Ternary Intermetallic Palladium Compounds with Anionic Partial Structures

Roman Demchyna, Yurii Prots, and Ulrich Schwarz

The description of chemical bonding in intermetallic compounds is a demanding task since the well known 8-N rule, which holds for insulating or semiconducting valence compounds, is in general not valid for metallic systems. In order to study the effects of factors like valence electron concentration or atomic volume on pattern formation, we started to systematically investigate atomic arrangements, homogeneity ranges and polymorphism of transition metal compounds comprising a main group element like germanium or gallium. Ternary equiatomic intermetallic compounds have been studied in some detail for systems $M_1 - M_2 - L$, where M_1 = rare-earth metal, M_2 = transition metal and L = aluminium, gallium, silicon or germanium. Most of these compounds adopt crystal structures which are distorted substitution varieties of the AlB_2 type and some of these are interesting as perspective materials, for example ZrRuSi [1], LaRhAl and YRhAl [2] exhibit superconducting properties at low temperatures. In order to study chemical bonding systematically, we investigated new compounds M_1 – Pd – {Ga,Ge} where M_1 = Ti, Zr and Hf.

The new ternary compounds are prepared from the elements by arc melting. Thermal treatment of the samples is performed in sealed alumina crucibles which are placed in evacuated silica ampoules and finally quenched in cold water. The crystal structures are studied by X-ray single-crystal diffraction or Rietveld refinement of powder diffraction data (TiPdGa). The compositions obtained from crystal structure refinements are in agreement with those determined by EDAX for all synthesized compounds with typical differences being less than one at. % for each element. With respect to physical properties, samples of TiPdGa and ZrPdGa exhibit high overall values of the electrical resistivity (Fig. 1). In combination with an almost linear increase with temperature the finding indicates that the compounds are bad metals.

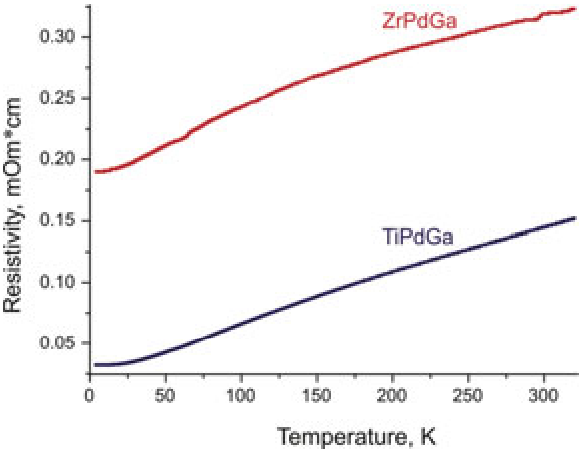


Fig. 1: Electrical resistivity of ZrPdGa and TiPdGa as a function of temperature. The experimental data exhibit an almost linear increase which is typical for metal-type conductors.

Among the investigated compounds, only $Ti_{1+x}Pd_{1-x}Ga$ exhibits a significantly broad homogeneity range from TiPdGa to about $Ti_{1.25}Pd_{0.75}Ga$ evidenced by varying unit cell parameters and analytically determined composition differences. The relation between volume and composition of samples $Ti_{1+x}Pd_{1-x}Ga$ is linear so that Vegard's rule is fulfilled. The crystal structure of TiPdGa ($P6_3/mmc$, a = 4.3924(1) Å, c = 5.4593(1) Å) is isotypic to that of ZrBeSi [3] and represents an undistorted, ordered decoration variety of the AlB_2 type.

The corresponding germanium compound, TiPdGe exhibits temperature polymorphism with a transition temperature of about 1240 °C. Thus, the low-temperature (LT) modification ($Pnma$, a = 6.3707(7) Å, b = 3.8574(3) Å, c = 7.5372(6) Å) was synthesized at 800 °C and exhibits a TiNiSi type atomic pattern [4]. The high temperature (HT) modification ($P\bar{6}2m$, a = 6.6030(4) Å, c = 3.6998(3) Å) is obtained by heat treatment at 1275°C and realizes a ZrNiAl type pattern [5]. Both atomic arrangements are deformation varieties of the AlB_2 type.

The atomic pattern of HfPdGa ($P\bar{6}2c$, a = 7.1572(2) Å, c = 6.8945(4) Å, HfRhSn type [6]) is a variety of the ZrNiAl type while zirconium palladium gallide ZrPdGa ($Pnma$, a = 6.9182(5) Å, b = 3.7186(4) Å, c = 15.975(2) Å) is isotypic to LaNiAl [7].

The crystal structure of HfPdGe represents a new crystal structure type. Analysis of reflections intensities in the initially detected hexagonal metric of

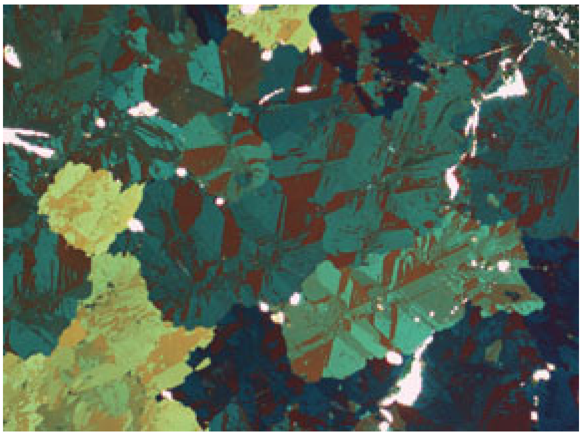


Fig. 2: View of the microstructure of HfPdGe in polarized light. The observed pattern is compatible with a multi-domain structure typical for twinned aggregates. White spots correspond to cracks.

the investigated crystals ($a \approx 13.30$ Å, and $c \approx 3.93$ Å) reveals disagreement with hexagonal Laue symmetry. Models based on the three possible ortho-hexagonal settings did not result in satisfying refinement results. An investigation of the microstructure of HfPdGe using polarized light (Fig. 2) reveals a large number of grain boundaries and straight lines. Both findings are characteristic features which are consistent with twinning planes. Assuming that the investigated specimens are multiply twinned agglomerates, a monoclinic structure model is developed ($P2_1/m$, $a = 11.4421(2)$ Å, $b = 3.93048(5)$ Å, $c = 6.65205(9)$ Å, $\beta = 90.0(1)°$). Here, the crystals exhibit reticularly twinned domains (I, II, III) rotated around a threefold axis parallel to the twofold monoclinic axis, thus resulting in partially overlapping lattices (Fig. 3). Additionally, the domains are pseudo-merohedrally twinned by a rotation of 180 ° around the monoclinic c axis (designated by + and –). A final decomposition of the collected data set into the constituting parts of each twin component allowed a verification of the structure model with the final least square refinement resulting in residuals of $R_F = 0.027$ and $R_w = 0.030$. This procedure indicates a ratio of twin components of 0.306(2) : 0.148(1) : 0.161(3) : 0.129(3) : 0.073(3) : 0.182(3) for I(+), I(–), II(+), II(–), III(+) and III(–) domains, respectively. Finally, the structure model with an ordered distribution of all atoms was successfully confirmed by Rietveld refinement (Fig. 4).

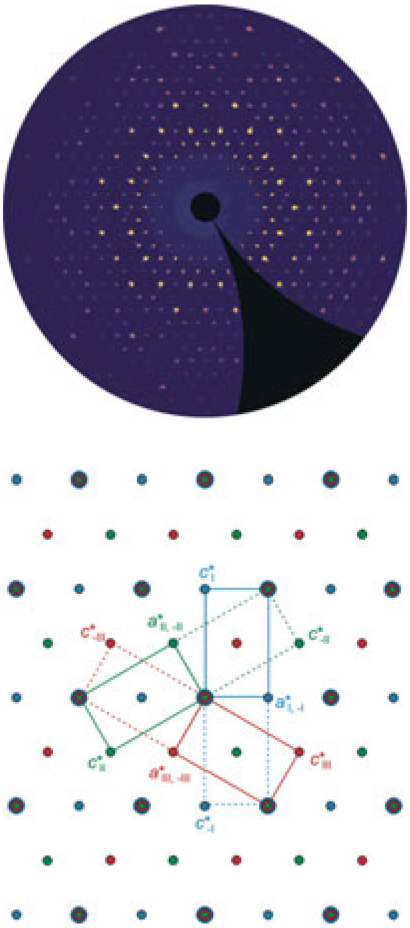


Fig.3: Reciprocal space representation of the 0^{th} layer perpendicular to [010] direction for a HfPdGe particle. In the lower part of the figure a schematic representation of the twin components is given. One-color dots correspond to individual reflections of each domain. Multicolored circles symbolize overlapping reflections.

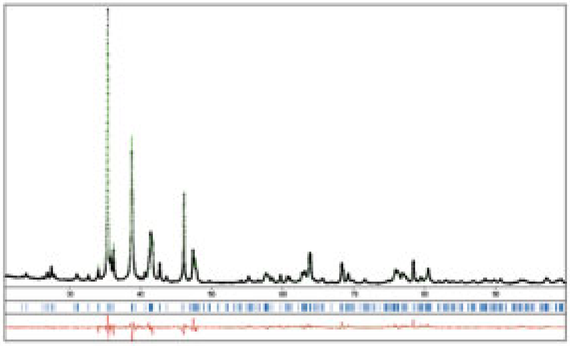
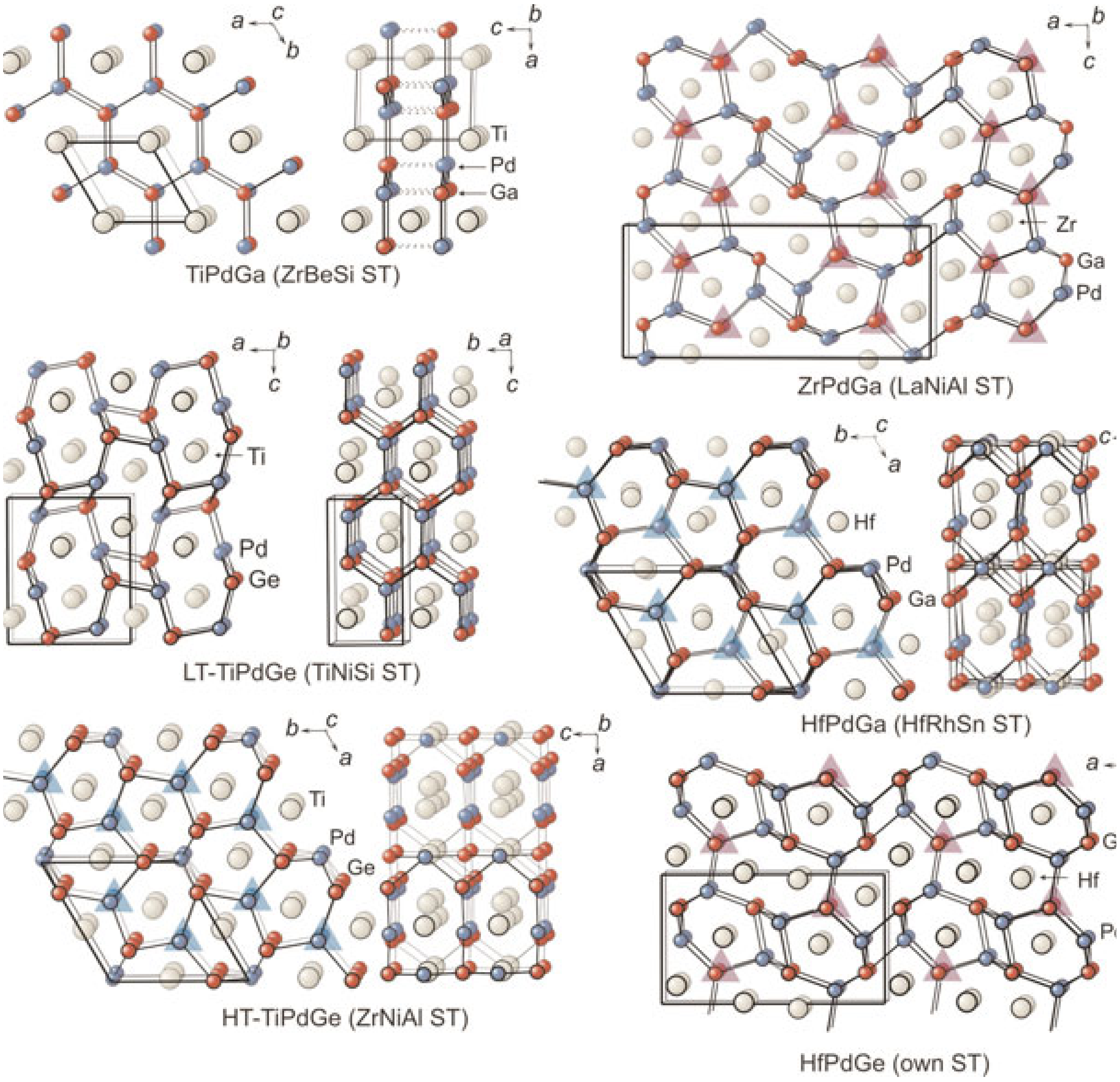


Fig 4: Refinement of the crystal structure of HfPdGe ($CuK\alpha_1$ radiation) using full profiles of powder diffraction data. Ticks below the experimental pattern indicate possible peak positions, the curve at the bottom reproduces the difference between observed (black hollow circles) and calculated (solid green line) intensities.

The crystal structures of the investigated compounds can be described as [PdGa] or [PdGe] frameworks embedding Ti, Zr or Hf atoms (Fig. 5). The nets are characterized by the absence of homonuclear contacts between Ga and Ge. The shortest Ga–Ga and Ge–Ge distances of 3.3226(8) Å and 2.953(1) Å, respectively, which are observed in the structures of HfPdGa and HT-TiPdGe, are significantly larger than the values of 2.703 Å observed in α-Ga (average value) and 2.450 Å in the diamond modification of Ge [8]. In contrast, the situation concerning Pd–Pd contacts is inconsistent. In LT-TiPdGe interatomic distances reveal that homonuclear palladium contacts are absent. For TiPdGa, HT-TiPdGe, ZrPdGa, HfPdGa and HfPdGe this is not unambiguously indicated since the shortest Pd–Pd contacts in these crystal structures (2.82 Å – 2.90 Å) are significantly longer than the sum of the covalent radii (2.56 Å) but only slightly larger than the interatomic distance of 2.751 Å in *ccp* palladium.

The frameworks in the atomic arrangements of HT-TiPdGe, ZrPdGa, HfPdGa and HfPdGe are built by three- as well as four-coordinated atoms. The fraction of three-bonded species (3b) in these crystal structures is 1/3 of the polyanion atoms in HfPdGa and HT-TiPdGe (3b-Pd), 1/4 in ZrPdGa



TiPdGa (ZrBeSi ST)

ZrPdGa (LaNiAl ST)

LT-TiPdGe (TiNiSi ST)

HfPdGa (HfRhSn ST)

HT-TiPdGe (ZrNiAl ST)

HfPdGe (own ST)

Fig.5: Frameworks in the crystal structures of TiPdGa, ZrPdGa, HfPdGe, LT-TiPdGe, HT-TiPdGe and HfPdGe. Three-bonded atoms are emphasized by colored triangles (ST = structure type).

(3b-Ga) and 1/6 in HfPdGe (3b-Ge). In the structure of HfPdGa and HT-TiPdGe some of the Pd atoms are 6 bonded, thus constituting a polyanion with 1/6 (6b-Pd). The [PdGe] network in the structure of LT-TiPdGe is three dimensional and consists of four-coordinated atoms exclusively with Pd–Ge distances ranging from 2.4589(9) Å to 2.586(1) Å. The finding that the distances Pd-Ge (2.46 Å – 2.62 Å) and Pd-Ga (2.54 Å – 2.66 Å) within the frameworks of the investigated compounds are close to the sum of the covalent radii (Pd–Ge 2.50 Å, Pd–Ga 2.53 Å) justifies the description as [PdGe] and [PdGa] networks. Consequently, the Pd–Ga distance of 2.710(1) Å between adjacent slabs in the crystal structure of TiPdGa is taken as evidence for a transition towards a two-dimensional building unit. Taking into account the more electropositive character of the embedded Ti, Zr or Hf atoms, the covalently bonded frameworks may be regarded as polyanions. A more detailed investigation of the chemical bonding in these intermetallic phases will be performed by band structure and ELF calculations.

References

[1] *I. Shirotani, K. Tachi, K. Takeda, S. Todo and T. Yagi, K. Kanoda,* Phys. Rev. B **52** (1995) 619.

[2] *D.C. Kundaliya and S.K. Malik,* Solid State. Commun. **131** (2004) 489.

[3] *J. Nielsen and N.C. Baenziger,* Acta Crystallogr. **7** (1954) 132.

[4] *C. B. Shoemaker and D. P. Shoemaker,* Acta Crystallogr. **18** (1965) 900.

[5] V. Ya. Markiv and P.I. Kripyakevich, Sov. Phys. Crystallogr. **11** (1966) 733.

[6] A. E. Dwight, J. Less-Common Metals **34** (1974) 279.

[7] *G. Cordier, G. Dorsam and R. Kniep,* J. Magn. Magn. Mater. **76** (1988) 653.

[8] *J. Donohue,* The structures of the elements, Wiley, New York (1974).