

## Low-Temperature Chemistry in the Binary Systems of Pt and Mn with Gallium

Iryna Antonyshyn<sup>1</sup>, Magnus Boström<sup>2</sup>, Stefan Hoffmann, Marcus Schmidt, Franz Weitzer<sup>3</sup>, Yurii Prots, and Yuri Grin

Most of the binary metallic systems are widely investigated and the information about the composition of the compounds, their crystal structure and formation conditions are represented by the respective phase diagrams (commonly in the composition – temperature coordinates) which are collected in the reference books and data bases [1]. Nevertheless, a careful re-examination of these data shows that some of the reported phases are not completely investigated. An application of the different preparation techniques, e.g., synthesis by using self-flux of one of the constituent component such as Al, Ga, or Bi, allowed us recently to shed new light on the phase equilibria in some binary systems and to synthesize a series of new binary compounds, most of them with unique crystal structures. For instance, the phase equilibria and phase formation in the binary system Bi–Rh depends on the cooling rate of the melt. Different phases can be obtained as single crystals in the Bi-rich region, e.g., by slow cooling of the melt below the liquidus, Bi<sub>14</sub>Rh<sub>3</sub> crystallizes, while Bi<sub>4</sub>Rh forms if the melt is rapidly cooled to below liquidus and then annealed [2].

Typically, the crystal structure determination of the so-obtained phases is hampered by the systematic twinning in the investigated specimens. Nevertheless, the structure solution and refinement can be significantly facilitated and accelerated by

utilizing state-of-the-art single crystal instruments, e.g., area detectors, in combination with the modern data reduction software which includes very useful graphical tools and allows a better analysis of the collected data [3]. Here we report on the synthesis and the crystal structure of binary phases which were initially reported as „PtGa<sub>6</sub>“ [4] and „MnGa<sub>6</sub>“ [5] about fifty years ago.

These new platinum and manganese gallium-rich compounds were synthesized by reaction of the respective precursors „PtGa<sub>3</sub>“ and „MnGa<sub>6</sub>“ with an excess of Ga at different temperatures (160 °C – 360 °C) and subsequent removing of the flux by high-temperature centrifugation-aided filtration (HTCAF) [6–8].

The crystal structure investigation of „PtGa<sub>6</sub>“ revealed PtGa<sub>5</sub> as the correct composition for this phase. According to the results of differential thermal analysis and *in situ* X-ray powder diffraction the platinum pentagallide decomposes peritectically at 294 °C: PtGa<sub>5</sub> → Pt<sub>3</sub>Ga<sub>7</sub> + L. The collected X-ray single crystal diffraction data can be described on the basis of two reticularly twinned domains that possess a primitive monoclinic unit cell (space group  $P2_1/m$ ,  $a = 6.3951(7)$  Å,  $b = 15.882(2)$  Å,  $c = 8.839(2)$  Å,  $\beta = 110.26(1)^\circ$ ) and which are related by the matrix  $10\frac{1}{2} \ 0\bar{1}0 \ 00\bar{1}$  (Fig. 1).

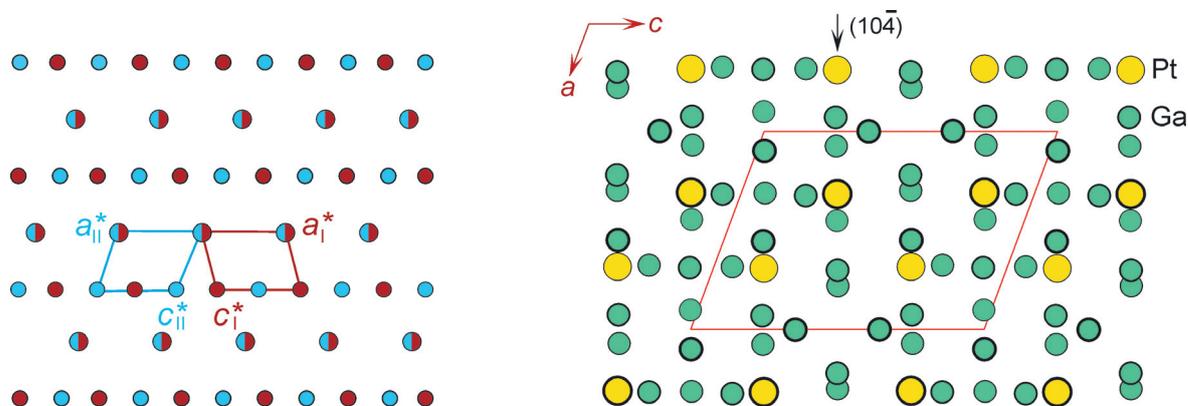


Fig. 1: (left) Schematic arrangement of the twinned components in the PtGa<sub>5</sub> crystal sketched in the projection of the reciprocal space along  $b^*$ . Single-coloured dots correspond to individual reflections of each domain. Circles of two colours symbolize overlapping reflections. (right) Projection of the structure of PtGa<sub>5</sub> along  $[010]$  with the pronounced densely packed slabs of atoms located within  $(10\bar{4})$  planes.

The structure solution performed by decomposition of the collected data set into the constituting parts and the subsequent refinement of the crystal structure resulted in residuals of  $R_F = 0.039$  and  $R_w = 0.103$  with a twin component ratio of  $0.596(2) : 0.404$ . The dominant part (5/6) of atoms in the crystal structure of  $\text{PtGa}_5$  is located on the pronounced planes perpendicular to the  $[001]$  direction (Fig. 1). The presence of such densely packed layers of atoms in the structure may be regarded as a reason for the twinning which obviously occurs during the crystal growth.

The investigation of the gallium-rich part of the binary Mn–Ga system clearly indicated that the composition designated in the literature as „ $\text{MnGa}_6$ “ is actually  $\text{Mn}_6\text{Ga}_{29}$  ( $\text{MnGa}_{4.83}$ ). Combining differential thermal analysis, X-ray single-crystal diffraction techniques and *in situ* high-temperature powder diffraction performed at beamline ID31 of ESRF we have established the existence of three modifications of the compound  $\text{Mn}_6\text{Ga}_{29}$ . The corresponding  $\alpha$ – $\beta$  and  $\beta$ – $\gamma$  phase transitions occur at  $\sim 145$  °C and  $\sim 210$  °C (Fig. 2). Whereas the  $\alpha$  and  $\beta$  modifications were examined at ambient conditions,  $\gamma$ - $\text{Mn}_6\text{Ga}_{29}$  (tetragonal, space group  $P4/m$ ,  $a = 6.3464(1)$  Å,  $c = 10.0235(4)$  Å) is not accessible by quenching the sample to room temperature. Rather, it is only detected in the powder diagrams collected at high temperatures. The upper limit of the existence of  $\gamma$ - $\text{Mn}_6\text{Ga}_{29}$  is  $\sim 390$  °C, where this phase undergoes a peritectic decomposition:  $\gamma\text{-Mn}_6\text{Ga}_{29} \rightarrow \text{MnGa}_4 + L$ .

The crystal structure models of the  $\alpha$  and  $\beta$  phases were determined from systematically twinned specimens: triclinic, space group  $P\bar{1}$ ,  $a = 6.3020(5)$  Å,  $b = 9.9388(7)$  Å,  $c = 18.911(2)$  Å,  $\alpha = 90.52(1)^\circ$ ,  $\beta = 90.79(1)^\circ$ ,  $\gamma = 90.43(1)^\circ$  for the  $\alpha$  phase and monoclinic, space group  $P2$ ,  $a = 6.2909(3)$  Å,  $b = 9.9685(5)$  Å,  $c = 31.431(2)$  Å,  $\beta = 90.79(1)^\circ$  for the  $\beta$  phase. The relation between two domains twinned by reticular merohedry is defined by the matrixes  $00\frac{1}{3} 0\bar{1}0 300$  and  $00\frac{1}{3} 0\bar{1}0 500$ , for the  $\alpha$  and the  $\beta$  modification, respectively. The formation of the twinned agglomerates could be easily explained taking into account the fact that low-temperature modifications are formed by displacive phase transitions accompanied by the stepwise deformation of the structural motif of the high-temperature tetragonal  $\gamma$ - $\text{Mn}_6\text{Ga}_{29}$  phase.

The characteristic building element of the investigated crystal structures is a distorted monocapped tetragonal antiprism formed by Ga species around the transition metal atom (Pt or Mn). In the atomic motif of  $\text{PtGa}_5$  each antiprism shares atoms with five neighboring polyhedra interconnected via four edges and one vertex resulting in a 3D network (Fig. 3). In the pattern of  $\text{Mn}_6\text{Ga}_{29}$  each tetragonal antiprism  $[\text{MnGa}_8]$  has again five neighbors, but their linkage is different. The tetragonal antiprisms are condensed in pairs by their pseudo-tetragonal faces and connected with four more antiprisms by the remaining four vertices (Fig. 3).

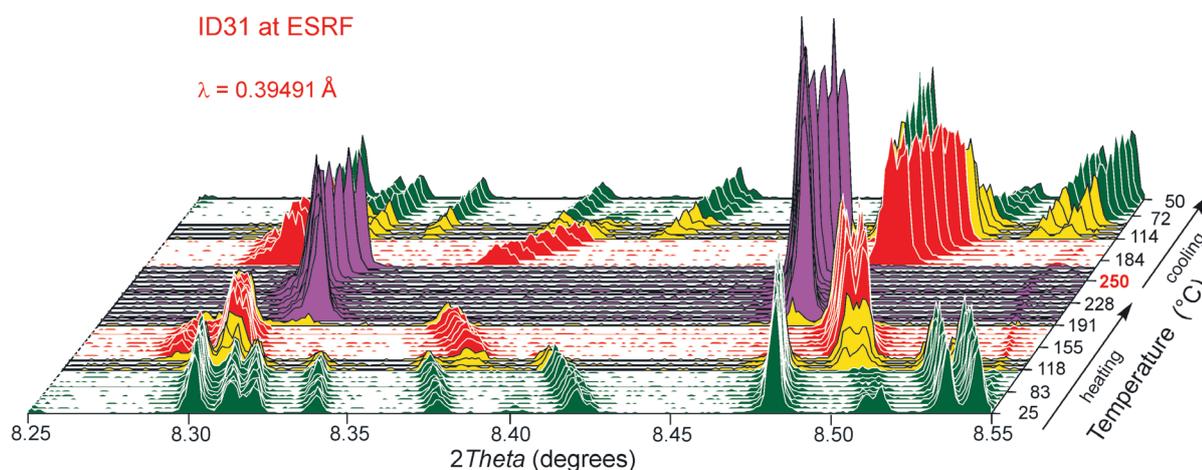


Fig. 2: Selected powder patterns collected upon heating from room temperature to 250 °C and subsequent cooling for the  $\text{Mn}_6\text{Ga}_{29}$  phases. Green, red and violet patterns correspond to the  $\alpha$ ,  $\beta$  and  $\gamma$  modifications, respectively. Regions of  $\alpha$ – $\beta$  and  $\beta$ – $\gamma$  transitions are indicated in yellow.

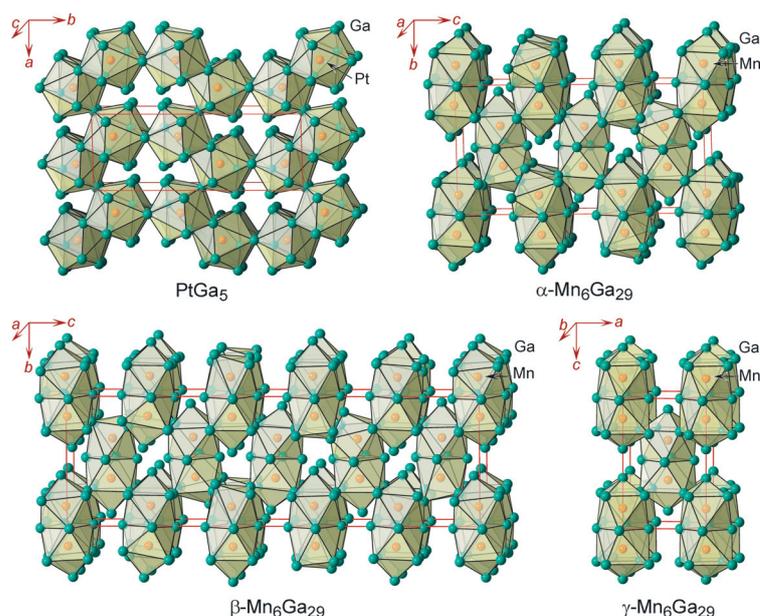


Fig. 3: Crystal structures of  $\text{PtGa}_5$ ,  $\alpha$ -,  $\beta$ -, and  $\gamma$ - $\text{Mn}_6\text{Ga}_{29}$  represented as condensed tetragonal antiprisms of gallium atoms formed around transition metal atoms.

The building unit just described (tetragonal antiprism around transition metal atoms) is typical for a series of the binary compounds, e.g.,  $\text{CuAl}_2$  [9,10],  $\alpha$ - and  $\beta$ - $\text{CoSn}_3$  [11],  $\text{PtSn}_4$  [12],  $\text{Co}_2\text{Al}_9$ ,  $\text{Rh}_2\text{Ga}_9$  [13],  $\text{PdGa}_5$  [14],  $\text{Rh}_4\text{Ga}_{21}$  and  $\text{Rh}_3\text{Ga}_{16}$  [15]. As expected, most of these structures are either tetragonal ( $\text{CuAl}_2$ ,  $\text{PdGa}_5$ ,  $\beta$ - $\text{CoSn}_3$ ) or some parts of the structures adopt a pseudo-tetragonal symmetry ( $\alpha$ - $\text{CoSn}_3$ ,  $\text{PtSn}_4$ ,  $\text{Rh}_4\text{Ga}_{21}$ ,  $\text{Rh}_3\text{Ga}_{16}$ ,  $\alpha$ - and  $\beta$ - $\text{Mn}_6\text{Ga}_{29}$ ). From this point of view the atomic arrangements of  $\text{Co}_2\text{Al}_9$ ,  $\text{Rh}_2\text{Ga}_9$  and  $\text{PtGa}_5$  are unique in this series, because the pseudo-four-fold axes of their tetragonal antiprisms are restricted to the building unit only and does not extend throughout the whole structure (e.g., layers, columns).

## References

- [1] *T. B. Massalski*, Binary Alloy Phase Diagrams, 2<sup>nd</sup> edition. ASM, New York, 1990.
- [2] *F. Weitzer, W. Schnelle, R. Cardoso Gil, S. Hoffmann, R. Giedigkeit, and Yu. Grin*, CALPHAD: Comput. Coupling Phase Diagrams Thermochem., **33** (2009) 27.
- [3] *H. Borrmann*, in Scientific Report 2006–2008, p. 171 (Max Planck Institute for Chemical Physics of Solids, Dresden, Germany, 2009).
- [4] *S. Bhan and K. Schubert*, *Z. Metallkd.* **51** (1960) 327.
- [5] *H. G. Meißner and K. Schubert*, *Z. Metallkd.* **56** (1965) 523.
- [6] *Z. Fisk and J. P. Remeika*, in K. A. Gschneider, L. R. Eyring (eds) Handbook on the physics and chemistry of the rare earth, Vol. 12, North-Holland, Amsterdam, p. 53 (1989).
- [7] *M. Boström and S. Hovmöller* *J. Alloys Compd.* **314** (2001) 154.
- [8] *M. Boström, Yu. Prots, and Yu. Grin*, in Scientific Report 2003–2005, p. 243 (Max Planck Institute for Chemical Physics of Solids, Dresden, Germany, 2006).
- [9] *J. B. Friauf*, *J. Am. Chem. Soc.* **49** (1927) 3107.
- [10] *Yu. Grin, F. R. Wagner, M. Armbrüster, M. Kohout, A. Leithe-Jasper, U. Schwarz, U. Wedig, and H. G. von Schnering*, *J. Solid State Chem.* **179** (2006) 1707.
- [11] *A. Lang and W. Jeitschko*, *Z. Metallkd.* **87** (1996) 760.
- [12] *B. Künnen, D. Niepmann, and W. Jeitschko*, *J. Alloys Compd.* **309** (2000) 1.
- [13] *M. Boström, H. Rosner, Yu. Prots, U. Burkhardt, and Yu. Grin*, *Z. Anorg. Allg. Chem.* **631** (2005) 534.
- [14] *Yu. Grin, U. Wedig, F. Wagner, H. G. von Schnering, and A. Savin*, *J. Alloys Compd.* **255** (1997) 203.
- [15] *M. Boström, Yu. Prots, and Yu. Grin*, *J. Solid State Chem.* **179** (2006) 2472.

<sup>1</sup> Ivan Franko National University of Lviv, 79005 Lviv, Ukraine

<sup>2</sup> Sandvik Materials Technology, SE-81181 Sandviken, Sweden

<sup>3</sup> Institute for Physical Chemistry, University of Vienna, 1090 Vienna, Austria