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DETERMINATION OF HEATS OF FORMATION OF PRASEODYMIUM ANTIMONIDES

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A systematic investigation of the heats of formation in the Pr–Sb system has been performed using a small-furnace, isoperibolic calorimeter. The compositions and the equilibrium states of the samples have been checked by metallographic and X-ray analyses. The following values have been found for the various compounds (kJ/g atom ±2): Pr_2Sb: −99; Pr_5Sb_3: −112; Pr_4Sb_3: −120; PrSb: −126; $PrSb_2$: −97.

The data available (both the results obtained in this work and those already known) are discussed briefly and related to the possible shape of the phase diagram.

During a systematic investigation of compounds and alloys of the rare earths, we recently reported on the heats of formation of gadolinium bismuthides [1] and cerium antimonides [2].

In this work we have studied the heats of formation of the Pr–Sb compounds.

The Pr–Sb system

For this system, as for other rare earth pnictides, several data have been reported in the literature concerning the intermediate phases, their crystal structures and their magnetic, electric, etc. properties; little is known about the thermodynamic properties and the shape of the phase diagram.

As far as the intermediate phases are concerned, their crystal data are listed in Table 1, both those from the literature and those obtained in this work.

Magnetic properties have been studied, for instance, by Mullen *et al.* [3], by Guertin *et al.* [4] (PrSb compound) and by Bucher [5] (ferromagnetic ordering in Pr_4Sb_3, while $PrSb_2$ is antiferromagnetic below $T_N = 5.1$ K and undergoes a first-order transition to ferromagnetic ordering in a field of 6.5 kOe at 1 K).

Among the thermodynamic investigations we may mention measurements of heat capacities at low temperature for LaSb, PrSb, LaBi and PrBi (Wallace *et al.* [6]); investigation of saturated solutions of Pr in Sb at 648–1012 K (Kober *et al.* [7]); evaluation of the heats of formation of a number of rare earth monoantimonides (Chua and Pratt [8]); vapor composition and evaporation enthalpies of monoantimonides (Viksman *et al.* [9]).

As concerns the Pr–Sb phase diagram, no determination has been reported in the literature.

However, considering the data relevant to other systems of rare earth antimonides (especially the determination of the Nd–Sb diagram [10] and the more

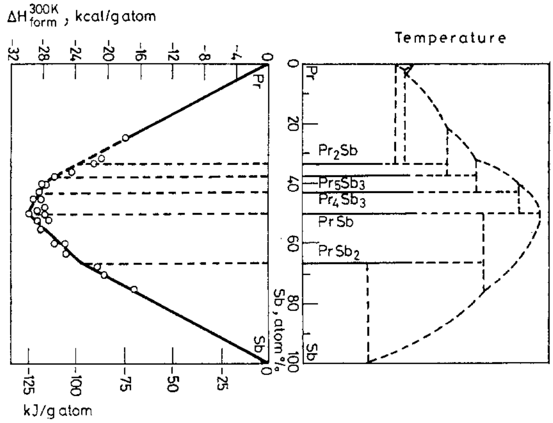

Fig. 1. Pr—Sb system. The trend in the heats of formation of the solid alloys is compared with a presumable shape of the phase diagram

recent investigation of the Tb—Sb system [11]) and the close analogies existing among the different rare earth antimonides, the sketch in Fig. 1 could be presumed to represent a reasonable approximation to the Pr—Sb phase diagram.

Experimental

The metals employed were Pr and Sb with nominal purities of 99.9 and 99.99 %, respectively.

A number of alloys of selected compositions was prepared by melting the metals in Ta crucibles (which were closed by welding under argon). These alloys were prepared in order to have a set of standard samples, to be considered as reference alloys for those prepared in the calorimeter, and to carry out a few crystallographic determinations.

After appropriate annealing, the samples were subjected to the X-ray and metallographic examinations described below.

Calorimetric measurements

These were carried out by using a direct, isoperibolic, aneroid calorimeter, fully described elsewhere [12]. It consists of a thick aluminium cylinder containing two small furnaces. The furnaces are used to start the reaction in the sample and for the electric calibration. The sample consists of a mixture of the two elements, which were first reduced to fine powders (this operation was carried out under argon for Pr) and then carefully mixed and compacted into an iron (or tantalum) crucible, which was subsequently closed by electric welding under argon. The crucible was then inserted inside the small furnace of the calorimeter. After thermal equilibration the mixture was heated until the reaction started. The temperature of the calorimeter is followed by a multiple-junction thermopile (differentially connected to the similar thermopile of another calorimeter, identical to the first one, used as a reference). The two calorimeters are symmetrically inserted in an aluminium block surrounded by a water ultrathermostat at 27 ± 0.01°. The electric energy dissipated in the calorimeter in the reaction run is compared with that evolved in a number of calibration runs. The formation heats can be considered as measured at 300 K (thermostat temperature) because the sample inside the calorimeter cools down to this temperature during measurement.

The overall instrumental uncertainty was estimated to be $\sim 1\%$ [12, 13], the error of ± 2 kJ/g atom generally ascribed to all measurements is considered to include both this uncertainty and the effects due to small variations of composition or to possible quenching of disorder, etc. from a certain temperature higher than 300 K. The complete range of composition was investigated and the different samples prepared in the calorimeter were subjected to a number of examinations, in order to check the composition and equilibrium state.

Metallographic examination

This was carried out (after dry polishing and etching in air) on the largest sections of the specimens, in order to check the uniformity of composition, the phase distribution and the completion of the alloying reaction. Some photomicrographs of alloys synthesized in the calorimeter are shown in Figs 2–4.

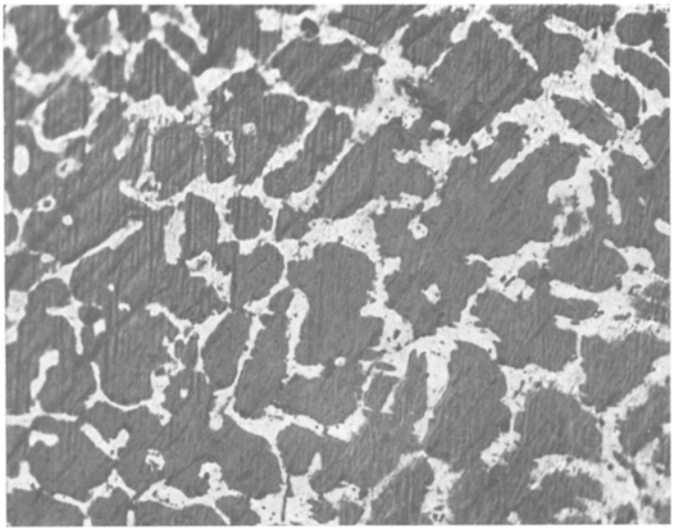

Fig. 2. A microphotograph of alloy 10 (Pr–Sb 45.0 at % Sb). Etched in air (500×)

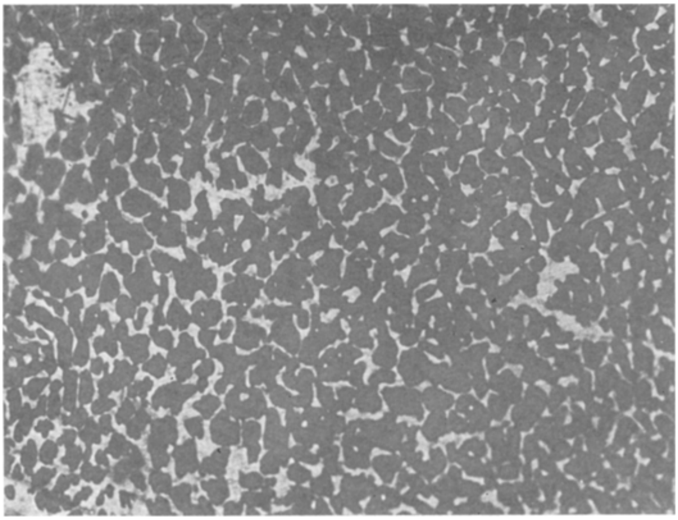

Fig. 3. A microphotograph of alloy 19 (Pr—Sb 60.0 at % Sb). Etched in air (500×)

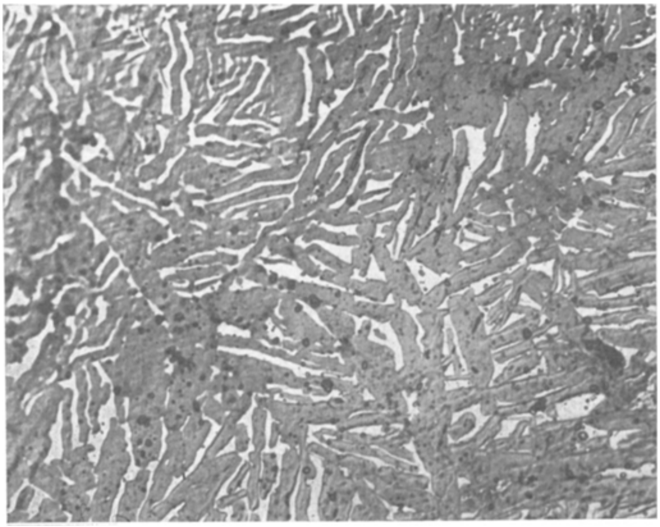

Fig. 4. A microphotograph of alloy 23 (Pr—Sb 75 at % Sb). Etched in air (500×)

X-ray analysis

Powders of the various alloys were examined by the Debye method, using CuK_α radiation. Powder photographs were used both for phase analysis and identification and for lattice parameter measurements. These were carried out with a least-squares fitting to the Nelson–Riley function [14].

Results and discussion

The crystal data measurements are reported in Table 1. The existence of the following phases was observed or confirmed: Pr_2Sb, Pr_5Sb_3, Pr_4Sb_3, PrSb and $PrSb_2$. We note the generally good agreement between the lattice parameters now measured and the values previously reported in the literature.

As was already known, the intermediate phases generally correspond to well-defined stoichiometries: on the basis of the data reported in Table 1, however, we cannot exclude the existence of small ranges of solid solubilities. Especially for the 1 : 1 and 4 : 3 compounds, which are stable up to very high temperatues (1800–2000°), it seems highly presumable that at these high temperatures there is an appreciable extension of the homogeneity field (compare also with Hulliger [20] and Abdusalyamova [21]).

Owing to the poor characteristics of the photographs for the compound Pr_5Sb_3, it was not possible to obtain accurate values of the lattice constants during this work.

For the compound $PrSb_2$, in contrast, the parameters now observed are in good agreement with those reported in a Figure of the paper by Eatough and Hall [19], (however, there seems to be a misprint in the data reported in a Table in the same paper).

Table 1

Crystal structure data of Pr–Sb phases

Phase	Structural type	Unit cell dimensions, Å	Reference
Pr_2Sb	Tetragonal	$a = 4.54_0$, $c = 17.74$	
	$tI12-La_2Sb$	$(c/a = 3.90_8)$	This work
Pr_5Sb_3	Hexagonal	$a = 9.233$, $c = 6.510$	
	$hP16-Mn_5Si_3$	$(c/a = 0.705)$	[15]
Pr_4Sb_3	Cubic	$a = 9.45 \div 9.48$	This work
	$cI28$-anti-Th_3P_4	$a = 9.458$	[16]
		$a = 9.36$	[17]
PrSb	Cubic	$a = 6.377 \div 6.382$	This work
	cF8 – NaCl	$a = 6.366$	[18]
$PrSb_2$	Orthorhombic	$a = 6.26_7$, $b = 6.12_5$	This work
	$oC24-LaSb_2$	$c = 18.18$	[19]

As a comment to these data we can remark on the very close analogy existing between the phase sequence now described and that observed, for instance, in the La–Sb system. This system was previously investigated [22]: crystallo-chemical characteristics of the different phases were also described. Special emphasis was given to a discussion of the trends of the coordination numbers and (as suggested by Kubaschewski [23]) to the relationship observed, at least for the La-richer compounds, between coordination and heat of formation.

The calorimetric data on the Pr–Sb alloys are given in Table 2.

The same Table includes a few data on samples for which the reaction was not complete (these data, however, can be useful in giving limiting values of ΔH). Table 2 also reports the values of ΔH_{form} interpolated for the different compounds.

Table 2

Heats of formation of solid Pr–Sb alloys at 300K; $(1 - x)\mathrm{Pr} + x\,\mathrm{Sb} = \mathrm{Pr}_{1-x}\mathrm{Sb}_x$

Alloy number	Nominal composition x_{Sb}	Micrographic appearance and remarks	Diffraction lines observed in the powder photograph	ΔH_{form}, kJ/g atom ± 2
1	0.25	Two phase	Pr_2Sb	−76
2	0.31_5	Not uniform sample (not in equilibrium)	$Pr_2Sb + PrSb$	(−88)
3	0.33	Sample not in equilibrium	$PrSb + Pr_4Sb_3$	(−91)
4	0.36	Not uniform	Pr_4Sb_3	(−103)
5	0.37_5	Nearly homogeneous	—	−112
6	0.40	Two phase	$Pr_4Sb_3 + PrSb$	−117
7	0.40	Two phase	$Pr_4Sb_3 + X$	−118
8	0.42_5	Nearly homogeneous	Pr_4Sb_3	−120
9	0.45	—	Pr_4Sb_3	(−119)
10	0.45	Two phase[a]	PrSb	−123
11	0.47_5	Not uniform	$Pr_4Sb_3 + PrSb$	(−117)
12	0.49	Not uniform sample	PrSb	(−121)
13	0.50	Not uniform	PrSb	(−117)
14	0.50	Homogeneous	PrSb	−125
15	0.52	Not uniform; the equilibrium state was not reached ($Q < -\Delta H$)	PrSb	(−115)
16	0.52_5	Nearly homogeneous	PrSb	−121
17	0.55	Two phase	PrSb	−119
18	0.60	Two phase	$PrSb + PrSb_2$	−106
19	0.60	Two phase[a]	$PrSb + PrSb_2$	−111
20	0.63	Not far from homogeneity	$PrSb + PrSb_2$	−105
21	0.68	—	$PrSb_2$	−90
22	0.70	Two phase	$PrSb_2$	−86
23	0.75	Two phase[a]	$PrSb_2 + Sb$	−70

[a] Microphotographs for alloys 10, 19 and 23 are given in Figs 2, 3 and 4 respectively

Interpolated values of ΔH_{form} for the various intermediate compounds:

Pr_2Sb: -99 ± 2.0; Pr_5Sb_4: -112 ± 2.0; Pr_4Sb_3: -120 ± 2.0; PrSb: -126 ± 2.0; $PrSb_2$: -97 ± 2.0 (kJ/g atom)

Table 3

Heats of formation of solid selected R.E.—Sb compounds at room temperature (kJ/g atom ± 2.0)

Compound	La	Ce	Pr	Nd	Y
R.E.$_2$Sb	−98	−103	−99		
R.E.$_5$Sb$_3$	−107	−109	−112	−108	−96
R.E.$_4$Sb$_3$	−119	−117	−120	−114	−100
R.E.Sb	−131	−126	−126	−123	−105
R.E.Sb$_2$	−92	−90	−97	−91	
Ref.	(22)	(2)		(26)	(27)

The trend in the calorimetric data is compared in Fig. 1 to the sketch of the presumed phase diagram. The sharp minimum in ΔH_{form} near the equiatomic composition can be related to a diagram showing a maximum in the melting temperatures for the 1 : 1 compound (the only congruently melting phase existing in the system). (For such general interrelationships between the $\Delta H/x$ curve and the trend of the liquidus in the diagram, see e.g. Kubaschewski [24]).

For the Pr-richer alloys the data have been corrected (obtaining the values represented by the dotted line), taking into consideration the incomplete formation of Pr_5Sb_3 generally observed.

In the Sb-rich part of the system, for $PrSb_2$, a clear discontinuity was observed in the ΔH curve (for other $RESb_2$ phases a discontinuity was hardly discernible).

As concluding remarks, we may note that the ΔH_{form} measured for the Pr antimonides (which are in good agreement with the values computed according to the semiempirical model by Miedema [25]) can be smoothly inserted into the sequence of ΔH_{form} already known for other rare earth antimonides (see Table 3).

We note the progressive decrease in the heat of formation on passing from the light to the heavy earths. There is also a regular decrease in the heat of formation on passing (for the same rare earth) from the arsenide to the antimonide and to the bismuthide [28].

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Zusammenfassung — Es wurde eine systematische Untersuchung der Bildungswärmen im Pr/Sb-System unter Verwendung eines Kleinofen-Isoperibolkalorimeters ausgeführt. Die Zusammensetzung und der Gleichgewichtszustand der Proben wurden durch metallographische und röntgenographische Analyse ermittelt. Für die einzelnen Verbindungen wurden folgende Werte ($kJ \cdot mol^{-1} \pm 2.0$) gefunden: Pr_2Sb: -99; Pr_5Sb_3: -112; Pr_4Sb_3: -120; PrSb: -126; $PrSb_2$: -97. Die als Ergebnis dieser Arbeit erhaltenen und aus der Literatur bereits bekannte Daten werden kurz diskutiert und mit einem möglichen Phasendiagramm in Verbindung gebracht.

Резюме — Проведено систематическое исследование теплот образования в системе Pr—Sb, используя изоперибольный калориметр с малой печкой. Состав и равновесное состояние образцов проверены металлографическим и рентгеноструктурным анализами. Для соединений различного состава были определены следующие величины теплот образования (приведены в кдж(г-атом)$^{-1}$ ± 2.0): Pr_2Sb — 99; Pr_5Sb_3—112; $PrSb_3$ — 120; PrSb — 126; $PrSb_2$— 97. Полученные данные кратко обсуждены наряду с известными в литературе и связаны с возможной формой фазовой диаграммы.