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論文名 「希土類金属フラライド  $RE_{2.75}C_{60}$  における混合原子価状態：  
格子—電子自由度の協奏的な振る舞い (Mixed-valence Rare-earth Fullerenes,  $RE_{2.75}C_{60}$ : Coupling of Lattice and Electronic Degrees of Freedom)」

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## 論文要旨

### Abstract of Thesis

The study of strongly correlated electron systems is at the forefront of contemporary condensed matter research because such materials, which include transition metal oxides (colossal magnetoresistive manganites, high- $T_c$  cuprates) and intermetallic heavy fermion systems, display remarkable electronic properties that challenge existing theory for satisfactory explanations. Coulomb repulsion between electrons leads to correlations between the particles, which opposes their natural tendency to form extended bands. A rich variety of behaviors occurs when these interactions become dominant *e.g.* when the on-site Coulomb energy (quantified by the Hubbard  $U$ ) is larger than that gained by delocalizing the outer electrons in the solid (measured by the bandwidth  $W$ ), the electrons become localized at each lattice site and the material exhibits vanishing electrical conductivity (Mott-Hubbard insulating state). Another manifestation of such many-body interactions is provided

by *f*-electron systems in which the correlations are so strong that the effective mass of the quasiparticles becomes several orders of magnitude higher than the bare electron mass, leading to intermediate valence, Kondo, and heavy fermion behavior. The interplay between charge, lattice, orbital, and magnetic degrees of freedom in such systems can be tuned sensitively both chemically (doping by isovalent or aliovalent ions) and physically (varying an external parameter such as pressure or magnetic field).

In this research project, hybrid *f*-/*p*-electron molecular materials have been researched; in particular, molecular-based strongly correlated *f*-electron fullerides in which the electronically-active C<sub>60</sub> anionic sublattice (*p*-electron) is combined with the mixed configuration behavior of selected rare earth cations (*f*-electron). The fullerene chemistry of the rare earths has not been explored extensively in a systematic way due to the difficulties in devising reliable protocols for preparation of single-phase materials. A representative example of such a material is provided by the samarium fulleride Sm<sub>2.75</sub>C<sub>60</sub>, which exhibits a temperature-induced valence transition on cooling at ambient pressure that is accompanied by a giant negative isotropic lattice response. This effect is reminiscent of the valence transitions in strongly correlated intermediate-valence Kondo insulators like SmS, which undergoes a pressure-induced abrupt catastrophic transition from a black semiconducting to a gold metallic phase. Additional experiments on Sm<sub>2.75</sub>C<sub>60</sub> have identified a pressure-induced valence transition, which is accompanied by a huge lattice collapse and a change in color, implying a drastic change in the conducting properties.

Here, we employed isovalent Ca substitution of Sm to afford the series of (Sm<sub>1-x</sub>Ca<sub>x</sub>)<sub>2.75</sub>C<sub>60</sub> ( $0 \leq x \leq 1$ ) fullerides in the attempt to map out in a systematic fashion the crystal structural features and electronic properties of the materials as a function of both chemical and physical pressure, shedding light on the mechanism determining the valence fragility of Sm cations and the electron reservoir role

played by the anionic  $C_{60}$  sublattice. This work comprised a combined study of Raman spectroscopy, synchrotron X-ray powder diffraction, and synchrotron X-ray absorption spectroscopy in both total and partial fluorescence yield modes (TFY-XAS/PFY-XAS). This thesis consists of seven Chapters summarized as following. The background of research and relevant literature review are described in Chapter 1, which is followed by the project outline and the motivation of research summarized in Chapter 2. Instrumentation, experimental methodology, and data treatment and analysis procedures used in this project are described in Chapter 3.

The influence of divalent calcium substitution on the mixed valency response of samarium cations in the parent  $Sm_{2.75}C_{60}$  material at ambient pressure and temperature is discussed in Chapter 4.  $Sm_{2.75}C_{60}$  adopts an orthorhombic superstructure of the commonly encountered face-centered-cubic structure of fullerides with stoichiometry  $A_3C_{60}$ , arising from the long-range ordering of Sm vacancies, and can be driven to a lattice-collapsed metallic state due to a valence transition towards  $Sm^{3+}$  upon pressurization. Here, we attempt to mimic the physical pressure effect on the electronic properties by co-intercalation of the smaller-size valence-precise  $Ca^{2+}$  ion to form the series of ternary solid solutions,  $(Sm_{1-x}Ca_x)_{2.75}C_{60}$  ( $0 \leq x \leq \frac{2}{3}$ ). Excellent miscibility of samarium and calcium ions aided by their similar ionic radii ( $Sm^{2+}$ ; 1.14 Å,  $Ca^{2+}$ ; 0.99 Å,  $Sm^{3+}$ ; 0.96 Å) leads to ideal solid solution formation with samarium and calcium cations randomly occupying the interstitial sites of the  $C_{60}$  anionic sublattice. This results in a linear dependence of the unit-cell volume on the calcium content,  $x$  obeying Vegard's law. Synchrotron X-ray absorption spectroscopy (XAS) at the Sm  $L_3$  edge in the partial fluorescence yield (PFY) mode at ambient conditions was employed to authenticate the mixed valence character of this family of materials, revealing the fact that chemical pressure acts as a fine parameter to continuously tune the average oxidation state of the rare-earth ions at ambient pressure and temperature from +2.07(3) ( $x = 0$ ) to +2.33(2) ( $x = \frac{2}{3}$ ). Assuming full charge transfer between the

metal ions and  $C_{60}$ , the charge on the  $C_{60}$  units remains invariant throughout the series at approximately  $-5.78$ , corresponding to fully occupied  $C_{60}$  orbital states ( $t_{1u}$ , LUMO).

The pressure-driven first-order electronic (valence) phase transition in the family of  $(Sm_{1-x}Ca_x)_{2.75}C_{60}$  fullerides is discussed in Chapter 5. Here we study their electronic response to the application of pressure in the range  $0 - 9$  GPa. Synchrotron X-ray absorption measurements in the total and in the high-resolution partial fluorescence yield modes (TFY-/PFY-XAS) at ambient temperature show the onset of an abrupt strongly hysteretic first-order reversible phase transition at  $\sim 4$  GPa, accompanied by a drastic increase in the average Sm valence towards  $3+$  and the emergence of a metallic phase. Raman spectroscopy provides complementary evidence of pressure-driven metallization appearing as reversible hysteretic pressure response of  $C_{60}$  intramolecular vibrational modes (disappearance/recovery of the well-resolved Raman peaks upon pressure increase/decrease) in excellent agreement with the high pressure region in which samarium valence evolution occurred. This behavior is reminiscent of the electronic and lattice response to pressure of highly correlated Kondo insulators like SmS and its ternary derivatives,  $Sm_{1-x}R_xS$  ( $R = Ca, Y$ ). However, a distinguishing feature of the fulleride systems is that the  $C_{60}$  anionic sublattice can act as an electron reservoir due to the availability of a close-lying band derived by the  $t_{1g}$  orbitals and can accept excess charge as the  $4f$ -electron occupation number decreases. The observed electronic response as a function of pressure is thus opening new possibilities for accessing metallic fullerides at elevated pressures.

The accompanying pressure-driven first-order structural phase transition in the family of  $(Sm_{1-x}Ca_x)_{2.75}C_{60}$  fullerides is discussed in Chapter 6. Of particular interest is the crystalline structure adopted by  $Sm_{2.75}C_{60}$  and its analogues. This derives from the conventional face-centered cubic (*fcc*) structure of  $A_3C_{60}$  alkali fullerides in which the metal ions fully occupy the available large octahedral

and smaller tetrahedral interstices. The non-stoichiometry of the Sm sublattice necessitates the absence of one of the eight tetrahedrally residing metal ions. The long-range ordering of these Sm metal defects leads to the formation of a  $2a \times 2a \times 2a$  superstructure whose orthorhombic unit cell (space group  $Pcab$ ) contains 2008 atoms (32  $C_{60}$  units and 88 metal ions) and has a very large lattice parameter on the order of  $\sim 28$  Å. Notably, the existence of the ordered tetrahedral defects in this non-stoichiometric phase leads to an equilibrium structure with significant shifts of the rare-earth metal ions away from the centers of the occupied octahedral and tetrahedral interstices by  $\sim 2.3$  and  $\sim 0.4$  Å, respectively at ambient condition (termed O phase). Synchrotron X-ray powder diffraction measurements at high pressure and ambient temperature reveal that  $(Sm_{1/3}Ca_{2/3})_{2.75}C_{60}$  is a compressible solid with a bulk modulus,  $K_0 = 24(1)$  GPa, that transforms to a more densely packed isostructural high-pressure phase (termed O' phase) above  $\sim 4$  GPa. The first-order phase transition retains the formation of the superstructure and is accompanied by a discontinuous lattice size decrease ( $\Delta V/V \sim 2\%$ ). The O' phase is stabilized by the release of the steric crowding that develops upon compression; the Sm/Ca metal ions, which reside in the tetrahedral and octahedral holes of the fulleride sublattice, shift from their off-centered positions at low pressure (O phase) to nest at the centers of the interstices (O' phase). The nearly exact coincidence of the pressure response of the reversible hysteretic  $O \leftrightarrow O'$  phase transformation with that of the samarium valence transition from  $+2.33(2)$  to  $+2.71(3)$ , as established before by synchrotron X-ray absorption spectroscopy, unambiguously establishes an intimate link between the crystal and electronic structures of the  $(Sm_{1/3}Ca_{2/3})_{2.75}C_{60}$  fullerides.

Comprehensive understanding of the emergent physics in which structural, optical, and electronic degrees of freedom are strongly coupled with each other in the family of  $(Sm_{1-x}Ca_x)_{2.75}C_{60}$  fullerides throughout the discussion of Chapters 4-6 is summarized in Chapter 7. The concept of hybrid  $f$ - and

*p*-electron systems realizes electronic interplay between rare-earth valence fluctuations and C<sub>60</sub> cage acting as electron reservoir paving the way towards unexplored physical responses. Especially important is the search for superconductivity in the collapsed metallic phases at high pressures where the coupling between the anion and cation sublattices is extremely enhanced. As superconductivity is also supported by the fulleride sublattice, the ability to tune band filling *via* the changes in the rare-earth electronic structure at high pressure opens a new route to unconventional superconductors as a future perspective.

## 審査結果の要旨

本論文は、希土類金属フラライド  $\text{RE}_{2.75}\text{C}_{60}$  が示す電子・構造物性の体系的理解に向けて、放射光 X 線回折測定・X 線吸収分光法により、化学・物理圧力下における希土類金属フラライドの価数・格子・伝導特性の評価に関する研究成果をまとめたものであり、以下の結果を得ている。

- (1) 混合原子価状態を示す希土類金属サマリウム(Sm)を含む  $\text{Sm}_{2.75}\text{C}_{60}$  に対し、二価イオン状態を安定的にとるカルシウム(Ca)によって置換した  $(\text{Sm}_{1-x}\text{Ca}_x)_{2.75}\text{C}_{60}$  系を調製した。放射光 X 線吸収分光測定により、 $\text{Sm}_{2.75}\text{C}_{60}$  での Sm 酸化状態は 2 価優位であることが示された一方で、Ca 置換量の増加に伴い Sm 価数が 3 価優位へと遷移することが明らかとなった。一方、 $\text{C}_{60}$  酸化状態は Ca 置換量に依存せず、LUMO が完全に充填された電子状態を安定的に取ることを示唆する結果が得られた。
- (2) 次に圧力セルを用いた放射光 X 線吸収分光測定によって、常温における Sm 価数状態の圧力依存性を調査し、4GPa 付近で圧力に誘起される 2 価 $\leftrightarrow$ 3 価の価数転移が発現することを明らかにした。物理圧力印加に誘起される Sm 価数転移によって、 $\text{C}_{60}$  の電子状態は LUMO が充填された絶縁体(低圧)から LUMO+1 に余剰電子が供給された金属状態(高圧)に遷移することが示された。
- (3) 圧力に誘起される Sm 価数・ $\text{C}_{60}$  酸化数転移が結晶構造に与える影響を調査した。圧力印加によって、Sm 価数転移点付近での急激な体積収縮を伴う isosymmetric な構造相転移を示すことが明らかとなった。リートベルト解析により金属配位構造を詳細に調査した結果、体積収縮は Sm 価数転移(2 価 $\rightarrow$ 3 価)に由来し、さらに価数転移は圧迫された四面体間隙での局所構造に起因するという、希土類金属とフラーレン分子の電子・格子自由度が協奏的に相関していることを明らかにした。

以上の諸成果は、炭素由来の  $p$  電子と希土類金属由来の  $f$  電子間に強い相関を示す希土類金属フラライドの物性を体系的に明らかにしたものであり、本分野における学術的發展に大きく貢献するものである。また、申請者が自立して研究活動を行うのに必要な能力と学識を有することを証したものである。学位論文審査委員会は、本論文の審査および最終試験の結果から、博士(工学)の学位を授与することを適当と認める。