JAIST Repository
https://dspace.jaist.ac.jp/

Title	金属ドープしたフラーレン化合物における構造相転移及び結合性質の研究
Author(s)	Dam, Hieu Chi
Citation	
Issue Date	2003-03
Type	Thesis or Dissertation
Text version	none
URL	http://hdl.handle.net/10119/2130
Rights	
Description	Supervisor:三谷　忠興，材料科学研究科，博士

JAIST
JAPAN
ADVANCED INSTITUTE OF
SCIENCE AND TECHNOLOGY

Japan Advanced Institute of Science and Technology

Study of Bonding Nature and Structural Transitions in Metal doped Fullerene Materials

Mitani Lab. 040014 Dam Hieu Chi

Introduction

The closed cage nearly spherical molecule C_{60} and related fullerene molecules, the third allotrope of carbon following diamond and graphite, have attracted a great deal of interest in recent years because of their unique structure and properties (Fig.1). For a variety of reason, fullerenes together with nanotubes are of broad-based interest to scientist in many fields, and are expected as key materials for nanotechnology.

Intercalation and polymerization of fullerene solids are known as effective method to functionalize fullerene based materials. The intercalation of fullerene solids yields a variety of compounds with different physical properties, which significantly change depending upon the intercalated species (Fig. 2). Thus the information on the bonding nature including charge transfer properties is essential in understanding the physical properties of fullerene intercalated materials. Another unique aspects of fullerene molecules is the formation of interfullerene bondings, which afford a rich variety of nanoscale network structures and electronic states. It is widely known that fullerene molecules can be connected either by 2+2 cycloaddition, by C-C single bonds depending on the electronic states of fullerenes (Fig. 3). Combination of intercalation and polymerization, in other words, bridging fullerenes with intercalated metals, which has not been known so far, might provide novel aspects of solid state fullerenes. To achieve this new state, intercalation of rare earth metals might be promising, because the interaction between metal ions and fullere anions are stronger than the case of alkali metals.

The main purposes of our research are:

- To explore the novel family of rare-earth metal doped fullerene materials.
- To clarify the bonding nature of the new compounds and to elucidate unique structural properties

Experiment

The compounds of metal doped fullerene materials have been synthesized by a solid-state reaction by mixing a stoichiometric amount of metal and fullerene powders. All of the mixed powder was sealed in a quartz tube under high vacuum. Heat treatments were carried out at 550∫C - 600∫C for several days.

The samples of M_6C_{60} (M= K, Ba, Eu, Sm) were synthesized with high crystallinity. A series of new stable materials RE_3C_{70} (RE= Sm, Eu, Yb) has been successfully synthesized.

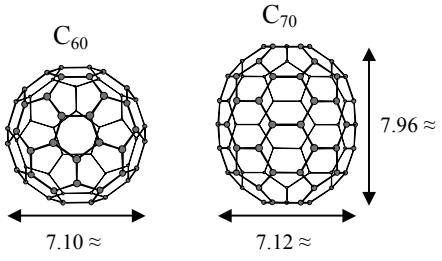

Figure 1. Molecular structure of C_{60} and C_{70}

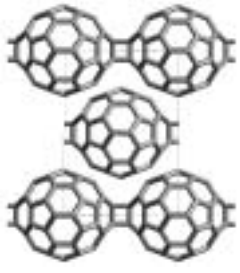

Figure 2. Crystal structure of polymerized C_{60}.

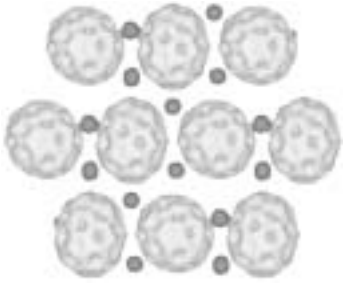

Figure 3. Electron density distribution map of metal bridged fullerene dimer.

All of the synthesized samples were sealed in thin quartz glass capillaries of 0.3 mm in outer diameter for high-resolution synchrotron x-ray powder diffraction experiments, which performed at SPring-8 and KEK. Synchrotron x-ray powder diffraction experiments were carried out for samples at high pressure and high temperature as well. In high-pressure experiments, quasi-hydrostatic pressure was generated by a diamond anvil cell. The high-temperature experiments were performed using a high temperature gas flow system.

The structure analysis in the electron density level was carried out using a combination of Rietveld method and Maximum Entropy Method (Rietveld/MEM analysis).

Result and Discussion

1. Experimental visualization of orbital hybridization in M_6C_{60} (M= K, Ba, Eu)

Figure 4 shows the electron density distributions of M_6C_{60} (M= K, Ba, Eu) estimated from synchrotron x-ray diffraction experiments *via* Rietveld/MEM analysis. A complete charge transfer behavior was observed for the case of K_6C_{60}. An electron integrate results entirely K^+ state of K atoms. The bonding in crystalline of K_6C_{60} is ionic and each C_{60} molecules binds six excess electrons. In contrast, electron density of Ba_6C_{60} and Eu_6C_{60} clearly exhibits an overlapping of electron density between metal atoms and C_{60}. Partial charge transfers (from metal to C_{60}) and covalency in these materials were experimentally confirmed for the first time. The hybridization between metal and carbon is stronger in Eu_6C_{60}, than that in Ba_6C_{60}. The present results clearly demonstrate that the bonding nature of fullerene intercalates significantly changes depending upon the intercalated species.

2. Covalent metal-carbon bonds and structural transitions in RE_3C_{70} (RE= Sm, Eu, Yb)

All of the diffraction patterns of RE_3C_{70} (RE= Sm, Eu, Yb) can be indexed on monoclinic cells, which derived by deformation of the f.c.c cells. Especially, a single phase of Sm_3C_{70} was synthesized allow us performing a full structural analysis of this compound. A Rietveld/MEM analysis was performed for the diffraction data of Sm_3C_{70}, and obtained electron density distribution is shown in Fig 3. A strong covalent Sm-C bond was discovered in Sm_3C_{70}, forming a unique C_{70}-Sm-C_{70} dimer structure. In contrast to the well known interfullerene bonding *via* 2+2 cycloaddition and C-C single bonds, the C_{70}-M-C_{70} type bonding in solids is quite new, possibly offering a new opportunity to investigate novel structural properties based on this interfullerene bonds. Particular interests are the pressure effect and thermal effect on this novel dimer structure, because they have provided numerous important and interesting information on the bonding properties in fullerites and fullerides.

Synchrotron x-ray powder diffraction profiles of Sm_3C_{70} and Eu_3C_{70} were collected at pressures between ambient and 5.0 GPa. A reversible first-order structural phase transition associated with almost 2.7-2.9% reduction of the unit

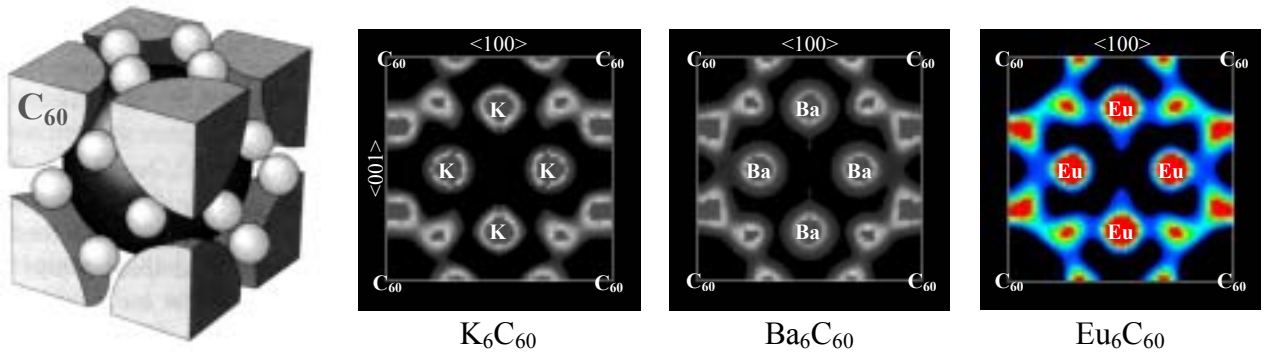

Figure 4. Structural model of <100> basal plane of M_6C_{60} structure (left), and experimentally determined electron density distribution for M=K, Ba, and Eu.

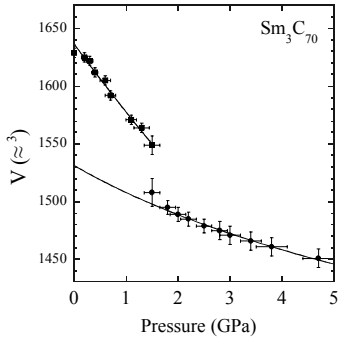

Figure 5. Pressure dependence of unit cell volume of Sm_3C_{70}.

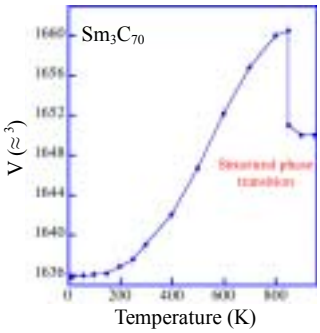

Figure 6. Temperature dependence of the unit cell volume of Sm_3C_{70}.

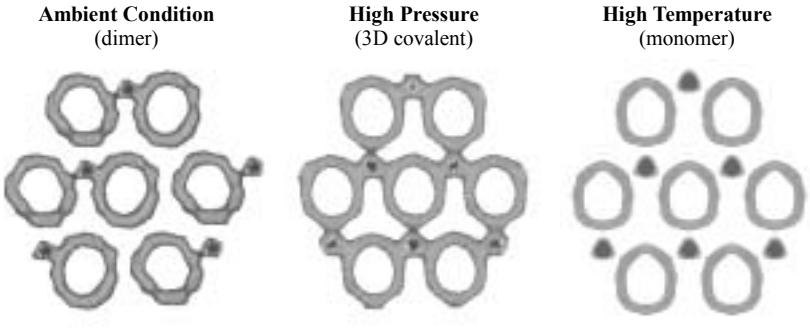

Figure 7. Cross section of electron density distribution map at various states of Sm_3C_{70}.

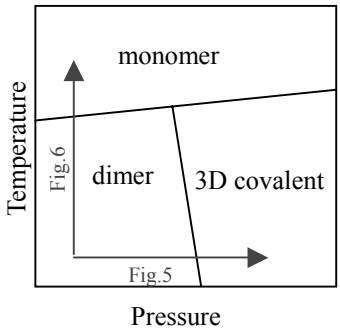

Figure 8. Schematic phase diagram of Sm_3C_{70}.

cell volume was discovered at about 1.5 GPa for both cases of Sm_3C_{70} and Eu_3C_{70} (Fig. 5). Structural analyses based on the Rietveld method combined MEM prediction have shown that the transition takes place when the size of the tetrahedral hollow is smaller than the ionic radii of Sm^{2+} and Eu^{2+}. Furthermore, the long axis of C_{70} molecules, which were aligned in zigzag pattern at ambient pressure, are realigned parallel to each other at high pressure (Fig. 7). High temperature powder x-ray diffraction experiments also have been carried out in a range of 20K-1000K, and a reversible first-order structural phase transition associated with reduction of the unit cell volume was discovered for three type of RE_3C_{70} (*RE*=Sm, Eu, Yb) at high temperature (Fig. 6). Structural analyses have shown that the transition takes place when the bond is broken, and C_{70} molecules rotate freely around their long (five fold) axis (Fig. 7). The phase diagram of Sm_3C_{70} is shown in Figure 8. These features at high pressure and high temperature, which have not been encountered so far in other fullerides, indicate that the phase transition observed is ascribed to the unique bonding nature of rare earth C_{70} compounds.

Conclusion

We have studied the bonding nature and phase transition in metals doped fullerenes. The result of our research are summarized as follows:

- The first demonstration of the hybridization of metal and C_{60} orbitals in M_6C_{60} system.
- Synthesis of new materials RE_3C_{70} (*RE*= Sm, Eu, Yb), which displayed a strong covalent bonding between metal and fullerene that causes a novel fullerene dimer structure (C_{70}-Sm-C_{70}).
- Discovery of pressure- and temperature-induced phase transition in RE_3C_{70}, associated with a significant changes of bonding nature between carbon and metals.

The results of this research will potentially open a new aspect in nano scale designing of fullerene materials.

Thesis contents:

1. Introduction 1
2. Rietveld analysis and Maximum Entropy Method 12
3. Bonding nature in C_{60} fullerides doped with metals M_6C_{60} (M= K, Ba, Sm,Eu) 33
4. Structural study of C_{70} fullerides doped with rare earth metals RE_3C_{70} (RE= Sm, Eu, Yb) 47
5. Pressure induced structural phase transition in C_{70} fullerides doped with rare earth metals RE_3C_{70} (RE= Sm, Eu) 65
6. Thermal induced structural phase transition in C_{70} fullerides doped with rare earth metals RE_3C_{70} (RE= Sm, Eu, Yb) 86
7. Structural studies of other metal doped fulleride materials 101
8. Conclusions 110
9. Appendix 115
10. Bibliography 123
11. Publication list 129

List of Publications:

1. Pressure-induced structural phase transition in fullerides doped with rare earth metals
   H. C. Dam, Y. Iwasa, K. Uehara, T. Takenobu, T. Ito, T. Mitani, E. Nishibori,
   M. Takata, M. Sakata, Y. Ohishi, K. Kato, and Y. Kubozono.
   Physical Review B, *in press* (2003).
2. Synthesis, structure, and magnetic properties of the fullerene-based ferromagnets Eu_3C_{70} and Eu_9C_{70}
   T. Takenobu, H. C. Dam, S. Margadona, K. Prassides, Y. Kubozono, N. Fitch, and Y. Iwasa.
   Journal of the American Chemical Society, *in press* (2003).
3. An experimental probe of bonding nature in rare earth metal doped fullerenes
   Dam Hieu Chi, Y. Iwasa, T. Mitani, M. Takata, E. Nishibori, and M. Sakata.
   American Institute of Physics Vol. 633, 51-54 (2002).
4. Correlation between Molecular Rotation and Electronic Properties
   Y. Iwasa, H. Shimoda, K. Ishii, T.Takenobu and Dam Hieu Chi.
   Solid State Physics, Vol. 37, No. 9, 595 (2002), (in Japanese).
5. Bridging fullerenes with metals
   Dam Hieu Chi, Y. Iwasa, X. H. Chen, T. Takenobu, T. Ito, T. Mitani,
   E. Nishibori, M. Takata, M. Sakata and Y. Kubozono.
   Chemical Physics Letters, Vol. 359, 177-183 (2002).
6. Dimmer Structure of Sm_3C_{70}
   H. C. Dam, X. H. Chen, T. Takenobu, T. Itou, Y. Iwasa, T. Mitani,
   E. Nishibori, M. Takata and M. Sakata.
   American Institute of Physics Vol. 590, 447 (2001).
7. Intralayer Carbon Substitution in the MgB_2 Superconductor
   T. Takenobu, T. Ito, Dam Hieu Chi, K. Prassides and Y. Iwasa.
   Physical Review B 64, 134513-134515 (2001).
8. Compressibility of the MgB_2 Superconductor
   K. Prassides, Y. Iwasa, T. Ito, D. H. Chi, K. Uehara, E. Nishibori, M. Takata,
   S. Sakata, Y. Ohishi, O. Shimomura, T. Muranaka, and J. Akimitsu.
   Physical Review B 64 012509 (2001)
9. Synthesis, structure, and transport properties of novel fullerides A_3C_{70} (A=Ba and Sm)
   X. H. Chen, D. H. Chi, Z. Sun, T. Takenobu, Z. S. Liu, and Y. Iwasa.
   Journal of the American Chemical Society Vol. 122, 5729-5732 (2000)
10. Structure and Magnetic Characterisation of $Ce@C_{82}$
    C. J. Nuttall, Y. Inada, Y. Watanabe, K. Nagai, T. Muro, D. H. Chi, T. Takenobu, Y. Iwasa and K. Kikuchi.
    Mol. Crys. and Liq. Crys., Vol. 340, 635-638 (2000).
11. Structure and properties of a fulleride Sm_6C_{60}
    X. H. Chen, Z. S. Liu, S. Y. Li, D. H. Chi and Y. Iwasa.
    Physical Review B 60, 6183-6186 (1999)
12. Crystal Structure and Physical Properties of Metal Intercalated fullerenes
    Dam Hieu Chi, X. H. Chen, T. Takenobu, Y. Iwasa.
    Proceedings of The Third International Workshop on
    Materials Science (IWOMS'99), Hanoi, November 2-4, 1999, p 407.
13. Structural and magnetic studies of the endohedral metallofullerene $Ce@C_{82}$
    C. J. Nuttall, Y. Watanabe, Y. Inada, K. Nagai, T. Muro, D. H. Chi,
    T. Takenobu, Y. Iwasa, and K. Kikuchi.
    American Institute of Physics Vol. 486, 115 (1999).