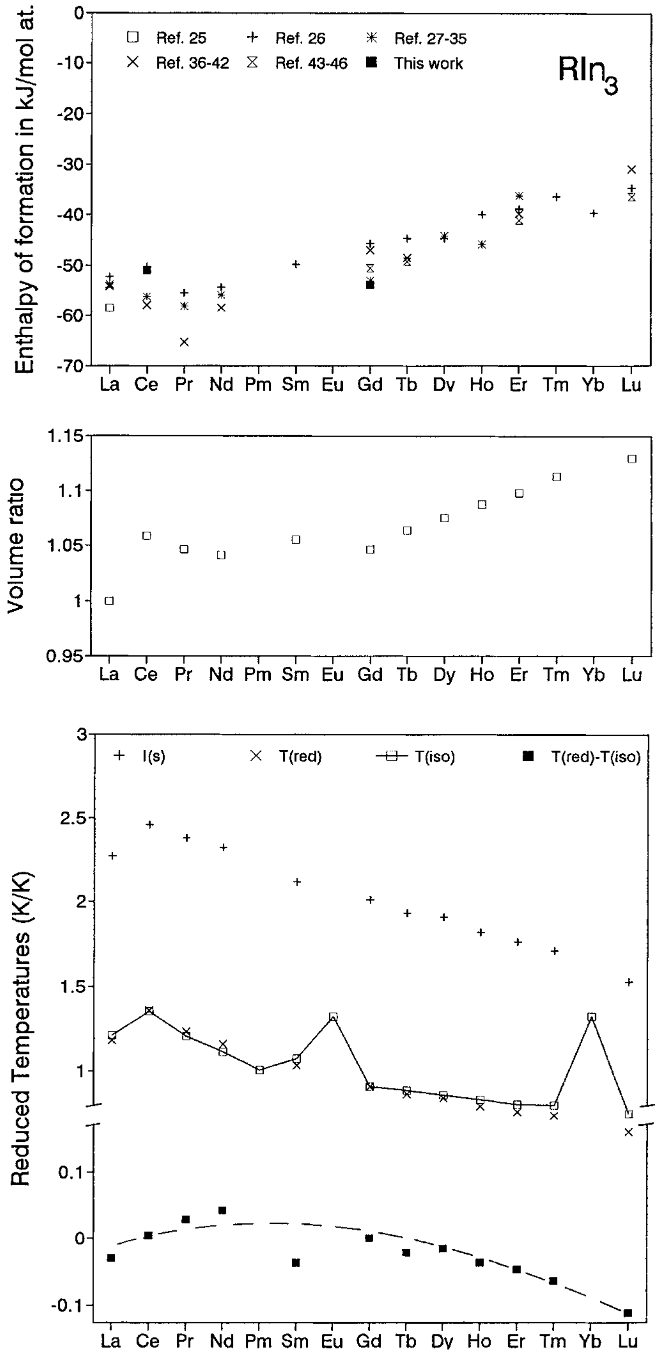

Fig. 1. $\Delta_f H$ and reduced parameters (see text) of a selected group of alloys (RIn_3) as functions of the atomic number R. For $CeIn_3$ and $GdIn_3$ the values obtained in this work have been inserted. We notice that, in this case, all the data indicate a decreasing stability of the phase on passing from the light to the heavy R. Volume ratio (r_{vol}); 'reduced temperature' (T_{red}); isomelting temperature (T_{iso}); stability index (I_s) are obtained according to Eqs. (1)–(4) respectively. For the reduced temperatures, notice the different scales for indexes and for the difference ($T_{red}-T_{iso}$), respectively.

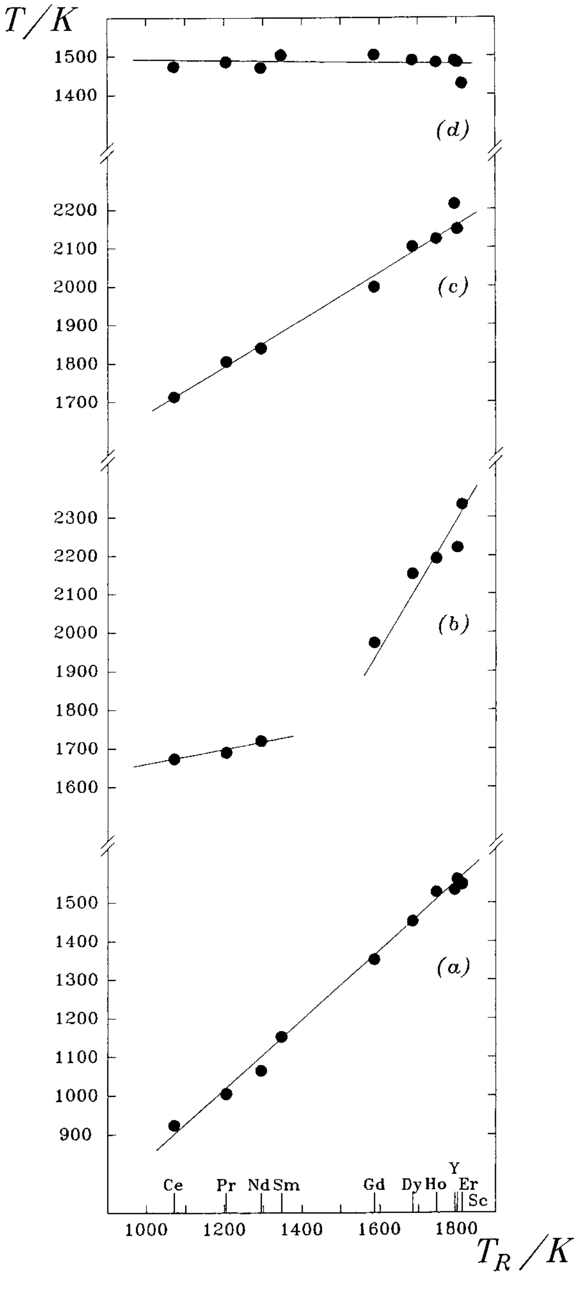

Fig. 2. Rare earth silicides. Melting temperature of the phases as a function of the melting temperature of R (adapted from [47]). Notice the change in the slope of the curves in relation to the R content in the alloy: (a) (R)+R_5Si_3 eutectics; (b) R_5Si_3 compounds; (c) R_5Si_4 compounds; (d) $RSi_{\sim 2}$+(Si) eutectics. The R_5Si_3 compounds have the Cr_5B_3-type (R=La, Ce, Pr, Nd) and the Mn_5Si_3-type (R=Sc, Y and heavy R) structures.

crystal structures have been in certain cases predicted, and it has been pointed out that such considerations may be useful for planning, designing and finely tuning alloys of given properties.

3. Comments on the state of the art of rare earth alloy thermodynamics

Tha data concerning the thermodynamics of formation of the rare earth alloys have recently been compiled and assessed (together with those relevant to the actinides) by Colinet and Pasturel [15]. Previously a review of the rare earth thermodynamics was reported by Bayanov [51]. The trends of these data have been commented on and discussed by Gschneidner [10,12]. Katayama and Takamici [52] periodically updates the thermodynamic data, as does Ansara [53] in THERMET (a bibliographical data base for inorganic substances and solutions).

In this paper we may just give an idea of the general alloying behaviour of the rare earths with the different elements and consequently of their capability of giving intermediate, more or less stable, compounds. A result of this inspection may also be a summary of the systems for which data are missing and/or new experimental investigation is needed.

Fig. 4 summarizes the compound formation capability of typical rare earth metals. As representatives of the behaviour of the trivalent rare earths, La and Gd have been chosen. La, the first lanthanide, may depict (as far as the constitutional properties of the alloys are concerned) the behaviour of the first group of lanthanides (the so-called light rare earths). Gd, on the other hand, may be considered a representative of the ‘heavy’ rare earths. We see that, in both cases, all the elements in the Periodic Table are (in a very similar way) subdivided into two sets. The first set contains all the elements which do not form any compound with the rare earths: the corresponding phase diagrams are generally of the simple eutectic type, often with a more or less large miscibility gap in the liquid state, and the $\Delta_f H$ or $\Delta_f G$ of the alloys are close to zero.

In the second set of elements, besides Be and Mg, the last transition metals are included and the metals and non-metals of the p-block of the Periodic Table. Often complex phase diagrams are formed with these

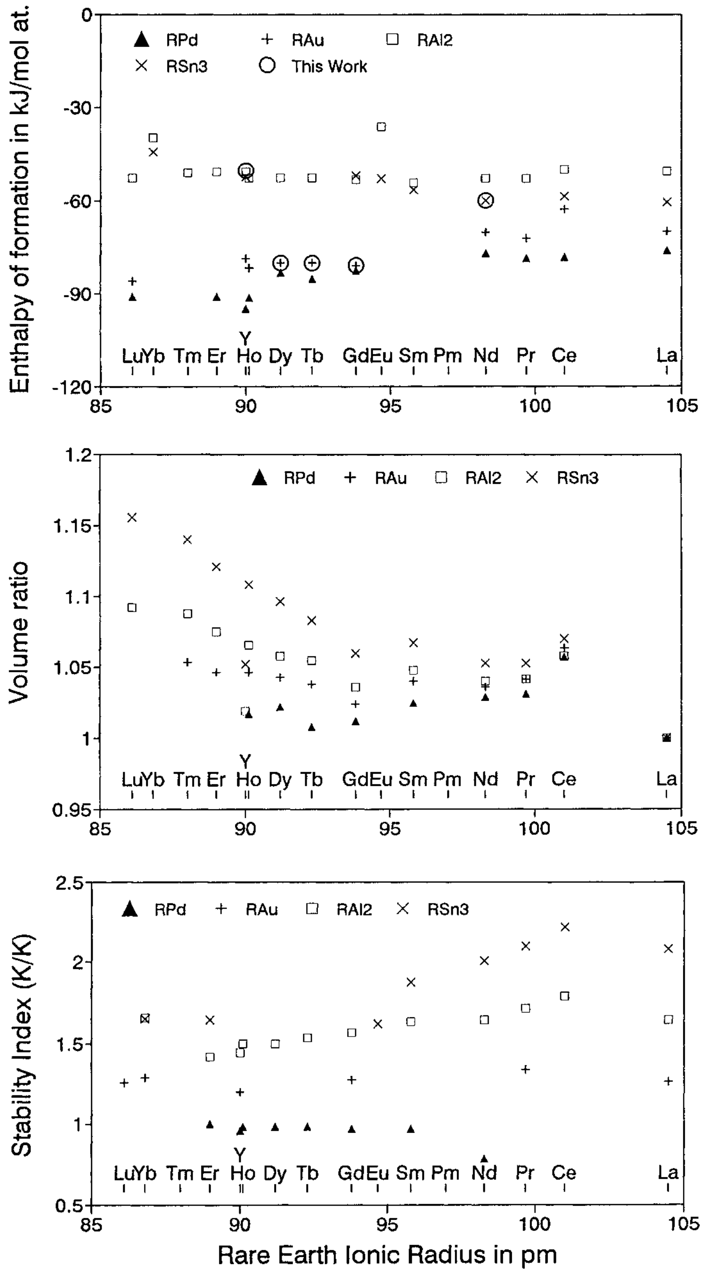

Fig. 3. $\Delta_f H$ and selected stability indexes for a few different series of compounds (RPd, RAu, RAl_2, RSn_3) plotted vs. the ionic radius of the rare earth. For a few RAu (R=Gd, Tb, Dy) compounds, for YAl_2 and for $NdSn_3$, the values obtained in this work have been inserted. In the volume ratio diagram the La value is 1, it is the reference R.

elements and negative or strongly negative values of the $\Delta_f H$ are observed, mainly with the 'noble metals' and the non-metals at the far-right of the table.

In the same figure the slightly different alloying behaviour of the divalent rare earths, Eu and Yb, is also presented.

La

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
1															
–	1											3	2	1	1
–	6											6	5	4	2
–	0	0	0	0	0	0	0	8	8	5	8	5	6	3	5
–	–	0	0	0	0	–	5	8	5	4	5	7	9	5	4
–	0	La	–	0	0	0	2	10	6	5	6	6	7	5	–
–	–														

Eu

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
1															
–	1											1	4	1	3
–	5											3	2	8	3
–	0	0	0	0	0	0	1	–	3	4	5	6	5	12	1
–	–	0	0	0	0	0	–	4	7	5	7	4	2	4	3
–	0	Eu	0	0	0	1	–	2	7	7	4	3	4	5	1
–	–														

Gd

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
2															
–	1											5	4	1	1
–	4											5	5	2	4
–	0	0	0	0	0	3	4	8	9	7	10	5	7	1	2
–	–	0	0	0	0	1	4	9	8	3	6	5	10	4	6
–	0	Gd	–	0	0	1	2	7	8	8	4	6	6	4	–
–	–														

Yb

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
2															
–	1											5	6	1	2
–	1											2	4	2	6
–	0	–	0	0	0	0	2	3	5	5	8	7	2	3	3
–	–	0	0	0	0	–	2	3	9	6	6	5	5	6	3
–	0	Yb	0	0	0	1	1	4	9	8	5	4	5	5	1
–	–														

Fig. 4. Compound formation capability in selected rare earth alloys. For the different elements the number of intermediate phases formed with La, Gd, Eu and Yb can be identified according to their position in the Periodic Table. The numbers have been updated to 96/97. Notice however, that very often changes (additions or deletions) have been reported in literature.

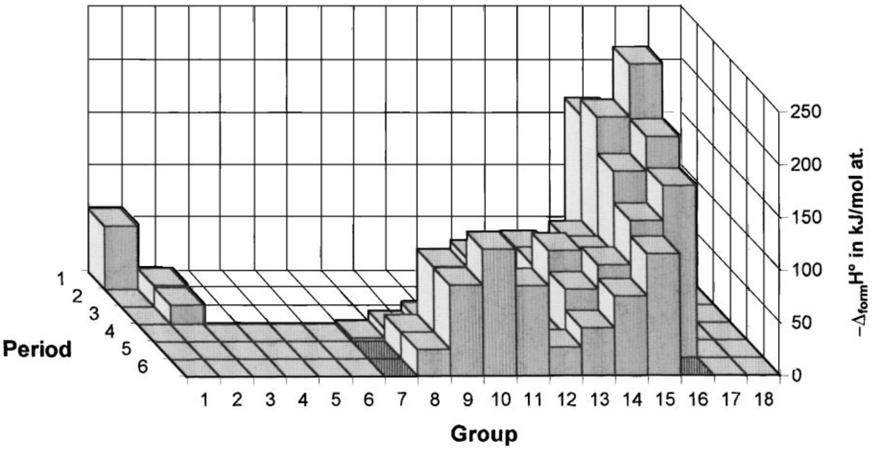

Fig. 5. Averaged values of the formation enthalpies of the trivalent rare earth alloys with the different elements in the Periodic Table. Generally, the more negative value observed in the R–M systems with a given M is reported. The hatched cells correspond to elements for which no reliable data are available. The halogenides have not been considered.

The trend in the stability of the intermediate phases is shown in Fig. 5. This figure gives the more negative values of the $\Delta_f H$ which have been reported, on average, for the trivalent rare earths. Notice however, that for systems such as R–Os, R–Cd, R–Hg and R–Ga only scant data are available.

4. Experimental problems in rare earth alloy thermodynamics

The peculiar properties of the rare earth metals and alloys and their high reactivity are reflected in the special techniques and devices which have to be used in the preparation and handling of these materials. In the specific case of thermodynamic measurements, special attention has been dedicated to these points. Just as an outline of this topic, we may mention the following comments based on a few authoritative references.

4.1. General questions concerning alloy preparation and handling

4.1.1. Role of impurities

Because the great effect that even small quantities of several impurities may have on the properties of the rare earth metals and alloys, the need for strict control of the purity has been underlined, particularly by Gschneidner et al. [54], who described also special techniques for obtaining high purity metals [55].

Emphasis has been given to the fact that, generally, even the best commercial sources of rare earth metals may have quite large quantities of a number of interstitial impurities such as H, C, N, O, F. It is rare to find a metal R with purity higher than 98 at% (even when the metal is said to be 99.9 wt% pure, this is generally true only with respect to the metallic impurities).

We may mention the papers [56,57] underlining the role that several impurities may play in the stabilization of certain crystal structures and consequently of certain compounds. Typical examples are the phases of Mn_5Si_3-type, such as La_5Sn_3 containing small quantities of C or O [56] and previously believed to be true binary R–M compounds. In another paper [57] special problems related to the presence of hydrogen have been described. The possible permeation of hydrogen through the walls of different types of crucible and especially through tantalum at high temperature has been underlined.

4.1.2. Reactions with crucibles and containers

This kind of reaction may frequently cause severe alteration of the sample, particularly at high temperature and with molten alloys. The reactivity of the rare earths with Al_2O_3 has been discussed in [54,58]. Comments on the possible effect of temperature and heating rates on the reaction extent, have been reported [54]. The recommendation of using a tantalum (or possibly better a tungsten) crucible in DTA and similar measurements on alloys involving rare earth metals is greatly emphasized.

Considering however that, in an alloy, together with the rare earth metal we will have other elements involved, the entire alloy reactivity will generally be more complex and may, for instance, also result in the attack of other crucible materials such as Mo, Ta, etc. See for instance in [58] a description of the difficulties met in the preparation and examination of R–Mn alloys, which are very reactive towards Ta, Al_2O_3, SiO_2, etc.

An interesting effect of the crucible material has been reported by Gschneidner and Calderwood [59] for the RAl_3 phases. Small differences in preparation methods and/or small amounts of impurities may alter their structures. For instance, van Vucht and Buschow [60] reported that the melting of $ErAl_3$ in a ZrO_2 crucible instead of an Al_2O_3 crucible changed this compound from cubic $AuCu_3$ type to rhombohedral $HoAl_3$ type.

A systematic use of W crucibles and containers in the preparation of several rare earth compounds (including sulphides, selenides, etc.) their electron-beam welding in vacuum and their use at very high temperature has been described by Kaldis [61].

The use of BN crucibles as a satisfactory alternative to other materials, convenient for its workability and chemical inertia has been described by Kleppa and Topor [62], together with a series of particular expedients used in high temperature calorimeters.

The problems mentioned have a special relevance in the case of Eu and Yb alloys due to the high volatility of these elements. The utilization of sealed non-reactive crucibles is in this case especially recommended.

4.2. Remarks on measurement techniques of formation thermodynamics and their application to the rare earth alloys

Besides the general problems in handling rare earths and their alloys, there are also specific ones regarding the techniques used in thermodynamic measurements. The consequent experimental difficulties and the particular expedients suggested for each individual case have been dealt with and explicitly described by some authors. Further illustration, however, may be found, not only in specific articles on rare earth alloys, but also in those on other metals such as the alkaline earths, the actinides, etc., which often show analogous behaviour and reactivity.

4.2.1. Differential thermal analysis

A review on the experimental methods (especially at high temperature) in phase diagram science has been presented by Ipser and Komarek [63]. In this article, questions concerning generation of high temperatures, temperature measurement and thermal analysis, and problems concerning selection of crucible and thermocouple materials were mentioned and discussed. Palenzona and co-workers employed, for instance, Mo containers, sealed by arc-welding under pure argon [64,65] for the investigation of the Ca–Pd and the Th–Sn systems up to about 1700 K. Additional problems with very high vapour pressures were encountered by Kaldis et al. [66–68] in their phase diagram studies of rare earth-chalcogen systems using a commercial DTA up to about 2500 K. Specially developed W-crucibles made by electro-erosion were filled with about 200 mg of the sample and sealed by electron bombardment using a special device to keep the main part of the crucibles cool. W/W-Re thermocouples and their standardization with the melting point of high purity Al_2O_3 were used.

Ta-crucibles (about 1.5 g sample weight) were employed by Abdusalyamova et al. [69] in their investigation of the Tb–Sb system with a commercial high-temperature DTA up to 2500 K, with W/W-20% Re thermocouples standardized at the melting points of different high purity materials. All measurements were performed under pure He. For compositions beyond 55 at% Sb, molybdenum or Al_2O_3 crucibles had to be used in order to avoid reactions between Sb and Ta. To cope with the high vapour pressure of Sb, the crucibles were placed in larger Ta-containers sealed with a corresponding lid. Reaction with Mo or Al_2O_3 cannot, however, be completely excluded. A similar technique was used by Yatsenko et al. [70] in their study of R–In phase diagrams up to about 1800 K.

In a series of papers [71], Hayes deals with the possible advantages of the Smith method in thermal analysis [72]. According to this technique, a constant difference in temperature is maintained between the specimen and the furnace. When the sample undergoes a reaction, the furnace ceases to heat/cool until the reaction is complete. In this way an amplification of the thermal effect is obtained and also a very good resolution between effects which are very close to each other may be observed. The application of this technique to rare earth alloys has been presented by [73] by using specially built tantalum crucibles.

The previously mentioned discussion by Gschneidner [54] on several expedients to be considered while performing thermal analysis of rare earth metals and alloys is also to be borne in mind.

Jorda [74] describes the use of W or ZrO_2 crucibles with a DTA apparatus working up to 2400°C. Gachon et al. [75] have discussed preparation and analysis techniques without the use of containers. Among these is the widely used preparation technique in an arc furnace under an argon-controlled atmosphere and on a water-cooled copper-heart. This technique has been employed by many researchers in the preparation of various rare earth alloys, especially with metals which are not very volatile and which have a high melting point.

Another much used technique is that for induction heating. Hukin [76] presented a short review on the variant of this method based on ‘flux concentration’ (mainly the ‘cold crucible’ method and its application to the melting of rare earth alloys and the ‘levitation’ method). The special multi-segment cold crucible devised by Hukin is described and its further application to single crystal growth of rare earths discussed. The effects of the presence of impurities in the atmosphere and the use of special glove-boxes were also considered. More recently these methods have been reviewed by Fukuzawa [77].

The induction techniques have been coupled with methods of thermal analysis (see for instance Gachon et al. [75]) and enthalpy measurements (drop calorimetry by Frohberg and Betz [78]).

4.2.2. Calorimetric measurements

As an introduction to this topic, we may remember that the need for performing a number of measurements by using different complementary techniques has often been underlined, see for instance Kubaschewski [79].

In the application of the different methods to the calorimetric analysis of the rare earth alloys, various comments have been reported and a number of measurement expedients have been suggested. High-temperature calorimetry in metallurgy has been discussed by Bros [80]. Hertz [81] suggested that in using the high temperature calorimetric method in the investigation of an alloy system, mainly in the case of reactive materials, for each composition, the minimum temperature should be chosen at which the desired reaction could advance with reasonable speed. Notin et al. [82] have discussed the thermodynamic properties of Ca intermetallic compounds (several calcium alloys show reactivity and properties comparable with those of rare earths). They observed that CaX compounds are instable in air atmosphere. For this reason, the most useful method is often direct precipitation calorimetry, in a solid–liquid two phase domain measuring the effect of the addition to the bath of small samples of pure Ca. They generally used a Setaram calorimeter. They observed however, that the geometry and size of the thermoelectric heat-detector was not suitable for high-temperature metallurgical applications and they suggested modifications in the experimental cell and the surrounding thermopiles. This point has fully been described and discussed by Bros [80]; in his review he mentions various aspects of calorimetric experimentation such as, for example, materials employed, special devices and different factors on which the achievement of reliable results may depend. Emphasis to these points was given also by Gather and Blachnik [83,84] in their description of a heat-flow calorimeter and its use in the measurement of excess mixing enthalpies.

Kleppa determined the heat of formation of several groups of rare earth alloys, for instance of Pt-group alloys, carbides, silicides, etc. In a review [85], he discussed systematic aspects of high temperature thermochemistry. He emphasized the advisability of working at a temperature as high as possible in order to avoid, for instance in direct calorimetery, the possibility of an incomplete reaction. In his paper too, a description is presented of the best structure to be given to the thermopile detectors in commercial equipment. The use of Zr-getter, BN crucibles and stirrer, and Pt–Rh liner has been presented [62]. He also discussed specific problems which may be met in calorimetry with different rare earth alloys (for instance, difficult synthesis reaction with Pt-group metals) and described the solute–solvent calorimetry method and its advantages. According to this method, the heats involved in dropping into a high temperature calorimeter the components and then the compound respectively, together with a third partner acting as a solvent, are compared. The third partner can facilitate the reaction between the two components, by lowering the melting point of the mixture. This method has been used, for instance, in the case of rare earth borides [86] by using Pt as a solvent and obtaining, in the case of the investigation of YB_4, in both runs an alloy $Pt_{0.70}B_{0.24}Y_{0.06}$ as the final product.

Palenzona [87] studied the alloying properties of Ca and rare earth alloys, mainly investigating $AuCu_3$-type compounds, by using dynamic differential calorimetry (DDC). In this method the heat evolved in the direct reaction of the two elements during a heating run carried out in a DTA apparatus, is evaluated by using the data treatment suggested and discussed by Faktor and Hanks [88]. Generally the samples were contained under ultra-pure argon in molybdenum crucibles. In the case of compounds congruently melting and formed with low-melting metals, reliable results could generally be obtained quickly and easily. Drawbacks were however, observed when measuring compounds for which the direct synthesis is slow and difficult. This may be the reason for the disagreement observed, in the case of R–Pd alloys, between the data by Palenzona and Cirafici [89] and those by Guo and Kleppa [90].

The special problems met in the rare earth reaction with a volatile element were already presented by Pratt and Chua in the investigation of RSb compounds [91,92] (see Fig. 6). The heart of their calorimeter is a cylindrical tantalum reaction cell which is tightly closed with a screw-top containing a central well to accommodate the calibration heater. The mode of operation is essentially similar to that of differential thermal analysis. The reaction run was generally performed after heating the calorimeter at a slightly lower temperature than the reaction temperature. ΔH was measured between 700 and 750 K.

The results obtained in many cases were in fair agreement with those obtained by other techniques. In a few cases (DySb, HoSb and TmSb), however, large scattering was observed. This could be ascribed to the reaction of Sb with the tantalum container or to antimony escaping through the unsealed lid.

For a number of rare earth alloys, thermochemical data have been obtained by means of solution calorimetry. Special devices and expedients have often been reported.

Only in a few cases was the acid solution method used. Recently, however, this method has generally been dismissed. This is in agreement with what was

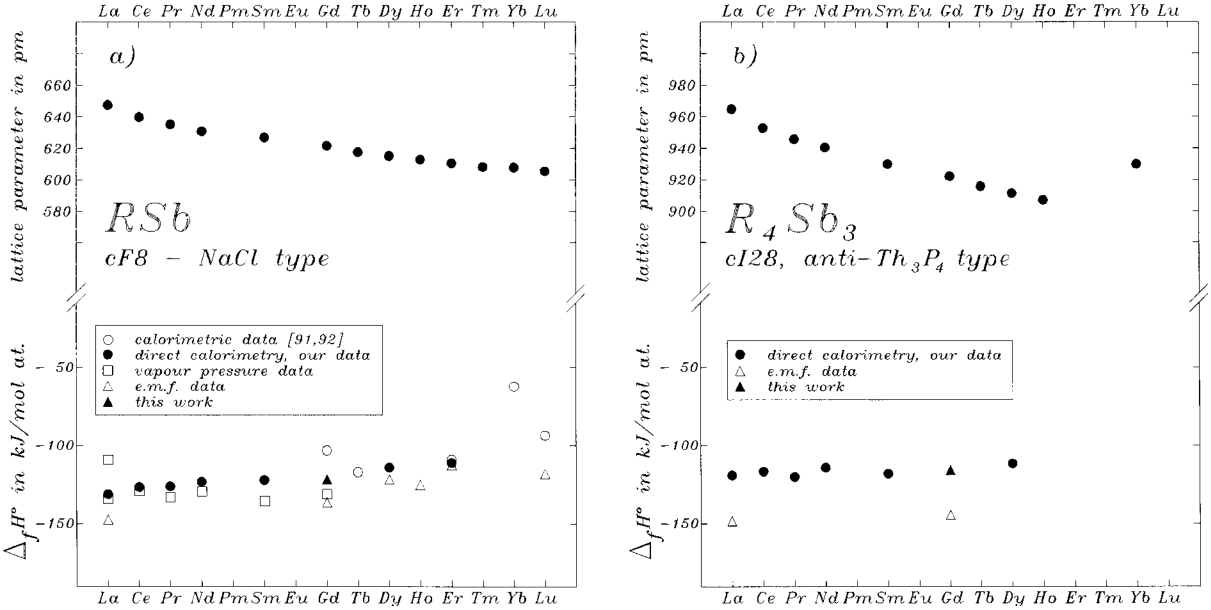

Fig. 6. Rare earth antimonides. Trends of lattice parameters and $\Delta_f H$ vs. atomic number of (a) the NaCl type RSb and (b) the anti-Th_3P_4 type R_4Sb_3 compounds. The enthalpy values obtained in this work for the Gd alloys have also been inserted.

observed by Kubaschewski and Alcock [93] who evidenced the large errors which may result from obtaining heats of formation, generally small, as the difference between two values, generally much greater, of the dissolution heats of the components and the compound in an acid. Solution calorimetry in acid (4N HCl) was nevertheless used by Kaldis in the investigation of very exothermic phases (for instance measurements on Ce–N and Sm–S compounds have been reported). Difficulties were noticed for Tm–Se alloys, for which the use of fluorine combustion calorimetry was developed [94].

As for mixing calorimetry in the liquid state and solution calorimetry in molten metals, we may mention a few reports and comments. The characteristics of high temperature mixing calorimeters have been reported by Mathieu et al. [95], Predel [96], Bros [80], Castanet [97], Sommer [98] and Stolz et al. [99]. The use of an association model in the description of liquid alloy thermodynamics has been discussed mainly by Sommer [98] and Stolz et al. [99]. Colinet [15,100] and Nagarajan and Sommer [101] were particularly interested in its application to the investigation of rare earth alloys. Experimental details have also been described by Nikolaenko [102] who noticed that the best working temperature was a compromise between the low rate of dissolution of solid samples in the melt, high vapour pressure of one or both components and their corrosive action at elevated temperature. The use of Al_2O_3 crucibles coated with protective layers of Y_2O_3 was indicated.

On the other hand solution enthalpies of salts (containing for instance La^{3+} ions) and high temperature enthalpies of mixing of binary liquid mixtures of rare earth halides have been described by Blachnik et al. [103,104].

4.2.3. Emf techniques

Emf methods with liquid and solid electrolytes and the conditions for their applications have been summarized in reviews by Komarek [105], Kubaschewski [79] and Mikula [106]. In a paper by Moser [107] the advantages and limitations of the emf method of high temperature concentration cells with liquid electrodes and electrolyte have been discussed with particular interest in the acquisition of partial thermodynamic functions and their use for further calculation by means of the Gibbs–Duhem equation and verification with the phase diagram. In this paper other problems taken into account are the preparation of the electrolyte, the choice of the material for construction of the cell and the application of suitable experimental arrangements.

General comments on the solid electrolyte electromotive force cells and their application to rare earth alloys have been reported by Colinet and Pasturel [108]. They observed that such experiments need careful preparation and the requisite criteria of the cell have to be checked. They mentioned moreover that the results obtained for a group of alloys of a certain system, from the emf of the different prepared cells, lead to a series of Gibbs energies of reactions. The Gibbs energy of formation of a given compound is then deduced by linear combination of these Gibbs energies of reaction. If in a certain system, therefore, the Gibbs energy of formation of a given compound is deduced from, for example, n Gibbs energy of reaction measurements, the quoted uncertainty is then n-time that of the first Gibbs energy measurement. The enthalpy of formation is deduced from the temperature variation of the Gibbs energies. Thus, the uncertainty also depends on the temperature range covered by the emf measurements and may be quite large in the rare earth-rich region.

However, Colinet and Pasturel observed that, nevertheless, emf measurements present the opportunity to obtain Gibbs energy, enthalpy and entropy of formation values all at the same time.

Several contributions to the application of these techniques to the rare earths alloys, mainly with low-melting metals, have been given by Yamshchikov et al. [109], Kober [28] and Vassiliev [110].

The use of solid oxygen and fluorine concentration cells for the study of thermodynamic alloy properties has been reviewed by Schaller [111]. Palladium alloys of Y, Ce, Gd and Th have been studied. The use of liquid two phase Ce–Bi alloy encapsuled in iron cups as a reference electrode instead of pure Ce was described: the reduced activity of Ce in this alloy helps to avoid oxygen contamination. The advantage of using fluorine concentration cells with CeF_3 as a solid electrolyte was discussed by Bretschneider and Schaller [112]. The method of coulometric titration was used to deposit Ce on thin Pd film and to control the composition of the alloys produced in situ. A discussion on the thermodynamics of Pd alloys with several electropositive metals, (Al, rare earth elements, thorium) and on the reliability of using emf methods has been reported by Hennemann and Schaller [19]. An original device containing a 'pin-point electrode' and its application to the investigation of alloys of electropositive elements (Ca alloys) has been described by Hertz and coworkers [113]. The point electrode can be used for electrochemical study of solid metal alloys characterised by non protective oxide. Measurements must be made in reducing gaseous atmosphere; the potential-time curves of depolarization, after highly-controlled oxidation of the point electrode, help to determine the activity of the most oxidizable component of the alloy. The results are almost of the same quality as those obtained by means of ordinary measuring cells; the cell response is however much faster.

4.2.4. Vapour pressure methods

Reviews on the vapour pressure methods have been reported by Komarek [105], Tomiska [114] and Neckel [115].

Vapour pressure measurements have been performed on a small number of rare earth alloy systems. These measurements, often show disadvantages similar to those of the emf methods because the enthalpies of formation are obtained indirectly. However, on selected groups of R alloys, different techniques have been employed.

A dewpoint apparatus has been used by Chiotti and Mason [116] in the investigation of Zn alloys of the light rare earths. This method is based on the fact that the vapour pressure of Zn over any sample at a given temperature is equal to the known vapour pressure of pure Zn placed in the same apparatus and maintained at the dewpoint temperature. Tantalum crucibles were generally used as containers of the alloys inside the dewpoint apparatus.

Similar in its working principle is the isopiestic method [105,117]. This method is based on the tendency toward equilibrium of a series of samples at various temperatures under an imposed vapour pressure of the more volatile component B (the vapour pressures of the two components should differ by, at least, three orders of magnitude). The apparatus contains a series of crucibles stacked in a vertical tube enclosed in a furnace with a temperature gradient. The crucible on the bottom (corresponding to the lowest temperature in the furnace) contains the pure volatile component B. The other crucibles (placed at progressively increasing temperatures) will contain, for instance, weighed samples of the other component. Each sample, after a sufficient length of time, will equilibrate with the volatile component vapour, giving the composition for which at its temperature the vapour pressure of B is equal to that over pure B.

This method has been used for some of the R alloys (Mg–Y [118], Mg–Y–Cu [119]). A discussion on the crucible material to be used is reported. A certain amount of the Mg–Y liquid alloy was found to creep out of the Ta crucible. This method may be useful (with a suitable choice of apparatus) for the investigation of Zn, Cd, etc. alloys or, possibly, of the alloys of Eu and Yb with high melting metals.

Effusion techniques have been applied to the investigation of several R alloys; general discussions on the Knudsen method, its variants and its combinations with other instrumental techniques (mass spectrometry) have been reported by Komarek [105], by Neckel [115] and by Tomiska [114]. Recoil momentum techniques (particularly torsion effusion methods) and the use of dual, triple or multiple cells have been discussed.

Examples of R alloy systems studied by using these methods may be:

R–Mg alloys: [120,121], measurement of the weight loss of a Ta effusion cell and a discussion on the preparation of alloys (outgassing, annealing, etc.) are presented.

Ce–Sb alloys: Schiffman and Franzen [122] employed a simultaneous weight-loss mass spectrometric Knudsen effusion technique. The use of different samples to confirm the existence of a congruent vaporizing composition is discussed. A detailed description of several auxiliary techniques is also reported.

Sc–P alloys: Mass-spectrometry and target-collection Knudsen effusion technique is described [123,124].

Lu–S alloys: The same techniques as above were used [123]. Preparation and heating methods are described in details. Homogeneity of the samples and their vaporization mechanism were checked and discussed.

5. Summary of the results obtained in our laboratory and of the work in progress on the thermodynamics of selected groups of rare earth alloys

5.1. Introduction and experimental details

For a long time our group has been involved in the investigation of alloy chemistry with special attention to the rare earth alloys. Intermetallic phase identification and characterization and phase diagram studies have been systematically carried out on several binary and ternary systems (see for instance the summaries reported in Refs. [125,126]).

On the same or similar systems, a methodical study of thermodynamics was also pursued. General information on this work has been reported for instance in Refs. [16,127,128].

In this paper, for some selected series of alloys, we report a summary of our experimental data previously obtained, with the results of a few new measurements and an indication of the work in progress and/or planned.

Our thermodynamic measurements were especially aimed at the determination of the heats of formation. This was generally performed by using ‘direct reaction calorimetry’ techniques (the alloys are synthesized from the elements inside the calorimeter itself).

The direct calorimeters (and a few other calorimetric instruments) built in our laboratory are briefly mentioned in the following:

Aneroid, isoperibolic, small furnace, direct reaction calorimeter.

A detailed description of this apparatus was published in [129] and its developments in [128].

The calorimeter, as sketched in Fig. 7, consists of a thick aluminum cylinder containing two small electric furnaces, which are used for starting the reaction in the sample and for electric calibration respectively. The sample (about 10–15 g) consists of a mixture of fine metal powder of the two elements, enclosed in a gas-tight inox crucible sealed by electric welding which is then inserted in the calorimeter and, after thermal equilibration, is heated until the reaction starts. The calorimeter, inserted in a thermostatted Al-block, is covered by the hot junctions of a thermopile differentially connected to similar reference calorimeter.

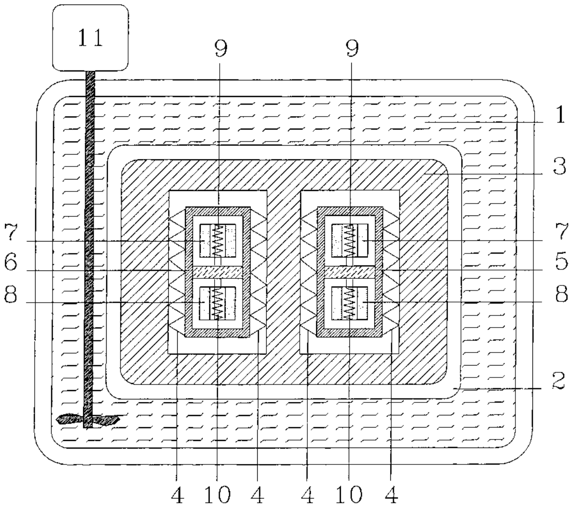

Fig. 7. Schematic representation of the aneroid isoperibolic, small furnace, direct reaction calorimeter [128,129]: (1) thermostatted water container, (2) vacuum tight container, (3) reference massive aluminum block for thermal uniformity, (4) thermopiles, (5, 6) identical calorimeters differentially connected, alternatively used as a measuring and reference instruments, (7) samples (compacts of finally mixed component metal powders), (8) metallic blocks as internal references, (9, 10) heating coils for priming the reaction and for electric calibration, respectively, (11) water ultrathermostat and propeller.

The heats of formation can be considered to be measured at 300 K because the sample inside the calorimeter cools down to this temperature during the measurement. The error of ± 2 kJ/mol at. generally ascribed to all satisfactory measurements, is considered to include both the instrumental errors and any uncertainties due to small compositional variations or inhomogeneities, not detectable in the subsequent micrographic and X-ray diffractometric examinations to which all the samples are subjected after the calorimetric measurement. (Previously a different version of an isoperibolic twin small furnace direct calorimeter was used. It was of the submerged type with the equipment plunged in a special liquid calorimetric bath, the temperature of which was measured by a multi-junction thermopile [128]). This kind of calorimeter is particularly convenient for studying exothermic and fast synthesis reactions, resulting in a complete transformation of the metals into final stable phases. This behaviour is most likely between two elements far apart in the Periodic Table, especially if one of the metals has a low melting point. The alloys of the rare earths with several p-block elements show these characteristics.

High-temperature, drop, direct reaction calorimeter. Several instruments of this type have been reported in literature. A variant, built in our laboratory, has been described in [130] and its performance and characteristics discussed. The working scheme of this calorimeter (sketched in Fig. 8) consists of the dropping,

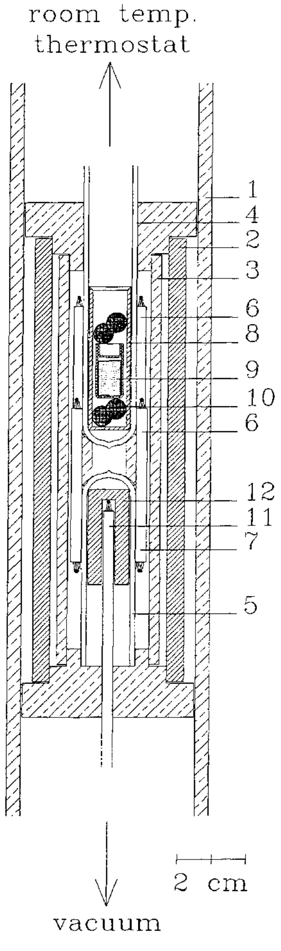

Fig. 8. Schematic section of the high temperature drop direct calorimeter [130]: (1) vacuum tight work tube, (2) 'nichrome' metallic cylinder, (3) alumina tube, (4, 5) silica tubes forming the measuring and reference cells respectively, (6, 7) sample and reference thermopile junctions, (8) sample-receiving metallic vessel, (9) sample enclosed in its metallic crucible, (10) Ag spheres for calibration, (11) thermocouple, (12) metallic reference block.

from an overhead room-temperature thermostat, into a high temperature calorimetric vessel, of a small sealed container containing the mixture of the two metals under study. The thermal effect is then compared with that observed in the subsequent dropping, from the thermostat into the calorimeter, of the alloy synthesized in the previous run. The evaluation of the effects is made by means of a series of standard specimens (for instance pure silver) which are dropped in the calorimeter in similar working conditions.

In comparison with the previously described instrument, this calorimeter has extended the range of alloys which can be studied by direct calorimetry. In a few cases for the investigation of some special alloys or for carrying out different thermodynamic measurements, other instruments have been built and used. We may mention an 'HCl solution calorimeter' which was used for the investigation of a few rare earth alloys with Mg and Zn [131]. In the case of the Nd–Zn system the values of the heat of formation obtained were satisfactorily used together with other experimental data for a thermodynamic optimization of the system.

A 'drop quasi-isodiabatic calorimeter', on the other hand, was built for the measurement of the incremental enthalpy of samples dropped, from an abovestanding furnace maintained at a determined high temperature, into a room temperature calorimeter characterized by an imposed constant heat flow towards a surrounding thermostatted metallic block. The system Mg–Pb has been studied with this instrument and the diagram enthalpy, temperature, composition determined [132]. Its use in rare earth thermochemistry is planned for the near future.

In a few cases, finally, in cooperation with the Marseille laboratory, particularly on R–Pb alloys, Cp measurements have been carried out by differential scanning calorimetry [133,134].

Electromotive force measurements, moreover, have been considered by using a potentiometric cell prepared, for instance in the case of Lu–Pb alloys [135], according to the following scheme:

$$(-)\mathrm{Lu}/\mathrm{LiCl\text{-}RbCl} + \mathrm{LuCl_3}/\mathrm{Lu}_x\mathrm{Pb}_{1-x}(+)$$

The electrolyte was a eutectic mixture of RbCl and LiCl with 0.05 mass% of lutetium chloride, which was dried by heating under vacuum, then under dry pure HCl gas flow and finally under pure argon flow. Reference and working electrodes were made of a W wire connected to a small block of alloy or of a reference metal.

5.2. Rare earth alloy systems studied and under investigation in our laboratory

The alloy systems most widely studied in our laboratory with different rare earth elements include the following.

R–Mg alloys. A number of phase diagrams have been assessed and determined in our laboratory; a summary of this work has been reported in [50,126]. A revision of some selected regions (Mg-rich) of these diagrams is in progress, using DSC [136] and special thermal analysis techniques (the Smith method as described by Hayes et al. [71]). As for thermodynamics, the literature data, obtained mainly by acid solution calorimetry, vapour pressure and, in the case of Ce alloys, by solution calorimetry in liquid Mg, seem to require a revision [15]. The data of the $\Delta_f H$ of the various phases obtained by different authors (even with similar techniques) show very large scattering. No reasonable trend may be deduced.

We are trying to determine the heat of formation by means of the direct drop calorimetry. Preliminary investigation has been carried out on a few Ce, Pr, Nd, Sm and Yb–Mg alloys [137].

R–Ag alloys. Only scarce data are available on thermodynamics. Calorimetric measurements have been reported by Kleppa and co-workers [138,139]. We have in progress (drop, direct reaction, high temperature calorimetry) an investigation of the La and Ce systems. Preliminary work has been performed on the congruent melting compounds $R_{14}Ag_{51}$ and RAg phases formed in the two systems. For the $R_{14}Ag_{51}$ phases, for which the following values were reported in literature: $La_{14}Ag_{51}$, (−21.4±2.0) kJ/mol at. [138] and $Ce_{14}Ag_{51}$, (−19.3±4.1) kJ/mol at. [139], we have obtained data in good agreement; slightly less exothermic values which are, on average, about 2 kJ/mol at. less, were observed. For the 1:1 phases, problems have been encountered in obtaining a well defined synthesis reaction advancement during the calorimetric measurements and the system is still being studied.

R–Au alloys. These systems are generally characterized by the formation of several compounds often having a congruent melting point. For a few of these systems a determination of the phase diagram has been performed in our laboratory [140,141].

For some of the same alloys the measurement of the formation heats is in progress. A number of systems, however, have already been studied by Kleppa [85]. For the 1:1 compounds, for instance, which generally represent the phases with the highest melting points in the different systems, the known data are reported in Fig. 3. The values obtained in this work for GdAu, TbAu and DyAu have been added. The good agreement may be noted. The high exothermicity of these alloys, which rises with the increasing of the atomic number R and the decreasing of the ionic radius is evident.

R–Al alloys. All these systems are characterized by the formation of several compounds. Typical of these are the RAl_2 phases (Laves phases) showing maximum stability with all congruent melting temperatures in the order of 1400–1500°C. For these alloys, several thermodynamic investigations have been reported. Different kinds of measurements (calorimetric, emf) have been performed. Generally, for the Al-rich alloys (containing more than ca. 65 at% Al), a good agreement was observed between the results of the different measurements and a reasonable, smooth trend of the $\Delta_f G$ or $\Delta_f H$ was reported. In the R-rich regions, however, greater difficulties were observed in the emf measurements and for a number of reasons not yet fully understood, erroneous values (and irregular, improbable trends) were observed for the $\Delta_f H$ obtained by this method (this point has been previously discussed for instance in [142]). A systematic calorimetric investigation of these alloys was therefore planned. The systems with La, Ce, Pr, Nd, Sm and Yb [143] have been studied. For the systems Ce–Al, Nd–Al and Sm–Al, moreover, all the available data have been used for a thermodynamic optimization [144].

New data recently obtained concern the Y–Al system. These data have been included, for the RAl_2 phases, in Fig. 3. The observed trends have already been discussed. We may now notice the good agreement seen for these compounds between the data obtained by different authors and using several different techniques. The values concerning these compounds, mainly for $CeAl_2$ and $PrAl_2$, may, therefore, be considered among the more reliable data relevant to the enthalpy of formation of intermetallic phases and their use may be suggested, for instance, in the field of alloy thermodynamics for the thermochemical calibration of new calorimetric devices or procedures.

As a final comment to this group of alloys, we may mention that in R–Al systems and in several complex R–Al–M systems, very often metastable and/or glassy alloys are obtained. Their formation and possible applications have been discussed by Inoue et al. [145]. An investigation into some aspects of this point has also been started in our laboratory [146,147]. The role of the excess liquid specific heat with respect to crystal phases in glass formation has been outlined.

R–In alloys. Previous work carried out in this laboratory mainly on phase diagram investigation, together with the work conducted along these lines by Yatsenko et al. [148] has been reviewed in [149]. The phase diagrams are characterized by the formation of several compounds. Generally, RIn, R_3In_5 and RIn_3 melt congruently.

As for the thermodynamic data, Kober et al. [27,28,30–32], Yamshchikov et al. [29,33–35], Bayanov et al. [36,37,39–42], Serebrennikov et al. [38] and Vasilev et al. [43–46], reported the results of emf measurements mainly in the In-rich regions, while Palenzona and Cirafici [26] systematically measured by differential dynamic calorimetry (DDC) the heat of formation of the RIn_3 phases. Previously, in our laboratory, an investigation of the La–In system was carried out by using the small furnace direct calorimeter [25]. Only partial data relevant to a portion of the system were obtained; a number of difficulties were, in fact, encountered because very often the reaction between the two components did not extend to the equilibrium state. In fact, as a first step in the reaction of synthesis, the $LaIn_3$ phase was generally formed even for the La-rich compositions. The subsequent advancement to the equilibrium was very slow.

Recently the thermochemical investigation of several R–In alloys has been undertaken, by using the direct drop calorimetry. The Gd–In system is now being studied. The new values just obtained for $GdIn_3$

and $CeIn_3$ are inserted in Fig. 1 together with the literature data.

R–Sn, R–Pb alloys. For a number of R–Sn system (La, Ce, Y) the heats of formation have been measured. The Nd–Sn system is under investigation. Fig. 3 shows the value obtained in this work for $NdSn_3$ in comparison with those from the literature relevant to the different RSn_3 phases.

For the R–Pb alloys, in cooperation with scientists from different laboratories, a number of thermodynamic properties have been studied (Cp measurements for RPb_3, R=La, Ce, Pr and Nd [133] and for several compounds of the Y–Pb [150], Yb–Pb [134,151] and Lu–Pb [135] systems. An investigation of the Gd–Pb alloys is in progress. The different data obtained, together with those from literature (by calorimetry, DDC, emf, etc.) have been summarized and commented on in a short review of the rare earth compounds with the elements of the 14th group (C, Si, Ge, Sn, Pb) [127].

Fig. 9 shows the trend of the highest values of the $\Delta_f H$ in this group. As can also be seen, in Fig. 5, we have in this part of the Periodic Table a typical trend with a minimum of the formation enthalpy in the central region of the curve. This may perhaps be related to the different bonding mechanism in the R–X phases according to the greater or lesser metallic character of the X element. Perhaps we should consider the existence, in the compounds with non-metallic X elements, of some residual X–X bonds.

R–Sb, R–Bi alloys. These systems are characterized by the formation of a number of compounds (the more frequent stoichiometries are R_2M, R_5M_3, R_4M_3, RM and RM_2) with very high congruent melting points for a stoichiometry generally corresponding to 1:1.

A number of phase diagrams have been determined by Abdusalyamova [152] and by Abulkhaev [153] for the R–Sb and for the R–Bi systems, respectively. As for the heats of formation, we have studied the systems with La, Ce, Pr, Nd, Sm and Dy (see [154] for a summary). The Gd–Sb and the Tb–Bi systems are under investigation. The values obtained in this work for GdSb and Gd_4Sb_3 are presented in Fig. 6 together with the literature data relevant to the other antimonides. In a number of cases, a thermodynamic optimization has also been carried out using the method and software developed by Lukas et al. [6]. The Pr–Sb and Nd–Sb systems have been optimized and the data obtained used for the computation of the ternary Pr–Nd–Sb system, for which then characteristic points were experimentally confirmed [155].

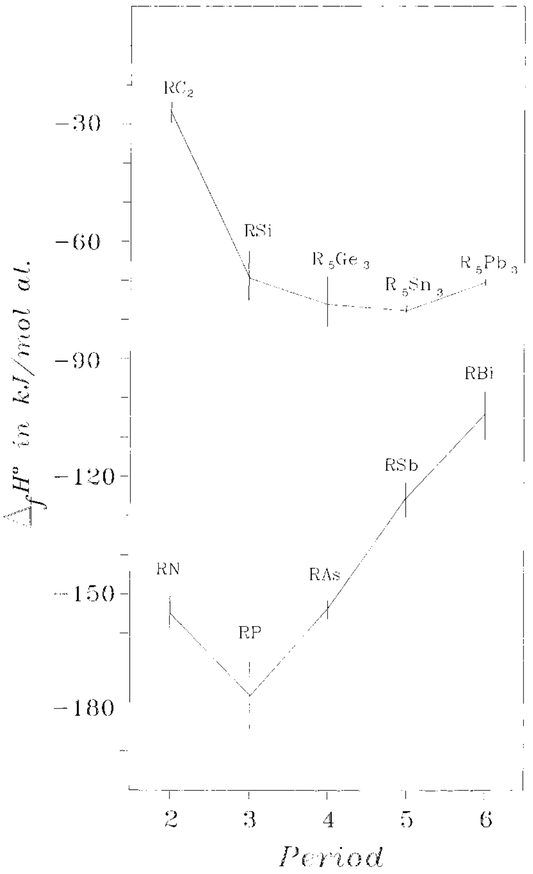

Fig. 9. Trends of the highest values of the $\Delta_f H$ observed in selected R–X systems of the lanthanides with the elements of the 14th and 15th groups. For the different R–X systems the range of values reported corresponds to the La–X and Gd–X alloys taken as examples.

For the R–Bi alloys, a summary of the work carried out is given in [156,157].

Yb–X alloys. After concentrating mainly on data and trends relevant to the trivalent rare earths, it may be worthwhile giving a few details about work carried out and in progress on the 'divalent' rare earths (particularly on Yb). While considering the properties of the different rare earths and their trends (see

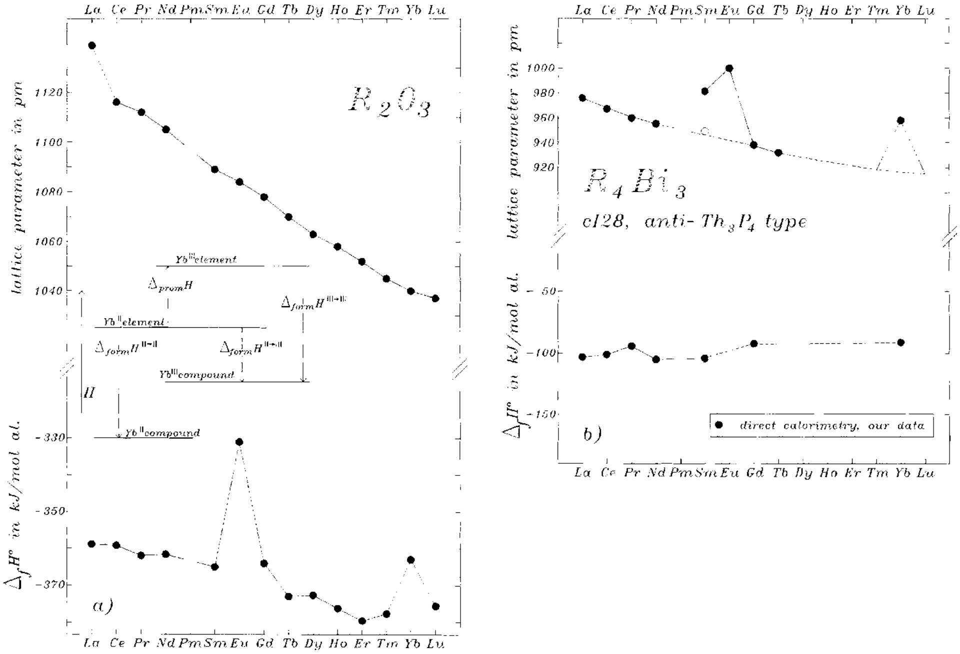

Fig. 10. Crystallochemical and thermochemical behaviour of Eu and Yb in comparison with the other rare earths: two series of compounds, oxides and bismuthides, are shown as examples. In the oxides Eu and Yb are trivalent, divalent in the bismuthides. The energy balance corresponding to the formation of compounds containing di- or trivalent Yb is shown in the inset in (a).

Fig. 10), we may notice the deviations often shown by the Eu and Yb alloys.

The role that thermochemical investigation may play in the study of this behaviour may be presented considering the data reported in this figure for the R_2O_3 oxides in which all the rare earths, including Eu and Yb, can be considered trivalent and which show a continuous trend of the lattice parameters and, therefore, of the atomic dimensions. We see the anomalies presented for $\Delta_f H$. In fact, starting from the elemental Eu and Yb in a divalent state, these become trivalent like the other rare earths in the compounds with oxygen. In the reaction of Yb metal 'promoted' to the trivalent state in the compound, an energy term (a 'promotion' $\Delta_{\mathrm{prom}}H$ value) different from that involved in other cases must thus be considered, which partially compensates for the $\Delta_f H$ experimentally observable.

It, therefore, seemed interesting to plan an experimental investigation of the Yb alloys with some elements in the right part of the Periodic Table. Contributions already given to this topic concern the compounds with Pb and Bi [151,157]. The data relevant to a group of bismuthides have been inserted in Fig. 10. The 'divalent' behaviour of Yb in these alloys is evident, in agreement with results of magnetic susceptibility, electrical resistivity, Hall effect and X-ray L_{III} absorption measurements [158]. As for the lattice parameters of the other bismuthides reported in Fig. 10, notice the behaviour of Eu similar to Yb and that of Sm_4Bi_3, for which two different values have been given in literature. For Sm_4Bi_3 an estimated valence of 2.2 has been reported in Röhler [159].

Ternary alloys

The systematic collection of thermodynamic data of ternary alloys will probably be a point of increasing interest in the future. The availability of a few $\Delta_f H$ on selected ternary compositions, together with the information on ternary compound formation and the well-assessed data concerning the binaries involved, will be very useful for an almost complete prediction or computation of the ternary equilibria.

For a systematic evaluation (experimental and/or theoretical) of ternary $\Delta_f H$, different approaches may be useful according to the characteristics of the binaries involved (compare with the different models adopted and used for the extrapolation from the binary systems of the $\Delta_{mix} H$ values).

As a first approach in this field, we are studying ternary alloys for which strong interactions (highly negative $\Delta_f H$) are known in all the three binary systems involved. Alloys such as R–Al–Ni are at present under investigation. The first results obtained [160], evidence the great exothermicity of all these alloys: $CeAl_2$ ($\Delta_f H = -50.0 \pm 2.0$ kJ/mol at.), NiAl ($\Delta_f H = -67.0$ kJ/mol at.), CeAlNi ($\Delta_f H = -54.0 \pm 2.0$ kJ/mol at.) are typical examples.

In the course of this research, a study of the Al-rich region of the Y–Al–Ni phase diagram [161] has been started and it has been found opportune to complete the data regarding the enthalpies of the binary Ce–Ni system. This work is now in progress.

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