The thesis reports the synthesis, crystal structure, stability of rhodium and gold-based binary intermetallic phases. The intermetallic compounds have been synthesized by the traditional high-temperature method starting from highly pure constituent metals. X-ray diffraction (XRD), and energy-dispersive X-ray spectroscopy techniques (EDX) have been employed for the structural characterization of the compounds. To understand the stability as well as the site distribution patterns in the as-synthesized intermetallic phases, electronic structure calculations have been carried out using tight-binding linear muffin-tin orbital employing atomic sphere approximation (TB-LMTO-ASA), Vienna ab-initio simulation package (VASP), and Quantum ESPRESSO package.

Our study on Cd rich part of the Rh-Cd system has uncovered two new compounds in close vicinity to RhCd (1:1). Both the compounds are structurally related to RhCd.

The non-stoichiometric, line phase $Rh_3Cd_{5-\delta}$ (δ~0.56) crystallizes in the body–centered cubic space group, $Im\bar{3}m$. It represents a defect 2^3 superstructure of bcc-type RhCd which accommodates a vacancy concentration of nearly 6% in its crystal structure. The first principles electronic structure calculation on a hypothetical ordered configuration of $Rh_3Cd_{5-\delta}$ reveals that Rh-Cd hetero-atomic interaction plays a major role in the stability of the compound. A combination of total energy, formation energy, and COHP calculations on a hypothetical model (a close approximation to the experimental model) establishes that the compound upholds an optimum vacancy concentration in one of the cadmium sites (Wyck off: 2a) for the stability of the phase.

Another compound Rh_2Cd_5 that crystallizes in the orthorhombic space group *Pbam* (55), adopts In_3Pd_5 structure type with an ordered vacancy. The compounds is viewed as a 2×4×1 modified superstructure of the CsCl type RhCd and is closely related to $Rh_3Cd_{5-\delta}$ as well. The crystal structure is made of two 2D atomic layers with the stacking sequence: ABAB. The presence of vacancy in Rh_2Cd_5 was investigated by the first-principles calculations.

A preliminary electronic structure calculations reveal that all these three structurally related compounds (RhCd, Rh_2Cd_5, and $Rh_3Cd_{5-\delta}$ (δ~0.56)) discern observable pseudogaps across the Fermi level in the DOS curves and, thereby, they are stabilized by the Hume Rothery mechanism. The chemical bonding analyses applying the crystal orbital Hamilton population (COHP) approach unveil that both the Cd-Cd and Rh-Cd interactions play a significant role in the stability of these compounds.

Our further investigation at the Cd rich region of the Rh-Cd system unearthed three new complex intermetallc phases. Those are related to γ-brasses: (a) a rhombohedral phase at 15.7 atomic % of Rh, (b) a monoclinic phase at approximately 14.7 atomic % of Rh and (c) a complex cubic phase at ca. 11 atomic % of Rh. The present thesis covers the rhombohedral phase Rh_8Cd_{43}. The two other γ-brass related phases are considerably more complex and will be the subject of future investigation.

The fully ordered compound Rh_8Cd_{43} crystallizes in the rhombohedral space group $R\bar{3}m$ (166) and contains 306 atoms per unit cell. This new compound is probably, the first example of a rhombohedral distortion of a $(2a_\gamma)^3$- superstructure of cubic γ-brass in particular, it is closely

related to Rh_7Mg_{44}. The structure is build up with by two main units: the 38-atom modified Pierce cluster and unions of three double sphenocoronae. The two main building units form 3D-networks. The structure is also described as a combination of flat and puckered atomic layers. The electronic structure of Rh_8Cd_{43} shows that the phase is stabilized by the Hume-Rothery mechanism.

In the course of our research investigation, the γ-brass region of Au-Cd, Au-Mg, and Au-Zn binary system have been reinvestigated to identify γ-brass or γ-brass related phases, their crystal structures and stabilization mechanism. In this dissertation, the structures and stability of two ordered compounds Au_3Cd_5 and Au_3Mg_5 and, a partially disordered complex $AuZn_{2.1}$ are detailed.

Both the Au_3Cd_5 and Au_3Mg_5 are isostructural with W_5Si_3. Both of them crystallize in the tetragonal space group *I*4/*mcm* (140). The structures consist of the columns of intergrown gold centered square anti-prisms, Mg or Cd-centered (Mg in Au_3Mg_5 and Cd in Au_3Cd_5) intergrown hexagonal antiprisms and a column of face sharing empty octahedra. Electronic structure calculations on the model structures show pseudogap at the Fermi level in the electronic density of the state curves, which is consistent with the Hume-Rothery phase. Both phases occur at a sharp valance electron concentration value (VEC) of 1.625 (e/a), which is in the VEC range of γ-brass type or related phases.

The hexagonal $AuZn_{2.1}$ phase that occurs in close vicinity to the rhombohedrally distorted γ-$Au_{5-x}Zn_{8+y}$, crystallizes in the trigonal space group *P*31*m* (No. 157) with ~227 atoms per unit cell and represents a $\sqrt{3}a \times \sqrt{3}a \times c$ superstructure of rhombohedrally distorted γ-$Au_{5-x}Zn_{8+y}$. The structure is largely tetrahedrally closed packed and is described by two types of building units: a 38-atom modified Pierce cluster and an intergrown 19-atom double icosahedron. The formation of γ1-$AuZn_{2.1}$ can be understood within the framework of a Hume-Rothery stabilization mechanism with a valence electron concentration of 1.68 e/a.

Keywords: Binary intermetallics; Gamma brass; Site preference; X-ray diffraction; Electronic structure; Hume-Rothery stabilization mechanism.