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Ternary rare earth (R) alloys occurring in the RAg_2–RGa_2 section

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Abstract

The intermetallic compounds of rare earths with $RAg_{0.5}Ga_{1.5}$ composition (R=Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Lu and Y) have been studied. Their crystal structures have been found to be related to the hP6–$CaIn_2$ type. The stability range of this structure, which often occurs when the valence electron concentration is near to 8/3, has been analysed for the Gd–Ag–Ga alloys. The study of the $GdAg_2$–$GdGa_2$ section has revealed that with increasing $GdGa_2$-content the following sequence of structure types occur: *oI*12-$CeCu_2$, *hP*6-$CaIn_2$, *hP*3-$CeCd_2$, *hP*3-AlB_2. The $YbAg_2$–$YbGa_2$ section has also been partially analysed.

Keywords: $CaIn_2$-type compounds; Rare earth ternary alloys; Rare earth silver gallides

1. Introduction

Previous investigations on ternary intermetallic compounds formed by the rare earth metals with transition metals and p-block elements of the Periodic Table, revealed the frequent occurrence of the *hP*6-$CaIn_2$ crystal structure or of its ordered variants. This crystal structure is found for valence electron concentration (v.e.c.) values near to 8/3 and for suitable dimensional ratios of the atoms involved [1]. In order to extend the systematic study of these compounds, the new series $RAg_{0.5}Ga_{1.5}$ has now been synthesised and characterised. To gain more information about the properties and the stabilities of these phases an investigation of RAg_2–RGa_2 sections, previously considered also by Dwight [2], was carried out for a few selected R elements. A detailed examination of the $GdAg_{2-x}Ga_x$ ($1\leq x\leq 2$) system was performed and some alloys in the Yb and Tm systems were studied. This allowed us to make a better comparison with other similar systems such as $GdZn_{2-x}Sn_x$ [1], $GdZn_{2-x}Al_x$, $GdZn_{2-x}Ga_x$ [3], $GdCu_{2-x}Ga_x$ [4,5] previously studied, in which this structure is present and the extension of its homogeneity range is known.

2. Experimental details

The rare earths employed in the preparation of the samples had a nominal purity of 99.9%, the other metals a nominal purity of 99.999%. All the metals were supplied by Koch Chemical Ltd, Hertford, UK, except Ag, supplied by Johnson Matthey and Co. Ltd., London, UK. Stoichiometric quantities of the three elements, enclosed in small tantalum crucibles, sealed by arc welding, under an argon atmosphere, were melted in an induction furnace (the reactions between the metals is generally strongly exothermic). The alloys were then generally annealed at 500°C for 1 week and finally water-quenched. All the samples resulted in brittle, well-melted compact ingots.

The samples were examined under a metallographic microscope after etching in a dilute solution of nitric acid (0.5–0.2 vol. %). An electronic micrographic examination was also carried out, using a scanning electron microscope equipped with an energy-dispersive X-ray analyser. The microprobe microanalysis (using pure elements as standards) was employed to check the overall compositions of the samples (which were generally found to be very close to the nominal ones) and to analyse the different coexisting phases.

Powders of the various alloys were examined by the Debye-Scherrer method, using Fe Kα radiation. The values of lattice parameters were computed and refined through a least-squares routine. The observed diffraction intensities

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were compared with the calculated values obtained by means of the program Lazy Pulverix [6].

3. Results

3.1. $RAg_{0.5}Ga_{1.5}$ alloys

Samples with the compositions $RAg_{0.5}Ga_{1.5}$ were prepared for most of the rare earth elements. The specimens were generally found to be nearly homogeneous and to have a composition very close to the nominal one. Diffraction patterns have been interpreted, for R=Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Lu and Y, on the basis of a hexagonal cell (see Table 1). A fair agreement was observed between the powder pattern experimental intensities and those computed on the basis of the following atomic positions in the $CaIn_2$-type structure (space group, $P6_3/mmc$): 2R in 2*b* (0, 0, 1/4), 1Ag and 3Ga in 4*f* (1/3, 2/3, *z*) with *z* ranging between 0.46 and 0.47. Derivative more ordered variants of the $CaIn_2$-type structure cannot, however be completely disregarded. The *z* parameter is in good agreement with the value reported by Dwight [7] for a similar Y alloy (reported in Table 1 and having a $YAg_{0.4}Ga_{1.6}$ composition) which was assigned to the said $CaIn_2$-type structure with $z=0.467$.

3.2. $GdAg_{2-x}Ga_x$ section

In the ternary Gd–Ag–Ga system a number of alloys were prepared along the $GdAg_{2-x}Ga_x$ section ($1\leq x\leq 2$). The results are presented in Table 2. It may be observed that starting from GdAgGa (orthorhombic, $CeCu_2$-type phase) we have a gradual variation in the lattice parameters of the unit cell which, in a seemingly continuous way, changes into the hexagonal $CaIn_2$-type cell (notice the trend of the axial ratios reported in Table 2). Apparently no intermediate two-phase region is formed between the stability fields of the orthorhombic and hexagonal alloys ($1.25<x<1.30$). For a still higher gallium content the atomic volume gradually decreases, and then for $1.60<x<1.65$ a change from the $CaIn_2$-type structure to the $CeCd_2$-type is observed. In this case no intermediate two-phase region has been identified. For $x>1.65$ another change in the crystal structure is observed: from the $CeCd_2$-type phase to the AlB_2-type which is stable up to $x=2$. A wide two-phase region is observed here: the AlB_2-type $GdGa_2$ dissolves only a very small amount of Ag.

The trend of the average atomic volumes is plotted in Fig. 1. A similar trend was described in the analogous systems: $RZn_{2-x}Ga_x$ (R=Ce, Sm, Gd, Er), $RCu_{2-x}Ga_x$ (R=Sm, Gd, Er), and $ErNi_{2-x}Ga_x$, by Iandelli [3] and Dwight [4].

For the $CeCd_2$-type structure observed as a one-phase alloy only for the 1:0.35:1.65 composition, a fair agreement between the experimental and calculated intensities was obtained for $z=0.45$. An ordered variant of this structure, however, cannot be excluded.

3.3. $YbAg_{2-x}Ga_x$ section

Instead of adopting the AlB_2-type structure as is the case for most of the RGa_2 phases, $YbGa_2$ is known to crystallise with the $CaIn_2$-type structure. This can be considered in agreement with the so called presumed bivalence of Yb: to this formula, indeed, a nominal v.e.c= 8/3 could be attributed, usually corresponding to the stability field of the $CaIn_2$-type structure. In connection with this point we notice that also the $YbAg_{0.5}Ga_{1.5}$ phase

Table 1
Crystal data of ternary hexagonal $RAg_{0.5}Ga_{1.5}$ alloys

Phase	Lattice parameters (pm)			$\bar{V}$[a] ($pm^3\times10^{-6}$)	$\Delta V/V$[b]	Ref.
	a	*c*	*c/a*		(%)	
$NdAg_{0.5}Ga_{1.5}$[c]	451.8	750.8	1.662	22.1	−8.01	this work
$SmAg_{0.5}Ga_{1.5}$	449.6	738.1	1.642	21.5	−9.07	this work
$GdAg_{0.5}Ga_{1.5}$	448.5	727.7	1.623	21.1	−10.7	this work
$TbAg_{0.5}Ga_{1.5}$	446.6	720.6	1.614	20.7	−11.0	this work
$DyAg_{0.5}Ga_{1.5}$	446.2	716.0	1.605	20.5	−11.3	this work
$HoAg_{0.5}Ga_{1.5}$	444.8	711.6	1.600	20.3	−11.7	this work
$ErAg_{0.5}Ga_{1.5}$	443.8	707.0	1.593	20.1	−12.2	this work
$TmAg_{0.5}Ga_{1.5}$	443.3	702.8	1.585	20.0	−12.3	this work
$LuAg_{0.5}Ga_{1.5}$	442.1	697.7	1.578	19.7	−12.5	this work
$YAg_{0.5}Ga_{1.5}$	445.4	721.5	1.620	20.7	−13.0	this work
$YAg_{0.4}Ga_{1.6}$	443.8_2	722.4_2	1.623	20.5	−13.5	[7]

[a] $\bar{V}$ (average atomic volume)$=V_{cell}/6$.

[b] Volume contraction values, $\Delta V/V(\%)=100\times(V_{cell}-\Sigma V_{at})/\Sigma V_{at}$, the atomic volumes of elements are from [8].

[c] Heterogeneous sample.

Table 2
Solid Phases in the $GdAg_2$–$GdGa_2$ system

$GdAg_{2-x}Ga_x$ Nominal Composition	Pearson symbol/ Prototype	Lattice parameters (pm)			Axial ratios		Average atomic volume[a] ($pm^3 \times 10^{-6}$)	Ref.[b]
$x=0.00$	$tI6$-$MoSi_2$	$a=373.5$	$c=928.2$		$c/a=2.485$		$\bar{V}=21.6$	[9]
$x=1.00$	$oI12$-$CeCu_2$	$a=456.9$	$b=715.3$	$c=781.9$	$b/a=1.566$	$c/a=1.711$	$\bar{V}=21.3$	[2]
$x=1.00$	$oI12$-$CeCu_2$	$a=456.6$	$b=715.2$	$c=783.3$	$b/a=1.566$	$c/a=1.715$	$\bar{V}=21.3$	t.w.
$x=1.10$	$oI12$-$CeCu_2$	$a=455.8$	$b=716.1$	$c=781.6$	$b/a=1.571$	$c/a=1.715$	$\bar{V}=21.3$	t.w.
$x=1.15$	$oI12$-$CeCu_2$	$a=454.6$	$b=717.4$	$c=780.3$	$b/a=1.578$	$c/a=1.717$	$\bar{V}=21.2$	t.w.
$x=1.20$	$oI12$-$CeCu_2$	$a=454$	$b=718$	$c=780$	$b/a=1.58$	$c/a=1.72$	$\bar{V}=21.2$	t.w.
$x=1.25$	$oI12$-$CeCu_2$	$a=452.2$	$b=719.4$	$c=780.1$	$b/a=1.591$	$c/a=1.725$	$\bar{V}=21.2$	t.w.
$x=1.30$	$hP6$-$CaIn_2$	$a=450.2$	$c=726.6$	$a\sqrt{3}=779.8$	$c/a=1.614$		$\bar{V}=21.3$	t.w.
$x=1.40$	$hP6$-$CaIn_2$	$a=449.1$	$c=727.5$	$a\sqrt{3}=777.9$	$c/a=1.620$		$\bar{V}=21.2$	t.w.
$x=1.50$	$hP6$-$CaIn_2$	$a=448.5$	$c=727.7$	$a\sqrt{3}=777.0$	$c/a=1.623$		$\bar{V}=21.1$	t.w.
$x=1.60$	$hP6$-$CaIn_2$	$a=446.5$	$c=733.0$	$a\sqrt{3}=773.4$	$c/a=1.642$		$\bar{V}=21.1$	t.w.
$x=1.65$	$hP3$-$CeCd_2$	$a=444.4$	$c=369.0$	$a\sqrt{3}=769.7$	$c/a=0.830$		$\bar{V}=21.0$	t.w.
$x=1.70$[c]	$hP3$-AlB_2	$a=422.3$	$c=414.1$		$c/a=0.981$		$\bar{V}=21.3$	t.w.
	$hP3$-$CeCd_2$	$a=442.1$	$c=372.0$		$c/a=0.841$		$\bar{V}=21.0$	t.w.
$x=1.75$[c]	$hP3$-AlB_2	$a=422.0$	$c=414.3$		$c/a=0.982$		$\bar{V}=21.3$	t.w.
	$hP3$-$CeCd_2$	$a=442.0$	$c=367.8$		$c/a=0.828$		$\bar{V}=21.0$	t.w.
$x=1.80$[c]	$hP3$-AlB_2	$a=422.4$	$c=413.6$		$c/a=0.979$		$\bar{V}=21.3$	t.w.
	$hP3$-$CeCd_2$	$a=444.3$	$c=368.4$		$c/a=0.829$		$\bar{V}=21.0$	t.w.
$x=1.90$[c]	$hP3$-AlB_2	$a=422.2$	$c=414.4$		$c/a=0.982$		$\bar{V}=21.3$	t.w.
	$hP3$-$CeCd_2$	$a=444.0$	$c=368.2$		$c/a=0.831$		$\bar{V}=21.0$	t.w.
$x=2.00$	$hP3$-AlB_2	$a=422.1$	$c=413.7$		$c/a=0.980$		$\bar{V}=21.3$	t.w.
$x=2.00$	$hP3$-AlB_2	$a=422.2$	$c=413.7$		$c/a=0.980$		$\bar{V}=21.3$	[4]

[a] $\bar{V}$ (average atomic volume)$=V_{cell}/12$ for $CeCu_2$ structure type, $V_{cell}/6$ for $CaIn_2$ and $MoSi_2$ structure types, $V_{cell}/3$ for AlB_2 and $CeCd_2$ structure types.
[b] t.w.=this work.
[c] Two-phase samples.

has a crystal structure different from that of the other R compounds with the same composition. In agreement with the sequence of structural types previously described for $GdAg_{2-x}Ga_x$ alloys, a $CeCu_2$-type structure has been assigned to $YbAg_{0.5}Ga_{1.5}$. The indexing for this and the other orthorhombic phases on the same section has been carried out by comparison with the intensities of the isostructural GdAgGa alloy. In the series $YbAg_{2-x}Ga_x$ the

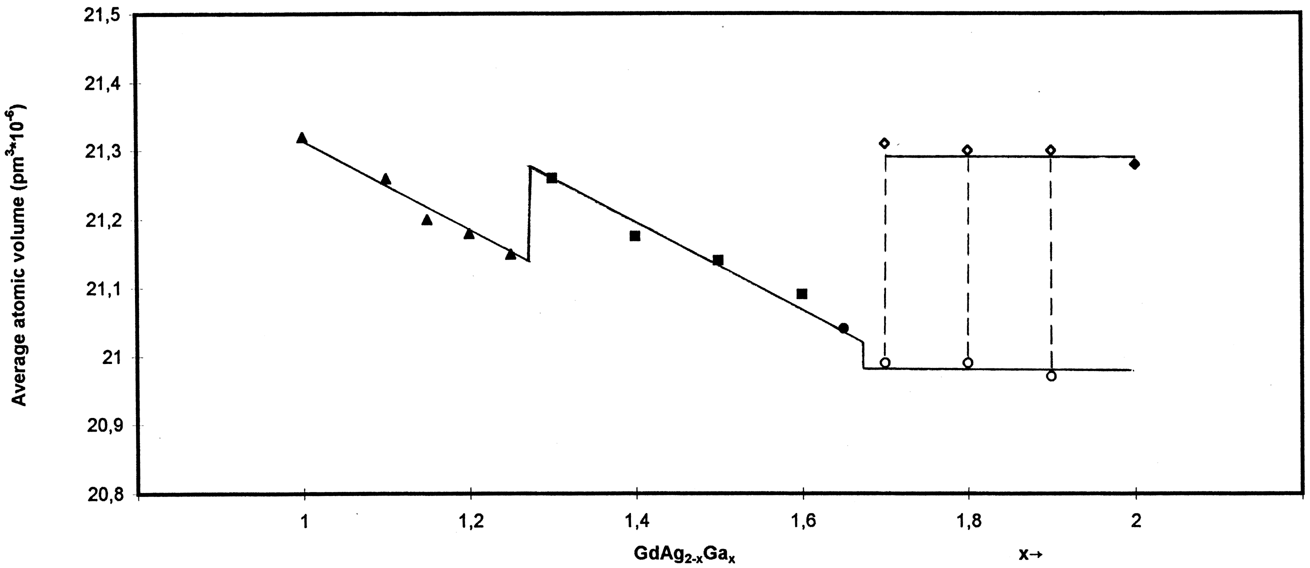

Fig. 1. Average atomic volume plotted as a function of the nominal composition of samples $GdAg_{2-x}Ga_x$ ($1 \leq x \leq 2$): ▲, orthorhombic $oI12$-$CeCu_2$ type; ■, hexagonal $hP6$-$CaIn_2$ type; ●○, hexagonal $hP3$-$CeCd_2$ type; ◆◇, hexagonal $hP3$-AlB_2 type. Filled symbols are used for homogeneous samples.

Table 3
Solid Phases in the $YbAg_2$-$YbGa_2$ system

$YbAg_{2-x}Ga_x$ Nominal composition	Pearson symbol/prototype	Lattice parameters (pm)			Axial ratios		Average atomic volume[a] ($pm^3 \times 10^{-6}$)	Ref.[b]
$x=0.00$	$oI12$-$CeCu_2$	$a=467.1$	$b=720.4$	$c=817.8$	$b/a=1.542$	$c/a=1.751$	$\bar{V}=22.9$	[10]
$x=1.50$	$oI12$-$CeCu_2$	$a=452.6$	$b=720.0$	$c=779.0$	$b/a=1.591$	$c/a=1.721$	$\bar{V}=21.2$	t.w.
$x=1.80$	$oI12$-$CeCu_2$	$a=451$	$b=719$	$c=777$	$b/a=1.59$	$c/a=1.72$	$\bar{V}=21.0$	t.w.
$x=1.90$	$hP6$-$CaIn_2$	$a=446.3$	$c=723.4$	$a\sqrt{3}=773.0$		$c/a=1.621$	$\bar{V}=20.8$	t.w.
$x=2.00$	$hP6$-$CaIn_2$	$a=445.6$	$c=718.7$	$a\sqrt{3}=771.8$		$c/a=1.613$	$\bar{V}=20.6$	[11]

[a] $\bar{V}$ (average atomic volume)$=V_{cell}/12$ for $CeCu_2$ structure type, $V_{cell}/6$ for $CaIn_2$ structure type.
[b] t.w.=this work.

Table 4
Solid phases in the $TmAg_2$–$TmGa_2$ system

$TmAg_{2-x}Ga_x$ Nominal composition	Pearson symbol/prototype	Lattice parameters (pm)			Axial ratios		Average atomic volume[a] ($pm^3 \times 10^{-6}$)	Ref.[b]
$x=0.00$	$tI6$-$MoSi_2$	$a=363.9$		$c=911.5$		$c/a=2.505$	$\bar{V}=20.1$	[14]
$x=1.00$	$oI12$-$CeCu_2$	$a=449.2$	$b=691.4$	$c=778.2$	$b/a=1.539$	$c/a=1.732$	$\bar{V}=20.1$	[2]
$x=1.00$	$oI12$-$CeCu_2$	$a=448.3$	$b=693.4$	$c=778.5$	$b/a=1.547$	$c/a=1.737$	$\bar{V}=20.2$	t.w.
$x=1.50$	$hP6$-$CaIn_2$	$a=443.3$	$c=702.8$	$a\sqrt{3}=767.8$		$c/a=1.585$	$\bar{V}=20.0$	t.w.
$x=2.00$	$oI12$-$CeCu_2$	$a=420.0$	$b=687.9$	$c=806.7$	$b/a=1.638$	$c/a=1.921$	$\bar{V}=19.4$	[12]
$x=2.00$	$oI12$-$CeCu_2$	$a=421.0$	$b=689.7$	$c=807.4$	$b/a=1.638$	$c/a=1.918$	$\bar{V}=19.5$	t.w.

[a] $\bar{V}$ (average atomic volume)$=V_{cell}/12$ for $CeCu_2$ structure type, $V_{cell}/6$ for $CaIn_2$ and $MoSi_2$ structure types.
[b] t.w.=this work.

transition between the $CaIn_2$ and $CeCu_2$-type structures occurs for $1.8<x<1.9$.

In Table 3 the crystallographic data of Yb alloys are reported.

3.4. $TmAg_{2-x}Ga_x$ section

The RGa_2 phases formed by the heaviest rare earths (Tm and Lu) have the $CeCu_2$-type structure [12,13]. A few

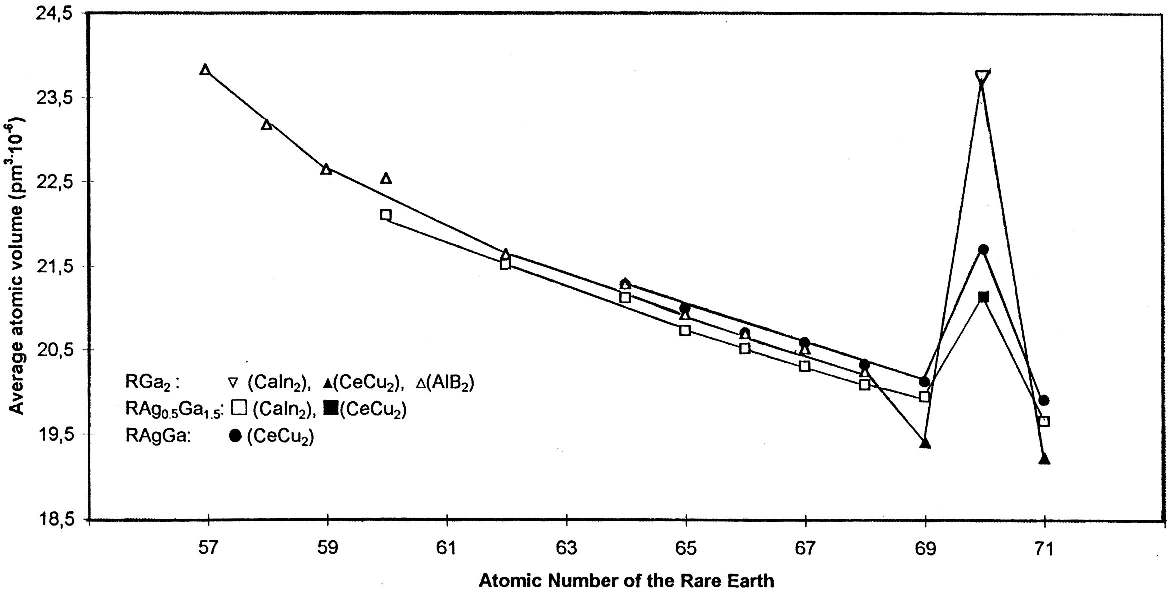

Fig. 2. Average atomic volume plotted as a function of the atomic number of the rare earth for the compounds $RAg_{0.5}Ga_{1.5}$ (□ and ■), RAgGa (●) [2] and RGa_2 (△ and ▲) [12,13,15,16]. Filled symbols are used for the orthorhombic $CeCu_2$-type structure, the empty ones for the hexagonal AIB_2 and $CaIn_2$ type structures.

samples along the $TmAg_{2-x}Ga_x$ section have been prepared in order to confirm the peculiar sequence of phases and structure types, already observed by Iandelli in the $TmZn_2$–$TmGa_2$ section [3]. The data obtained are reported in Table 4 together with the literature data. Notice for the $CeCu_2$-type phases (both for $x=1$, TmAgGa and for $x=2$, $TmGa_2$) the fair agreement between the literature values and those obtained in this work.

4. General remarks

The trend of average atomic volume for $RAg_{2-x}Ga_x$, RAgGa, RGa_2 compounds is reported in Fig. 2. The typical behaviour of Yb may be noticed.

As for the $GdAg_{2-x}Ga_x$ system we see from Table 2 that the stability range of the $CaIn_2$ type phase occurs between $x=1.27$ and 1.62. This corresponds to values of the v.e.c. between 2.52 and 2.75. Notice the close relationship between the unit cell dimensions of the $CeCu_2$ and $CaIn_2$ type structures.

These data may be compared with those of the $YbAg_{2-x}Ga_x$ system and with those of a number of other systems in which the stability field of $CaIn_2$-type structure has been studied and in which there is also a transformation from $CeCu_2$ to $CaIn_2$ type structure (see Table 5).

The range of homogeneity of the $CaIn_2$ phases generally corresponds to a nominal valence electron concentration (v.e.c.) between 2.52 and 2.78 (close to the value 8/3). Different groups of $RT_{2-x}X_x$ alloys (T=transition metal, X=p-block metal) are reported in Table 5. We may note that in each group of alloys formed with the same T and X metals by the different rare earths, the structure for the phases containing smaller rare earths changes from the $CeCu_2$ to the $CaIn_2$ type for a smaller value of x (first limiting value of x reported in the table). This change shows a regular trend versus the ionic radius of the rare earth (see Fig. 3).

Table 5
Composition range and valence electron concentration range of some $CaIn_2$-type $RT_{2-x}X_x$ alloys

$RT_{2-x}X_x$	$CaIn_2$-type phase		Ref.
	Composition range	Valence electron concentration range	
$ErNi_{2-x}Ga_x$	$1.55<x<1.76$	2.55<v.e.c.<2.76	[3]
$CeCu_{2-x}Ga_x$	$1.47<x<1.58$	2.65<v.e.c.<2.72	[3]
$SmCu_{2-x}Ga_x$	$1.45<x<1.62$	2.63<v.e.c.<2.75	[3]
$GdCu_{2-x}Ga_x$	$1.35<x<1.55$	2.55<v.e.c.<2.70	[3]
$ErCu_{2-x}Ga_x$	$1.25<x<1.65$	2.50<v.e.c.<2.67	[3–5]
$GdAg_{2-x}Ga_x$	$1.27_5<x<1.62_5$	2.52<v.e.c.<2.75	this work
$YbAg_{2-x}Ga_x$	$1.85<x$	2.57<v.e.c.	this work
$SmZn_{2-x}Al_x$	$1.05<x<1.25$	2.68<v.e.c.<2.75	[3]
$GdZn_{2-x}Al_x$	$0.95<x<1.35$	2.65<v.e.c.<2.78	[3]
$ErZn_{2-x}Al_x$	$0.65<x<1.32$	2.55<v.e.c.<2.77	[3]
$CeZn_{2-x}Ga_x$	$0.95<x<1.35$	2.65<v.e.c<2.78	[3]
$SmZn_{2-x}Ga_x$	$0.77<x<1.35$	2.59<v.e.c.<2.78	[3]
$GdZn_{2-x}Ga_x$	$0.75<x<1.35$	2.58<v.e.c.<2.78	[3]
$ErZn_{2-x}Ga_x$	$0.55<x<1.35$	2.52<v.e.c.<2.78	[3]
$TmZn_{2-x}Ga_x$	$0.55<x<1.35$	2.52<v.e.c.<2.78	[3]
$GdZn_{2-x}Sn_x$	$0.33_5<x<0.65$	2.56<v.e.c.<2.77	[1]

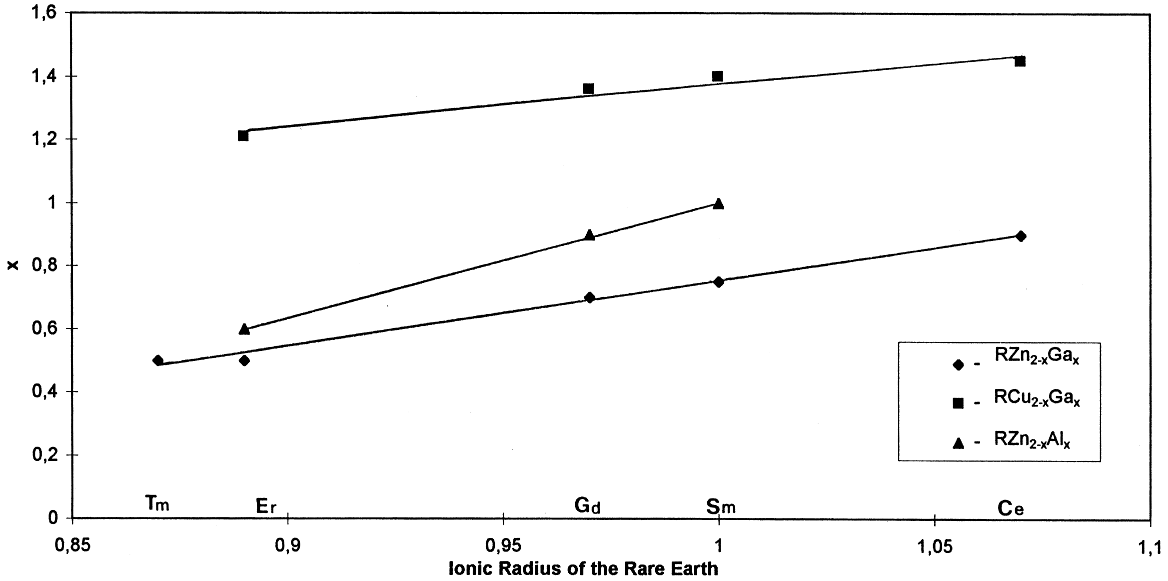

Fig. 3. Maximum value for the composition field of the $RT_{2-x}X_x$, $CeCu_2$ type phase (x) plotted as a function of ionic radius of rare earth metal.

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