7. Summary

This thesis deals with the development of novel colloidal synthetic approaches for various magnetic alloy nanocrystals as well as with the theoretical understanding of phenomena governing the nanocrystal nucleation and growth. Highly crystalline particles of platinum – iron, $CoPt_3$ and $CoPd_2$ magnetic alloys can be prepared in a predictable and reproducible manner via high temperature synthetic routes. The key point of the synthesis is the use of the novel bulky stabiliser 1-adamantancarboxylic acid. All samples were synthesised in the form of stable colloids. The possibility of the shape control of nanocrystals, e.g. controllable formation of spherical, cubic $CoPt_3$ nanocrystals and $CoPt_3$ nanowires was demonstrated. Elemental analysis, powder XRD, TEM, and HRTEM and SAXS data were used to characterised magnetic alloy nanocrystals. Detailed investigation of the effect of various reaction conditions (reaction temperature, concentration of the precursors and stabilisers) on the size of forming nanocrystals revealed the purely kinetic nature of the nanocrystals growth and the absence of the Ostwald ripening stage. The turning of the nanocrystal size in this case can be achieved via control over the balance between the nucleation and growth rates. To the best of our knowledge, this is the first attempt of a systematic experimental study of the "hot" organometalic synthesis of metal nanocrystals and the mechanism of homogenous nucleation of metal alloy nanocrystals. The experimental results indicate that nucleation of alloy nanocrystals occurs through the formation of some clusters from the precursor of transition metal playing the role of nucleation seeds for further growth of the alloy. The formation of these clusters is the rate-limiting step for the whole nucleation process whereas the concentration of platinum or palladium precursors does not affect the nucleation rate.

The development of novel effective and predictable methods of precise size control of $CoPt_3$ nanocrystals allowed the investigation of their size-dependent magnetic properties. The magnetic measurements (hysteresis loops and ZFC/FC scans) revealed a superparamangetic behaviour of these magnetic alloy nanocrystals at room temperature. The blocking temperature, coercivity and saturation magnetisation strongly depend on the nanocrystals sizes.

The monodisperse magnetic alloy nanocrystals can be organised in one-, two- and three-dimensional superstructures. Mixing different size nanocrystal sample with an appropriate ratio in size and packing fraction lead to the formation of mixed superlattices with high

packing densities. Crystallisation of monodisperse magnetic alloy nanocrystals in ordered three-dimensional superlattices is achieved via controllable destabilisation of toluene solution of nanocrystals. Perfectly faceted macroscopic (~20 – 30 nm) colloidal crystals of magnetic alloy nanocrystals ($CoPt_3$ and PtFe) have been obtained for the first time. HRSEM investigation showed the long range ordered nanocrystals with coherence over ten of microns. An external magnetic field has the strong influence on the arrangement of magnetic nanocrystals into 2D or 3D superstructures. Novel superstructures consisted of magnetic nanocrystals were prepared in an external magnetic field. Formation of periodic concentration stripes of $CoPt_3$ nanocrystals was observed in the parallel external magnetic field. When the external magnetic field was applied perpendicular to the substrate different types of needle-like nanocrystal assemblies were obtained. In relatively strong magnetic fields (~0.1 – 1 Tesla) mainly glassy solids with short-range ordering of magnetic nanocrystals were found while in weak magnetic fields (~0.01 – 0.02 Tesla) colloidal "supercrystals" can be formed.