新規高温超伝導体の創製に向けた球状カーボン分子C60への内外双方向ドーピングによる電子特性制御

Towards the Fabrication of Novel High-Temperature Superconductors: Control of Electronic Properties by Bidirectional Internal and External Doping of Spherical Carbon Molecules C60

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Most superconductors have simple structures built from atoms, but superconductors made from molecules arranged in solid structures also exist. Prominent examples are those of nanocarbon superatoms, the fullerenes (C_{60}) - they show the highest superconducting transition temperature, T_c (38 K) and do not lose their zero resistance performance even under extremely high magnetic fields (>90 Tesla). In this research, we are using a new building block for molecular superconductors beyond C_{60}. This is [Li@C_{60}], an endohedral metallofullerene, which incorporates a Li^+ ion inside the C_{60}^- cage. We have developed a scalable method to obtain neutral Li^+@$C_{60}^{(-)}$ by chemical reduction of Li_+@C_{60} using decamethylferrocene. Investigation of solid [Li@C_{60}] revealed the presence mainly of dimers (Li@C_{60})$_2$, together with the co-existence of a small fraction of the EPR-active monomer form. However, although this preparative route does not demand long reaction times, it leads to poorly crystalline materials. This is unlike electrolytic reduction routes, which afford very crystalline materials but in small quantities.

Nonetheless this allows the in-depth structural characterization, which has unveiled a highly symmetric hexagonal crystal structure comprising disordered dimer units in analogy with $(C_{59}N)_2$ or molecular dihydrogen. To date, we have achieved a full structural characterization of the structural properties of the endohedral metallofullerene as a function of temperature down to liquid helium temperatures and as a function of pressure up to applied hydrostatic pressures of 12 GPa.

研究目的

本申請研究においては、炭素系材料を基盤とした新規超伝導体の創製を目的とする。そのために、高純度試料の合成手法の確立と基礎物性の理解及び超伝導発現の原理解明を推進する。申請者は分子材料中で最も高い超伝導相転移温度（38 ケルビン）と上部臨界磁場（90 テスラ）を有する炭素系材料を開発した［Nature Mater. 2008, Science 2009, Nature 2010, Nature Communications 2012, Science Advances 2015, Nature Communications 2017 他］。

この成果をさらに発展させ、フラーレン（C60）を基盤物質としてより高い超伝導相転移温度を示す新たな炭素系分子材料を創製する。

概　　要

Superconductors have no electrical resistance and carry electricity without losing energy. The development of new materials in order to achieve transition temperatures to zero-resistance as high as possible is at the extreme forefront of current challenges in materials science. C_{60} superconductors played leading role in materials research in the last 30 years achieving a robust zero-resistance state at record temperatures and surviving at extremely high magnetic fields. But they have reached their upper limit. Here we are facing the challenge of surpassing the past performance of C_{60} superconductors. We are targeting to achieve this by developing the uncharted field of high-symmetry superatomic carbon frameworks with metal ions inside the cages and using unprecedented mechanisms of electronic control by dual-direction internal and external electron doping. To-date we have achieved the first milestone of producing and characterizing in the bulk the parent neutral lithium endohedral C_{60} fullerene both as a function of temperature and pressure - this constitutes the starting material, the synthon of our eventual targets.

In addition, we addressed the family of rare-earth (RE) metal C_{60} fullerides, which constitute an intriguing class of strongly-correlated molecular systems as they present the possibility of strong coupling between two electronically active sublattices, the anionic $p\pi(C_{60})$ and cationic 4f,5d(RE) sublattices both of which are dominated by strong electronic correlations. Here the properties are dominated by the extreme narrow-band behaviour of the rare-earth cation f-electron sublattice with the supporting anion sublattice again playing a charge-balancing structural-spacer role. As electronically active anion solids, the rare-earth fullerides can have properties intrinsically distinct from comparable rare-earth compounds with closed shell anions, and the emergence of novel phenomena such as co-existence of Kondo f-electron behaviour with C60-based pπ-electron superconductivity may be anticipated.

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