



# On the ternary calcium-containing phases $\text{CaM}_x\text{Ga}_{4-x}$ ( $M \equiv \text{Pd}$ , $\text{Pt}$ , $\text{Cu}$ , $\text{Ag}$ , $\text{Au}$ ) with $\text{BaAl}_4$ structure

Yu. Grin<sup>a</sup>, M. Ellner<sup>a</sup>, B. Predel<sup>a</sup>, G. Cordier<sup>b</sup>

<sup>a</sup>Max-Planck-Institut für Metallforschung, Institut für Werkstoffwissenschaft, Seestrasse 92, D-70174 Stuttgart, Germany

<sup>b</sup>Eduard-Zintl-Institut, TH Darmstadt, Hochschulstrasse 10, D-64289 Darmstadt, Germany

Received 8 April, 1994

## Abstract

The intermetallic compounds  $\text{CaM}_x\text{Ga}_{4-x}$  ( $M \equiv \text{Pd}$ ,  $\text{Pt}$ ,  $\text{Cu}$ ,  $\text{Ag}$ ,  $\text{Au}$ ) were synthesized in order to investigate the stability of the  $\text{BaAl}_4$  structure type in ternary gallium-containing systems.

The crystal structures have been studied on samples with the composition  $\text{CaM}_{0.5}\text{Ga}_{3.5}$  ( $M \equiv \text{Cu}$ ,  $\text{Au}$ ,  $\text{Pd}$ ,  $\text{Pt}$ ) by means of single-crystal and powder diffraction methods and have been found to be isotypic to  $\text{BaGa}_4$  and the homologous ytterbium compounds ( $\text{BaAl}_4$  structure type, space group  $I4/mmm$ ). In samples with this composition the transition metal atoms replace the gallium atoms in the sites with tetragonal antiprismatic environment.

All phases obtained have homogeneity ranges with constant calcium content. The non-linear dependence of the unit cell parameters on composition can be explained by gallium-transition metal substitution in various positions.

The  $\text{CaM}_x\text{Ga}_{4-x}$  compounds are diamagnetic in the temperature range 100–300 K.

**Keywords:** Gallium; Calcium; Ytterbium

## 1. Introduction

Gallium-containing phases with the  $\text{BaAl}_4$  structure form in the ternary systems  $\text{R-M-Ga}$  ( $\text{R}$ , light rare earth;  $\text{M}$ , d-transition metal of nickel or copper group) [1]. In the systems of the heavy rare earths such phases were found only with ytterbium [2]. Ytterbium-containing phases have homogeneity ranges corresponding to replacement of gallium by transition metal. This replacement leads to a contraction of the unit cell in comparison with the binary compound  $\text{YbGa}_4$ . Magnetic measurements showed either temperature-independent paramagnetism or a weak temperature dependence of the magnetic susceptibility with an effective moment value of about  $1 \mu_{\text{B}}$  per ytterbium atom. Both phenomena point particularly to a change in the electronic state of ytterbium ( $\text{Yb}^{\text{II}} \leftrightarrow \text{Yb}^{\text{III}}$ ).

Calcium and ytterbium have comparable atomic radii ( $r_{\text{Ca}} = 1.97 \text{ \AA}$ ,  $r_{\text{Yb}} = 1.933 \text{ \AA}$ ) and show similar crystal chemical behaviour with respect to the formation and crystal structure of ternary phases. A change in valence is not possible for calcium. Therefore the calcium compounds may serve as reference materials for a better understanding of the influence of valence changes on the properties of the  $\text{YbM}_x\text{Ga}_{4-x}$  phases.

The  $\text{BaAl}_4$  structure was found previously in ternary calcium-containing systems at the compositions  $\text{CaCu}_{0.5}\text{Ga}_{3.5}$  [3],  $\text{CaAg}_{0.5}\text{Ga}_{3.5}$  and  $\text{CaAu}_{0.8}\text{Ga}_{3.2}$  [4]. The latter two structures were refined using single-crystal data [4]. There are no further literature data on  $\text{CaM}_x\text{Ga}_{4-x}$  phases.

The aim of the present work is to find all  $\text{CaM}_x\text{Ga}_{4-x}$  phases with d-transition metals of the nickel and copper groups and to compare them with the corresponding  $\text{YbM}_x\text{Ga}_{4-x}$  compounds.

## 2. Experimental details

Alloys, each of about 2.5 g, with compositions  $\text{CaM}_x\text{Ga}_{4-x}$  ( $0.1 \leq x \leq 2.25$ ;  $M \equiv \text{Ni}$ ,  $\text{Pd}$ ,  $\text{Pt}$ ,  $\text{Cu}$ ,  $\text{Ag}$ ,  $\text{Au}$ ) were synthesized in a high frequency furnace in tantalum crucibles under argon (Messer-Griesheim 5.0). Compact metals were taken as initial components: calcium (Heraeus 99.9%), gallium (Ingal, 6N), copper (Heraeus 99.999%), nickel (Ventron, m4n8), silver, gold, palladium and platinum (Heraeus 99.99%). For the homogenization the samples were wrapped in molybdenum foil and heat treated in vacuum-sealed silica tubes at 600 °C for 350 h.

Table 1  
Crystallographic data of  $\text{CaM}_x\text{Ga}_{4-x}$  compounds (BaAl<sub>4</sub> structure type, space group *I4/mmm*)

Composition	<i>a</i> (Å)	<i>c</i> (Å)	<i>a/c</i>	<i>V</i> (Å <sup>3</sup> )
$\text{Ca}_{20}\text{Cu}_4\text{Ga}_{76}^a$	4.2430(5)	10.952(2)	0.387	197.17(8)
$\text{Ca}_{20}\text{Cu}_5\text{Ga}_{75}$	4.2394(1)	10.9585(4)	0.387	196.95(2)
$\text{Ca}_{20}\text{Cu}_{10}\text{Ga}_{70}$	4.1883(4)	11.033(1)	0.380	193.53(6)
$\text{Ca}_{20}\text{Cu}_{15}\text{Ga}_{65}$	4.1718(3)	11.049(1)	0.378	192.30(5)
$\text{Ca}_{20}\text{Cu}_{20}\text{Ga}_{60}$	4.1327(2)	11.0358(6)	0.375	187.48(3)
$\text{Ca}_{20}\text{Cu}_{25}\text{Ga}_{55}^a$	4.1252(5)	11.011(2)	0.375	187.38(8)
$\text{Ca}_{20}\text{Ag}_4\text{Ga}_{76}^a$	4.2820(6)	10.910(2)	0.392	200.04(9)
$\text{Ca}_{20}\text{Ag}_5\text{Ga}_{75}$	4.2807(2)	10.9186(6)	0.392	200.08(3)
$\text{Ca}_{20}\text{Ag}_{10}\text{Ga}_{70}$	4.2688(3)	11.008(1)	0.388	200.60(5)
$\text{Ca}_{20}\text{Ag}_{15}\text{Ga}_{65}$	4.2665(2)	11.0212(7)	0.387	200.61(4)
$\text{Ca}_{20}\text{Ag}_{22}\text{Ga}_{58}^a$	4.2826(3)	10.9687(9)	0.390	201.17(5)
$\text{Ca}_{20}\text{Au}_4\text{Ga}_{76}^a$	4.2850(6)	10.980(2)	0.390	201.61(9)
$\text{Ca}_{20}\text{Au}_5\text{Ga}_{75}$	4.2777(2)	11.0062(9)	0.389	201.40(4)
$\text{Ca}_{20}\text{Au}_{10}\text{Ga}_{70}$	4.2187(3)	11.232(2)	0.376	199.90(6)
$\text{Ca}_{20}\text{Au}_{15}\text{Ga}_{65}$	4.1888(6)	11.345(4)	0.369	199.06(13)
$\text{Ca}_{20}\text{Au}_{25}\text{Ga}_{55}^a$	4.1785(2)	11.398(1)	0.367	199.01(4)
$\text{Ca}_{20}\text{Pd}_5\text{Ga}_{75}^a$	4.2143(2)	11.0187(9)	0.382	195.70(3)
$\text{Ca}_{20}\text{Pd}_8\text{Ga}_{72}$	4.2250(2)	11.0253(7)	0.383	196.81(4)
$\text{Ca}_{20}\text{Pd}_{10}\text{Ga}_{70}$	4.2137(2)	11.0331(8)	0.382	195.90(4)
$\text{Ca}_{20}\text{Pd}_{15}\text{Ga}_{65}^a$	4.2259(4)	11.022(1)	0.383	196.83(5)
$\text{Ca}_{20}\text{Pt}_2\text{Ga}_{78}^a$	4.2700(8)	10.940(1)	0.390	199.47(9)
$\text{Ca}_{20}\text{Pt}_3\text{Ga}_{77}$	4.2662(2)	10.9436(7)	0.390	199.18(4)
$\text{Ca}_{20}\text{Pt}_5\text{Ga}_{75}$	4.2580(2)	10.9846(7)	0.388	199.16(4)
$\text{Ca}_{20}\text{Pt}_{10}\text{Ga}_{70}$	4.2285(2)	11.034(1)	0.383	197.29(4)
$\text{Ca}_{20}\text{Pt}_{12.5}\text{Ga}_{67.5}$	4.2205(2)	11.005(1)	0.384	196.03(4)
$\text{Ca}_{20}\text{Pt}_{15}\text{Ga}_{65}^a$	4.2195(2)	10.938(1)	0.386	194.64(4)

<sup>a</sup>Multiphase samples.

X-Ray characterization was done by the powder method (Enraf–Nonius Guinier camera FR552, Cu  $K\alpha_1$  radiation) with germanium (Ventron, m5n) as internal standard. Diffraction angles and intensities were measured with a line scanner (KEJ Instruments LS20). Unit cell parameters were refined with a least-squares method.

The single crystals for structure investigation were separated from the crushed bulk alloys. Laue class and systematic absences were distinguished by means of Weissenberg photographs (Cu  $K\alpha$  radiation). Diffraction intensities were measured with a Philips PW1100 four-circle diffractometer (Mo  $K\alpha$  radiation, graphite monochromator). Absorption correction was performed empirically [5]; isotropic extinction was considered. For the crystallographic calculations we employed the program package CSD [6]. The magnetic susceptibility was measured using the Faraday method in the temperature range 100–300 K ( $H \leq 2$  T).

### 3. Results and discussion

#### 3.1. Formation and homogeneity ranges

The chemical compositions of the alloys used for studying the homogeneity ranges are listed in Table 1.

Guinier photographs of heat-treated samples were indexed with a b.c.t. lattice. Refined unit cell parameters are given in Table 1. The homogeneity ranges of the  $\text{CaM}_x\text{Ga}_{4-x}$  phases at 600 °C were determined from the dependence of the unit cell parameters and unit cell volume on the composition (Fig. 1). Hence the phases of the copper group transition metals are stable in approximately the same concentration region. No indications were found for the existence of the phase  $\text{CaNi}_x\text{Ga}_{4-x}$  with the BaAl<sub>4</sub> structure. The homogeneity range of the palladium-containing phase is very narrow ( $0.33 \leq x \leq 0.57$ ). However, for the  $\text{CaPt}_x\text{Ga}_{4-x}$  phase this range is considerably larger ( $0.13 \leq x \leq 0.67$ ). For all  $\text{CaM}_x\text{Ga}_{4-x}$  phases obtained, the unit cell parameter vs. concentration dependence deviates considerably from linearity. For the  $\text{CaCu}_x\text{Ga}_{4-x}$ ,  $\text{CaAg}_x\text{Ga}_{4-x}$  and  $\text{CaPt}_x\text{Ga}_{4-x}$  phases a maximum of the *c* parameter within the homogeneity range occurs.

A comparison of the  $\text{CaM}_x\text{Ga}_{4-x}$  and  $\text{YbM}_x\text{Ga}_{4-x}$  phases shows that there is a close correspondence in the size and location of the homogeneity ranges for the phases with  $M \equiv \text{Cu, Au, Pd, Pt}$ . A clear difference is obtained only for silver-containing phases ( $0.25 \leq x \leq 0.43$  for  $\text{YbAg}_x\text{Ga}_{4-x}$  in comparison with  $0.23 \leq x \leq 1.0$  for  $\text{CaAg}_x\text{Ga}_{4-x}$ ). Similarly to ytterbium, calcium does not form a phase with the BaAl<sub>4</sub> structure with nickel and gallium.

#### 3.2. Crystal structure determination

A full structure determination was performed on the single crystals separated from the samples  $\text{CaM}_{0.5}\text{Ga}_{3.5}$  with  $M \equiv \text{Cu, Au, Pd, Pt}$ . Table 2 gives the important experimental details and crystal data as well as interatomic distances. In agreement with Guinier photographs, Weissenberg photographs indicated tetragonal symmetry and Laue class *4/mmm* with systematic extinctions characteristic of a body-centred lattice (*hkl* reflections only with  $h+k+l=2n$  were found). The symmetry and unit cell shape suggest the isotypism of all four compounds with  $\text{YbAu}_{1.075}\text{Ga}_{2.925}$  (BaAl<sub>4</sub> structure type, space group *I4/mmm*).

The structure refinement of  $\text{CaPt}_{0.5}\text{Ga}_{3.5}$  and  $\text{CaAu}_{0.5}\text{Ga}_{3.5}$  definitely showed statistical occupation of the 4(*e*) position by gold/platinum and gallium atoms, the 4(*d*) position being occupied by gallium atoms. The 4(*e*) position has a tetragonal antiprismatic environment of atoms (Fig. 2). The composition obtained from the refinement agrees with the initial sample composition within the standard deviation.

In case of the  $\text{CaPd}_{0.5}\text{Ga}_{3.5}$  structure the location of the palladium atoms in the 4(*d*) position leads to a larger *R*(*F*) value than a location in the 4(*e*) position. A statistical distribution of palladium in both positions gives the smallest *R* value in comparison with the previous two cases. However, the standard deviation

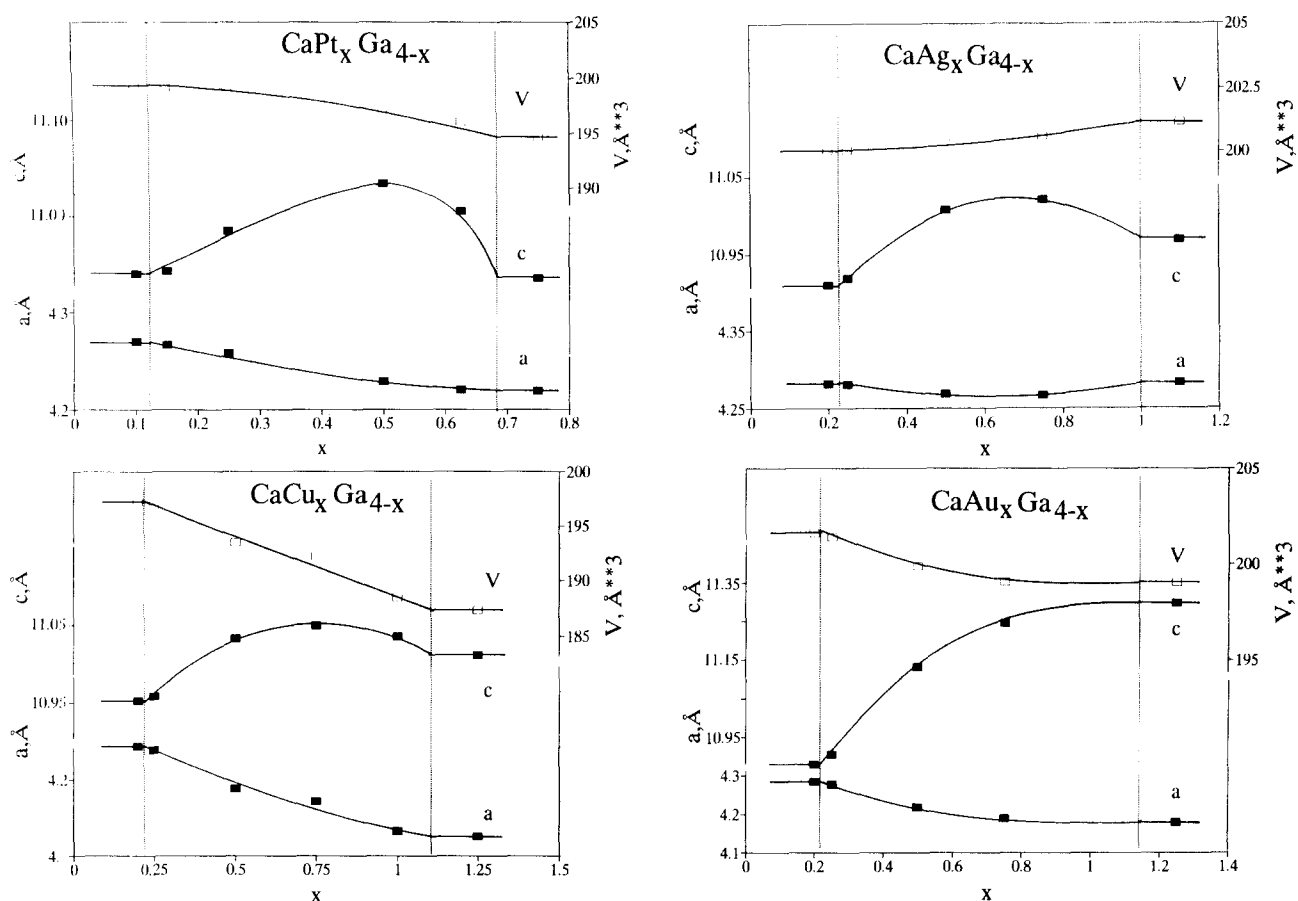


Fig. 1. Concentration dependence of the unit cell parameters and homogeneity ranges for the phases  $\text{CaPt}_x\text{Ga}_{4-x}$ ,  $\text{CaCu}_x\text{Ga}_{4-x}$ ,  $\text{CaAg}_x\text{Ga}_{4-x}$  and  $\text{CaAu}_x\text{Ga}_{4-x}$ .

for the occupation parameter of palladium in the 4(*d*) position is nearly as large as the value itself and the decrease in  $R$  value in comparison with the 4(*e*) occupation ( $R_{\text{exp}} = R(F)_{4(e)} / R(F)_{4(e)+4(d)} = 1.039$ ) is smaller than the statistically required value ( $R_{2,95,0.1005} = 1.065$  [7]). Therefore palladium preferably occupies the 4(*e*) position.

Despite the very low  $R(F)$  value, it was not possible to determine the distribution of copper atoms over the 4(*e*) and 4(*d*) positions in  $\text{CaCu}_{0.5}\text{Ga}_{3.5}$ . Because of the small difference in scattering factors between copper and gallium, the refinement of the occupation coefficients for the 4(*e*) and 4(*d*) positions does not give a statistically relevant indication of a preferred occupation of one of these positions.

Similarly to the recently studied  $\text{YbM}_x\text{Ga}_{4-x}$  phases [2], the  $\text{CaM}_x\text{Ga}_{4-x}$  phases belong to the  $\text{BaAl}_4$  structure type in which the transition metal occupies various positions depending on  $x$ . In the range  $x \leq 0.5$  the transition metal atoms preferably occupy the 4(*e*) position in both phase groups. An analysis in terms of Pearson's nearest-neighbour model [8] shows that the  $d(X_2-X_2)$  interatomic distances are responsible for the unit cell parameters, similarly as in other  $\text{RM}_x\text{Ga}_{4-x}$  phases [9]. Therefore the non-linear dependence of

the unit cell parameters on the concentration can be explained by different kinds of Ga/M substitutions in the various concentration ranges. In the concentration range  $x \leq 0.5$  the transition metal prefers the 4(*e*) position; therefore the  $c$  parameter increases overproportionally and the  $a$  parameter decreases strongly (Fig. 1). In the range  $x \geq 0.5-0.6$  the transition metal occupies both possible positions. In this range the increase in the  $c$  parameter is stopped (see  $\text{CaAu}_x\text{Ga}_{4-x}$  in Fig. 1); in the case of  $\text{CaPt}_x\text{Ga}_{4-x}$  and  $\text{Ca}(\text{Cu}, \text{Ag})_x\text{Ga}_{4-x}$  the  $c$  parameter even decreases. The change in the  $a$  parameter also became smaller. The unit cell volume decreases by this substitution (Cu, Pt and Au compounds) or does not change much (Ag and Pd compounds).

### 3.3. Magnetic measurements

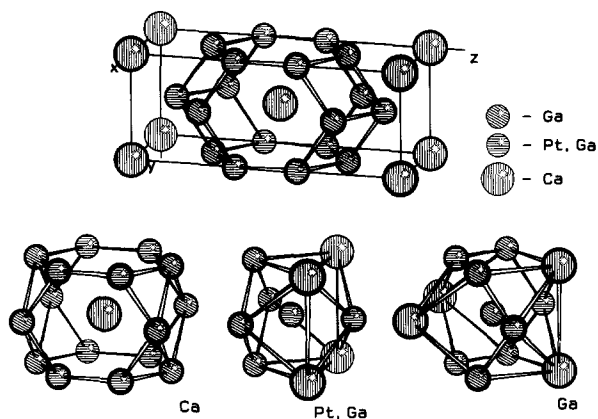
Magnetic susceptibility measurements were performed on the  $\text{CaM}_{0.5}\text{Ga}_{3.5}$  samples. The results are given in Table 3.

The samples are diamagnetic in the temperature range 100–300 K. A comparison with the measurements on the  $\text{YbM}_x\text{Ga}_{4-x}$  compounds [2] shows that the transition metals do not contribute much to the par-

Table 2

Structural data of  $\text{CaM}_{0.5}\text{Ga}_{3.5}$  compounds ( $M \equiv \text{Cu, Au, Pd, Pt, BaAl}_4$  structure type, space group  $I4/mmm$ )

	Cu	Au	Pd	Pt
$a$ (Å)	4.1883(4)	4.2187(3)	4.2137(2)	4.2285(2)
$c$ (Å)	11.033(1)	11.232(2)	11.0331(8)	11.034(1)
2Ca in $2(a) 000$				
$B$	0.89(5)	1.53(11)	1.05(13)	0.78(10)
4X1 in $4(d) 0\frac{1}{2}$				
X1	0.50Ga + 0.50Cu <sup>a</sup>	1.0Ga	0.89(9)Ga + 0.11(9)Pd <sup>a</sup>	1.0Ga
$B$	1.00(2)	1.43(4)	0.94(5)	0.60(4)
4X2 in $4(e) 00z$				
X2	0.50Ga + 0.50Cu <sup>a</sup>	0.75(3)Ga + 0.25(3)Au	0.85(9)Ga + 0.15(9)Pd <sup>a</sup>	0.69(7)Ga + 0.31(7)Pt
$z$	0.3888(1)	0.3900(2)	0.3870(3)	0.3844(1)
$B$	0.89(2)	1.18(3)	1.01(5)	0.71(3)
Number of measured reflections	568	301	175	280
Number of symmetrically independent reflections used for refinement	109	110	106	102
Number of refined parameters	11	11	11	11
Goodness of fit (GOF)	1.7	2.9	3.7	3.2
$R(F)$	0.0259	0.0342	0.0477	0.0352
Interatomic distances (Å)				
$d(\text{Ca}-\text{X1})$	3.4631(8)	3.512(2)	3.4709(6)	3.4755(8)
$d(\text{Ca}-\text{X2})$	3.2056(6)	3.229(1)	3.230(1)	3.2506(8)
$d(\text{Ca}-\text{Ca})$	4.1883(3)	4.2187(3)	4.2137(3)	4.2285(2)
$d(\text{X1}-\text{X1})$	2.9616(4)	2.9831(3)	2.9795(2)	2.9900(2)
$d(\text{X1}-\text{X2})$	2.5944(9)	2.631(2)	2.593(2)	2.583(1)
$d(\text{X2}-\text{X2})$	2.453(2)	2.473(3)	2.494(5)	2.551(3)

<sup>a</sup>See text.Fig. 2. Unit cell of the  $\text{CaPt}_{0.5}\text{Ga}_{3.5}$  structure (structure type  $\text{BaAl}_4$ ) and coordination polyhedra of the atoms.

amagnetism of these phases and that the electronic state of ytterbium is presumably responsible for the temperature-dependent paramagnetism of  $\text{YbM}_x\text{Ga}_{4-x}$ .

### Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft.

The authors thank Dr. K. Hiebl for his help with the magnetic measurements.

Table 3

Magnetic susceptibilities of  $\text{CaM}_x\text{Ga}_{4-x}$  and  $\text{YbM}_x\text{Ga}_{4-x}$  compounds (temperature range 100–300 K)

M	$x$ for $\text{CaM}_x\text{Ga}_{4-x}$ <sup>a</sup>	$\chi$ ( $\text{cm}^3 \text{g}^{-1}$ ) for $\text{CaM}_x\text{Ga}_{4-x}$ <sup>a</sup>	$x$ for $\text{YbM}_x\text{Ga}_{4-x}$ <sup>b</sup>	$\chi$ ( $\text{cm}^3 \text{g}^{-1}$ ) for $\text{YbM}_x\text{Ga}_{4-x}$ <sup>b</sup>
Cu	0.5	$-3.2 \times 10^{-7}$ to $-3.7 \times 10^{-7}$	0.75	$2.3 \times 10^{-6}$ to $1.0 \times 10^{-6}$
Ag	0.5	$-2.8 \times 10^{-7}$ to $-3.3 \times 10^{-7}$	0.375	$2.3 \times 10^{-7}$ to $0.5 \times 10^{-7}$
Au	0.5	$-1.7 \times 10^{-7}$ to $-2.0 \times 10^{-7}$	0.5	$6.1 \times 10^{-7}$ to $1.8 \times 10^{-7}$
Pd	0.5	$-0.4 \times 10^{-7}$ to $-1.2 \times 10^{-7}$	0.25	$1.1 \times 10^{-6}$ to $0.4 \times 10^{-6}$
Pt	0.5	$-1.0 \times 10^{-7}$ to $-1.5 \times 10^{-7}$	0.5	$2.1 \times 10^{-6}$ to $1.0 \times 10^{-6}$

<sup>a</sup>This work; <sup>b</sup>Ref. [2].

### References

- [1] Yu. Grin and R.E. Gladyshevski, *Gallide*, Nauka, Moscow, 1989, pp. 28–48.
- [2] Yu. N. Grin, M. Ellner, K. Hiebl and P. Rogl, *J. Alloys Comp.*, 196 (1993) 207.
- [3] K.S. Gyo, *Thesis*, Lvov University, 1985.

- [4] G. Cordier, G. Dörsam and C. Rohr, *J. Less-Common Met.*, 166 (1990) 115.
- [5] N. Walker and D. Stuart, *Acta Crystallogr. A*, 39 (1983) 193.
- [6] L.G. Akselrud, Yu.N. Grin, P.Yu. Zavaliy, V.K. Pecharski and V.S. Fundamenski, *Collected Abstracts, Twelfth Eur. Crystallography Meet., Moscow, 1989*, Institute of Crystallography of Academy of Sciences of the UdSSR, Moscow, 1989, Vol. 3, p. 155.
- [7] W.C. Hamilton, *Acta Crystallogr.*, 18 (1965) 502.
- [8] W.B. Pearson, *J. Less-Common Met.*, 96 (1984) 103.
- [9] Yu.N. Grin, K. Hiebl, P. Rogl and H. Noël, *J. Less-Common Met.*, 162 (1990) 361.