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The phase diagram of the Ce–Ru system

A. Palenzona
Istituto di Chimica Fisica, Universita' di Genova, Palazzo delle Scienze, 16132 Genova (Italy)

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Abstract

The phase diagram of the Ce–Ru system has been investigated using differential thermal analysis, metallographic analysis, X-ray diffraction and electron microscopy. The ruthenium-rich side (75–100 at.% Ru) has not been studied owing to the high melting temperature. The compounds Ce_7Ru_3 (Th_7Fe_3 type) and $CeRu_2$ ($MgCu_2$ type) have been confirmed; Ce_3Ru not previously known was found to crystallize with the Fe_3C structure type. Moreover, two new intermetallics have been found, *i.e.* $Ce_{16}Ru_9$ and Ce_4Ru_3 which are new structure types. None of these phases exhibits appreciable ranges of solid solubility. Additions of ruthenium do not significantly affect the transition temperature of cerium. The Ce–Ru phase diagram is rather different from those of the neighbouring rare earths lanthanum and neodymium, indicating once more an anomalous behaviour for cerium.

1. Introduction

In a recent investigation devoted to the study of the crystal chemistry of ruthenium with rare earth elements [1] several phase diagrams were studied: La–Ru and Nd–Ru [2], Sm–Ru [3] and Er–Ru [4]. About twenty new intermetallics were identified, three of which were found to be new structure types.

One of the results of this research was the evidence for an anomalous behaviour of cerium if compared with neighbouring lanthanum and neodymium. Literature data range from the existence of no compounds except $CeRu_2$ as reported by Obrowski [5] to the completely hypothetical presence of four intermediate phases, in addition to Ce_7Ru_3 and $CeRu_2$, as reported by Moffatt [6]. For these reasons and because it is well known that cerium can often give rise to interesting intermediate phases exhibiting valence instabilities and other singular physical properties, we have undertaken the determination of the Ce–Ru phase diagram and report here the results obtained.

2. Experimental details

Elemental cerium was a commercial product obtained from Koch-Light Laboratories, U.K. (purity, 99.8 wt.%) while ruthenium was obtained from

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Johnson–Matthey, U.K. (purity, 99.9 wt.%) and was outgassed under a dynamic vacuum for 5 h at 800 °C.

Samples of mass about 1.0 g each were prepared by melting weighed amounts of the two elements in the form of fine turnings for cerium and powder for ruthenium, pressed into small pellets in a semilevitation high frequency induction furnace. The samples were then transferred to the differential thermal analysis equipment and one or two thermal cycles were performed at heating and cooling rates of 10 or 20 °C min^{-1}. For compositions richer than 50 at.% Ru only one heating run was carried out. The temperature measurements were accurate to $\pm$ 5 °C. Strong difficulties were encountered for alloys in the range 20–40 at.% Ru owing to high undercooling effects and owing to the slowness of the alloys in reaching the equilibrium conditions. After several thermal cycles it was decided to take into account mainly thermal effects obtained on heating.

X-ray investigations were carried out on powders and on single crystals using a Guinier–Stoe camera with silicon as an internal standard and an Enraf Nonius CAD 4 automatic four-circle diffractometer with graphite-monochromated Mo Kα radiation. The powder intensities were calculated using the LAZY-PULVERIX program [7].

Metallographic examination was carried out using standard techniques; a diluted $FeCl_3$ solution was used as the etching agent.

Further identification of unknown phases was performed with the aid of electron microscopy and microprobe analysis. The standards used for semiquantitative determinations were pure metals and the other known phases of the system.

3. Results and discussion

Figure 1 shows the phase diagram of the Ce–Ru system as derived from the analyses carried out as described in Section 2. Table 1 contains the crystallographic data for the intermediate phases formed in the system. The melting point and transformation temperature for cerium were taken from the compilation of Gschneidner [14] for pure elements. The values obtained for the metal used in this investigation exhibit deviations which are in the range of experimental temperature determinations.

The solubility of ruthenium in cerium seems to be negligible as no marked effect on the transition temperature was observed. The solubility of cerium in ruthenium has not been investigated owing to the high melting temperature of the corresponding alloys. All intermediate phases in this system appear as "line compounds".

3.1. Ce_3Ru

The presence of a phase around this composition has already been claimed [8] but no information concerning the crystal structure was available. Single-crystal investigations made it possible to identify this compound as Ce_3Ru (Fe_3C type) which fits well into the R_3Ru series [15]. The refined

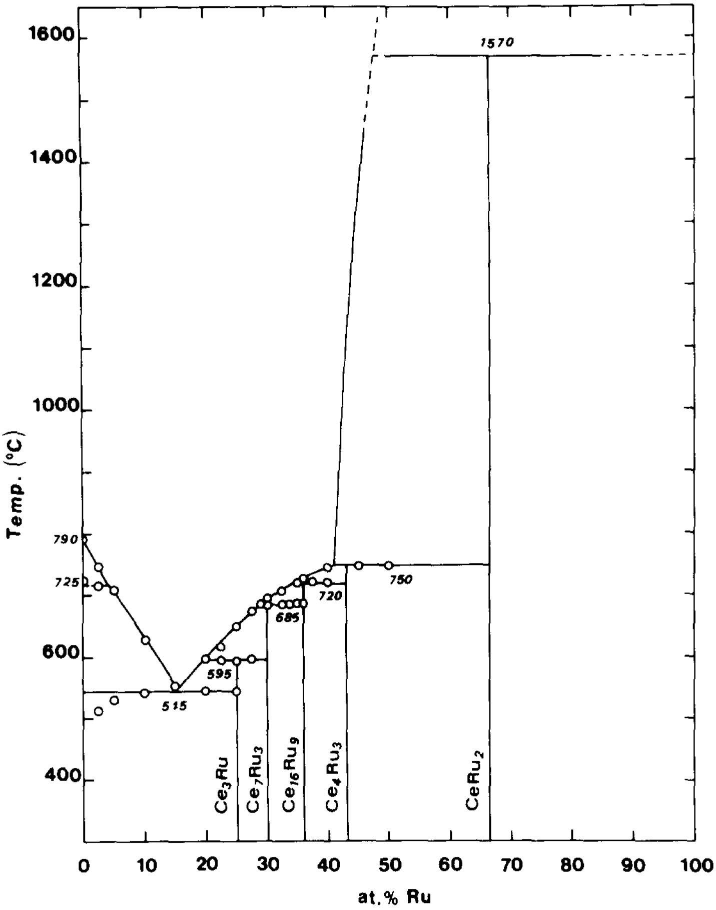

Fig. 1. The phase diagram of the Ce–Ru system.

positional parameters in the *Pnma* space group are as follows:

		x	y	z
Ce1	8(d)	0.1728	0.0651	0.6683
Ce2	4(c)	0.0468	0.25	0.1480
Ru	4(c)	0.3696	0.25	0.9668

3.2. Ce$_7$Ru$_3$

Sharifrazi *et al.* reported the existence of Ce$_7$Ru$_3$ (Th$_7$Fe$_3$ type) obtained on a sample of the composition Ce$_3$Ru [8]. This phase is the most difficult to study in this system: samples are compact and powder patterns are always faint and diffuse. Accidently, during the solidification of a sample in its tantalum crucible, a portion of material was extruded in a spherical form, made up of flat and thin crystals whose composition, when checked by the electron microprobe, corresponded to the Ce$_7$Ru$_3$ stoichiometry. These crystals

TABLE 1

Crystallographic data for the intermediate phases in the Ce–Ru system

Compound	Structure type	Lattice constants				Notes	Reference
		a (Å)	b (Å)	c (Å)	β (deg)		
Ce_3Ru	Fe_3C (oP16, $Pnma$)	7.242	9.863	6.419	–	sc, p	This work
Ce_7Ru_3	Th_7Fe_3 (hP20, $P6_3mc$)	9.802	–	6.261	–	sc, p	This work
		9.864	–	6.305	–	–[a]	[8]
$Ce_{16}Ru_9$	$Ce_{16}Ru_9$(hR150, $R\bar{3}m$)	13.645	–	22.742	–	sc, p	[9]
Ce_4Ru_3	Ce_4Ru_3 (mS28, $C2/m$)	8.400	13.837	5.985	117.90	sc, p	[10]
$CeRu_2$	$MgCu_2$ (cF24, $Fd\bar{3}m$)	7.545	–	–	–	p	This work
		7.543	–	–	–	–	[11]
		7.535	–	–	–	–	[12]
		7.570	–	–	–	–	[8]
		7.536	–	–	–	–	[13]
		7.779	–	–	–	–	[5]

[a]Obtained for the Ce_3Ru composition. sc, single crystal; p, powder.

were rather soft and of not very good quality but could be used for single-crystal work. This made it possible to confirm the structure and a coarse refinement of the positional parameters in the $P6_3mc$ space group gave the following values:

		x	y	z
Ce1	6(c)	0.540	0.460	0.041
Ce2	6(c)	0.124	0.876	0.250
Ce3	2(b)	0.333	0.667	0.039
Ru	6(c)	0.818	0.182	0.289

3.3. $Ce_{16}Ru_9$

This phase corresponds to a new structural type in the $R\bar{3}m$ space group with lattice parameter values $a = 13.645$ Å and $c = 22.742$ Å. A complete structure determination was made which will be discussed in a separate report [9]. Refined positional parameters are as follows:

		x	y	z
Ce1	18(h)	0.4254	0.5746	0.0419
Ce2	18(h)	0.5832	0.4168	0.2133
Ce3	18(h)	0.7571	0.2429	0.0848
Ce4	18(g)	0.2970	0.0	0.5
Ce5	18(f)	0.2837	0.0	0.0
Ce6	3(b)	0.0	0.0	0.5
Ce7	3(a)	0.0	0.0	0.0
Ru1	18(h)	0.4475	0.5525	0.2619
Ru2	18(h)	0.5430	0.4570	0.0823
Ru3	18(h)	0.5447	0.4553	0.4464

3.4. Ce_4Ru_3

This phase corresponds to a new structural type in the $C2/m$ space group with lattice parameter values $a = 8.400$ Å, $b = 13.837$ Å, $c = 5.985$ Å and $\beta = 117.90°$. The complete structure determination will be discussed separately [10]. Refined positional parameters are as follows:

		x	y	z
Ce1	8(j)	0.2561	0.1343	0.1655
Ce2	4(i)	0.6519	0.0	0.2799
Ce3	4(h)	0.0	0.1656	0.5
Ru1	8(j)	0.1186	0.3022	0.2535
Ru2	4(i)	0.0035	0.0	0.2479

3.5. $CeRu_2$

This compound corresponds to the well-known Laves phase, $MgCu_2$ type. The lattice constant obtained in the present investigation agrees well with the literature data. The peritectic decomposition temperature reported in the phase diagram is the mean value between those reported in refs. 5 and 13.

4. Concluding remarks

The Ce–Ru phase diagram determined in the present work and the comparison of this system with those of the neighbouring rare earths, lanthanum and neodymium, show once more the anomalous behaviour of cerium. The Ce–Ru diagram mainly differs from the La–Ru and Nd–Ru diagrams in the shape and in the melting properties. Moreover, different structures, two of which correspond to new types, have been found and their appearance cannot be related to the characteristic "lanthanide contraction". More probably, this singular behaviour should be ascribed to the well-known possibility of cerium to give rise to valence instabilities. Further investigations are in progress to obtain information on the valence state of cerium in these compounds by means of magnetic and transport properties, explored in a wide temperature range.

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