Hessisches Kompetenzzentrum
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Structure Discrimination and Magnetic Properties of $FeSn_N$ with N =8–15

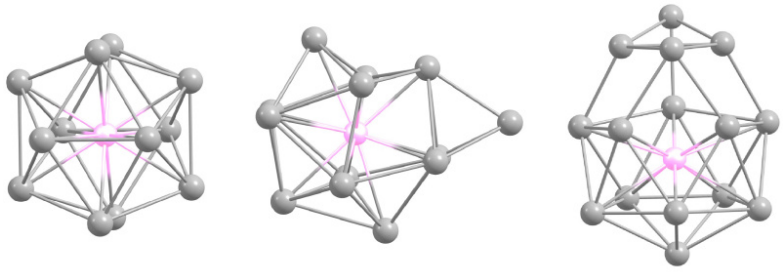


Figure 1: Predidcted ground state structures (GM) for Sn_NFe with N = 12, 13 and 15 at the PBE0/def2-TZVPP level of theory with their corresponding symmetry and calculated g-factors. Tin atoms are displayed as gray spheres while the iron atom is shown in pink.

Introduction

In the framework of the Collaborative Research Center (CRC 1487), iron is studied as a substitute for rare-earth metals in environmentally friendly technologies, since they are toxic or obtained by disputable methods. For this, iron is required to be investigated in varying compositions in order to reveal its characteristics, often being tunable in nature. In this regard, we want to study the influence of tin atoms as ligands on the iron atom and investigate their intriguing magnetic properties. We could already synthesize iron-doped tin probes and generate molecular beams which could then be investigated in electric and magnetic beam deflection experiments. To further validate and interpret the electric and magnetic deflection profiles, we want to examine computationally the geometries and the magnetically-relevant properties comprising *g*-factors and spin-rotation coupling constants. The latter properties are also to be calculated for $Pb_{12}X$ clusters (X = Al, Ga, In) which are predicted to possess very high *g*-factors.

Methods

Energetically-favored initial geometries were generated using a plane-wave Density Functional Theory-based (pw-DFT) Genetic Algorithm (GA) developed in our group. From the generated pool of structures candidates in the range of 1 eV relative to the energy of the energetically lowest-lying isomer are optimized on the PBE0/def2-TZVPP level of theory and verified by frequency analyses. The magnetic properties are then calculated with a relativistic Hamiltonian (ZORA).

Project Manager
Filip Rivic

Researchers
Andreas Lehr, Alexander Macion and Timo Schwab

Principal Investigator
Prof. Dr. Rolf Schäfer

Project Term
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Clusters
Lichtenberg Cluster Darmstadt

Software
GAUSSIAN, ORCA, Quantum ESPRESSO

Institute
Eduard-Zintl-Institut

University
Technische Universität Darmstadt

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Philipps Universität Marburg

Results

The geometric structures of Sn_NFe with N = 8–15 were calculated within this project. For most of the cluster sizes only one isomer is found within the considered energy range of 0.1 eV which is assumed to be a conceivable energy range for our experimental setup. However, the found geometries cannot be assigned clearly to the experimental data. Further, we calculated the electronic g-factors of the clusters $Sn_{12}Fe$, $Sn_{13}Fe$ and $Sn_{15}Fe$ to investigate the size-dependency of this property which allows good insight into the magnetic properties. Here, we could observe no such dependency, since these clusters all showed very similar g-factors of 2.1 slightly increased relative to the g-factor of a single electron ($g \approx 2$).
Additionally, the magnetic properties of $Pb_{12}X$ clusters (X = Al, Ga, In) were calculated. Here, highly increased g-factors of about 4 were calculated for the $Pb_{12}Al$ and $Pb_{12}In$ clusters. In contrast to that, the g-factor of the $Pb_{12}Ga$ cluster is decreased to g = 1.6.

Discussion

Since the iron atom has a spin multiplicity of S = 2, the calculation of the geometrical structures of Sn_NFe clusters is more complex than for the previous calculated S = ½ systems. This was also evident in the computing time needed to optimize one cluster structure on the higher level of theory. Single optimization steps needed more time than initially assumed. However, the used computing resources were still within the range of the estimation. The increased computing time is most likely due to the computational routine of the GA. Here, the spin multiplicity is not considered, since the cluster is treated as a unit cell of a solid to reduce the needed computational resources. However, the resulting initial geometric structures are not suited as good starting points for the further optimization and need much more time to converge. To circumvent this problem to either verify the calculated structures for the respective sizes or be able to calculate even larger clusters with more tin atoms, the initial structures have to be more accurate. This can be achieved by either introducing the spin multiplicity into the calculation routine of the GA or by choosing the initial structures without the GA by considering other already calculated open shell systems with higher spin multiplicity. The calculated magnetic properties indicate also that the cluster possess a considerable high zero-field splitting constant in the range of (10–30)cm^{-1}.
Furthermore, the strongly increased g-factors in the $Pb_{12}Al$ and $Pb_{12}In$ cluster can be explained on the one hand by a very high spin-orbit coupling constant of Pb (three times higher than the one for tin) and on the other hand by the nonvanishing angular momentum in the contributing molecular orbitals. These molecular orbitals, however, do not contribute to the g-factor in the case of the $Pb_{12}Ga$ cluster. This can be understood by considering the d-block contraction in the gallium atom which leads to an icosahedral rather than a pyritohedral structre.

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Publications

Lehr, A., Rivic, F., & Schäfer, R.: "Enhanced Electronic g-Factors in Magic Number Main Group Bimetallic Nanoclusters", Journal of the American Chemical Society, 145(4), 2070–2074, 2023
https://doi.org/10.1021/jacs.2c12959

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