Further studies using chemically produced silicon nanoparticles confirm the relation between blue luminescence, small cluster sizes and localised transitions. Zhong and co-workers report XRD diffraction peaks similar to the diamond structure of bulk crystalline silicon (Zhong et al., 2013). Size distributions were measured by TEM, for which an average size of 2.2 nm was found (Zhong et al., 2013). Li and co-workers observed very high quantum yields of blue fluorescence, up to 75%, which were attributed to surface treatement with nitrogen-containing agents (Li et al., 2013). Furthermore, Li showed that the fluorescence wavelength can be tuned by different ligands attached to nitrogen-capped silicon clusters (Li et al., 2016). Also, the quantum yield could be increased further, up to 90% and the emission bandwidth could be narrowed. They attribute their observations to localised transtions at the cluster surface and propose a 'ligand-law' controlling the photoluminescence (Li et al., 2016).

1.7 Conclusions

Silicon clusters consisting of a small number of atoms are fascinating objects through which one can study the evolution of material properties with complexity and size. Free clusters produced in molecular beams have properties that are unfavorable for light emission. However, when passivated or embedded in a suitable host, they may emit fluorescence. The current available data show that both quantum confinement and localised transitions, often at the surface, are responsible for fluorescence. By building silicon clusters atom by atom, and by embedding them in shells atom by atom, new insights into the microscopic origins of fluorescence from nanoscale silicon can be expected.

The methods needed to perform such experiments, such as spectroscopy in droplets of argon (Felix et al., 2001) and helium (Feng et al., 2015; Katzy et al., 2016), have recently been developed. It can be hoped that they will be used