Hessisches Kompetenzzentrum
für Hochleistungsrechnen

Structure Optimization, Dielectric and Magnetic Properties of Pure Silicon as well as Iron-Doped Silicon and Tin Clusters

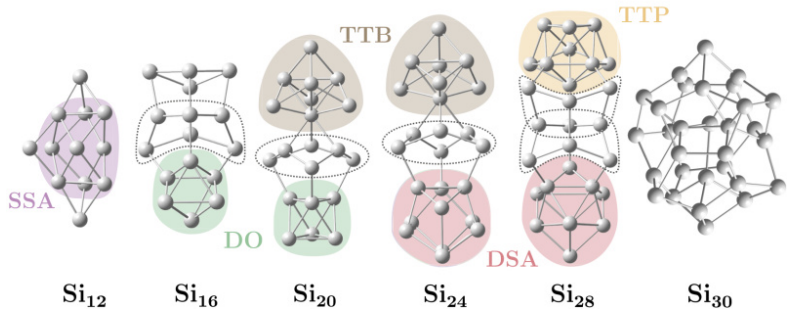

Figure 1: Exemplary selected geometric structures of SiN clusters to indicate the prolate growth patter up to the cluster Si30 which is quais-spherical. The reappearing sub-units are highlighted by different colours: distorted octahedron (DO, green), pentagonal bipyramid (PB, blue), triple-cappedtrigonal bipyramid (TTB, brown), double-capped trigonal prism(DTP, yellow), triple-capped trigonal prism (TTP, orange),single-capped square antisprism (SSA, purple) and a double-capped square antiprism (DSA, red). Additionally, reoccurring bowl-shaped Si6 units are circled with a dashed line.

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Clusters
Lichtenberg II Cluster Darmstadt

Software
GAUSSIAN, ORCA, Quantum ESPRESSO

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Introduction

The previous investigation of Sn_N clusters with N = 6−40 showed that below a clusters size of about 30 atoms, a prolate structure growth is dominant. However, larger clusters with 30 < N < 40 show again a quasi-spherical shape. Silicon is also a tetrel and the physico-chemical properties of clusters made of silicon and tin are shown to be very similar on the nanoscale. Therefore, it is interesting to investigate the geometric structures of silicon clusters and to compare both systems to get a deeper insight on the growth pattern of tetrel clusters. Additionally, we investigated the magnetic properties of endohedrally doped Sn_{12}TM clusters with TM = Cr, Mn and Fe. It was already observed that Sn_{12}Mn has very special magnetic properties, since it shows a high spin relaxation time within the time scale of the beam deflection experiment. To get a better understanding of the magnetic properties of doped tetrel clusters in general, we investigated the Sn_{12} clusters doped by Cr and Fe which are adjacent to Mn in the periodic table experimentally and by quantum chemical calculation.

Methods

Energetically-favored initial geometries were generated using a plane-wave Density Functional Theory-based (pw-DFT) Genetic Algorithm (GA) developed in our group. These calculations are performed using the Quantum Espresso software package.

Possible candidates are then optimized on the PBE0/def2-TZVPP level of theory. The existence of local minima has been verified by frequency analysis. These calculations were carried out with the quantum chemical program Gaussian16.
Additionally, for the endohedrally doped Sn12 clusters the magnetic properties are calculated with ORCA v5.0.4 on the DFT level of theory. Since it was shown that the results often do not match the experimental values, complete active space self-consistent field calculations (CASSCF) are carried out, for the first time for such large systems, to get a better description of the electronic structure and, thus, more accurate results on the magnetic properties.

Results

The comprehensive study of the geometrical structure of Si_N clusters with N = 12 − 30 shows that for this system the growth pattern is also dominated by prolate structures which are built of reappearing, very stable sub-units. Starting with the cluster Si_{27} quasi- spherical shapes appear again. For Si_{30} no more prolate shapes are found by quantum chemical calculations.
The calculation on the CASSCF level of theory of the g-factor which represents the magnetic properties revealed that the very different values observed experimentally for the three Sn_{12} clusters doped with Cr, Fe and Mn originate from spin-orbit coupling (SOC) between the tin cage and the dopant. Since there is no SOC in $Sn_{12}Mn$, the g-value is equal to the value of the free electron, g = 2, as already predicted by DFT.

Discussion

For most of the Si_N clusters with N = 12 − 30 an assignment of one structural isomer to the experimental data is possible. Additionally, it could be shown that, in contrast to Sn_N , for no cluster size two isomers are simultaneously present in the molecular beam. However, no distinct assignment of a structural isomer is possible for Si_{26} and Si_{28} based on our experiment, since the dielectric properties of all found isomers are very similar. Furthermore, it could be seen that a change of the exchange-correlation functional has a huge impact not only on the calculated value of the electric dipole moment but also on the energetic order of the structural isomers.
A more detailed analysis of the electronic excitations in $Sn_{12}TM$ with TM = Cr, Mn and Fe, firstly confirmed that no significant spin-orbit effects influence the g-factor of $Sn_{12}Mn$. Because of this, the value for the g-factor was already predicted correctly by DFT calculations. For $Sn_{12}Cr$ and $Sn_{12}Fe$ the g-factor is slightly lower and much higher, respectively, than the value of the free electron. The much more time consuming CASSCF calculations reveal that the different shifts originate from different kinds of electronic excitations relevant for the g-factor.

Publications

Rivic, F.; Schäfer, R. Magnetism of single-doped paramagnetic tin clusters studied using temperature-dependent Stern–Gerlach experiments with enhanced sensitivity: impact of the diamagnetic ligand field and paramagnetic dopant. Phys. Chem. Chem. Phys. 26, 12982-12992 (2024) https://doi.org/10.1039/D4CP00890A Rivic, F.; Lehr, A.; Schäfer, R. Dielectric Behavior and Prolate Growth Patterns of Silicon Clusters SiN with N = 12–30 by Cryogenic Electric Beam Deflection. J. Phys. Chem. A 128, 1853-1862 (2024) http://dx.doi.org/10.1021/acs.jpca.3c08432

Rivic, F. Influence of size and composition on the dielectric and magnetic properties of pure and doped tetrel clusters. PhD thesis, TU Darmstadt, (2024)

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