

Title	フラーレン・インターカレーション化合物の合成と固体物性
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Citation	
Issue Date	2001-03
Type	Thesis or Dissertation
Text version	none
URL	<a href="http://hdl.handle.net/10119/2102">http://hdl.handle.net/10119/2102</a>
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Description	Supervisor:岩佐 義宏, 材料科学研究科, 博士

# Synthesis and solid state properties of fullerene intercalation compounds

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## 1. INTRODUCTION

Generally, the carbon cluster is called fullerenes. It is well known that the Nobel Prize was awarded for the discovery of the soccer ball-shaped fullerene,  $C_{60}$ . Fullerenes usually form van der Waals solids with large interstitial sites, which are a few angstrom in diameter. These interstitial sites can be occupied by not only metal ions but also small molecules. Moreover, because of its very specific spherical shape, fullerene molecules are able to rotate easily with a fixed center of gravity. They are sole molecules that have a rotational degree of freedom which should provide novel aspect in fullerene based solids. The present research is concerned with two specific features of fullerenes, namely, the molecular rotation and intercalation, and has derived new science from

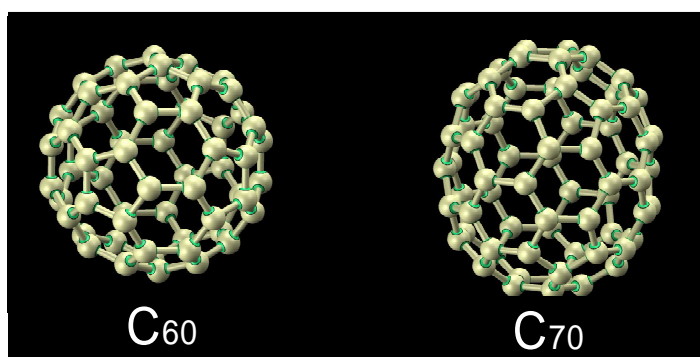


Figure 1. Molecular structures of  $C_{60}$  and  $C_{70}$ .

the two abundant fullerenes  $C_{60}$  and  $C_{70}$  (Figure 1). In  $C_{60}$  compounds, the author has synthesized new types of fullerene-based antiferromagnets with the highest Neel temperature ( $T_N$ ) among molecular materials. Moreover, we found that the orientational ordering of molecules are closely correlated with the magnetic spin structure *via* molecular orbital. For  $C_{70}$  fullerenes, several new intercalation compounds of alkaline earth metals and rare earth metals have been discovered, including the first  $C_{70}$  based ferromagnets.

## 2. $C_{60}$ COMPOUNDS

Fullerene  $C_{60}$  is known to form a vast variety of compounds including superconductors, by intercalation of alkali (*A*) metals, alkaline earth metals, rare earth metals, and molecules. Especially,  $A_3C_{60}$  superconductor has attracted considerable interest due to its high superconducting transition temperature ( $T_C$ ), which is 33 K at its maximum at ambient pressure, only surpassed by copper oxide high  $T_C$  superconductors. For example,  $K_3C_{60}$  is the most well known superconductor with

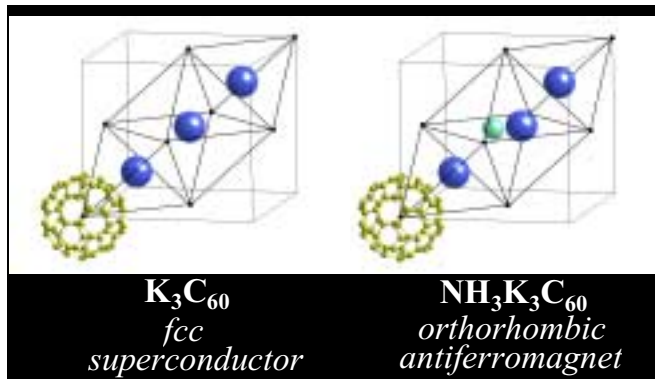


Figure 2. Schematic structures of  $K_3C_{60}$  and  $NH_3K_3C_{60}$ .  $C_{60}$ s,  $K^+$  ions,  $NH_3$  molecule are represented as dots, big and small balls, respectively.

$T_C=19$  K. The intercalation of neutral ammonia molecules into *fcc*  $K_3C_{60}$  transforms the crystal structure to orthorhombic and changes its ground state drastically from superconductivity to antiferromagnetism (Figure 2). Because the crystal and electronic structures of these materials are very similar to each other, the strong correlation between superconductivity and antiferromagnetism is expected. The goal of this study is to clarify the feature of this important antiferromagnetic phase. For this purpose, the author adopts two kind of approach. One is a detailed structural research of  $(NH_3)K_3C_{60}$ . A combined analysis of the

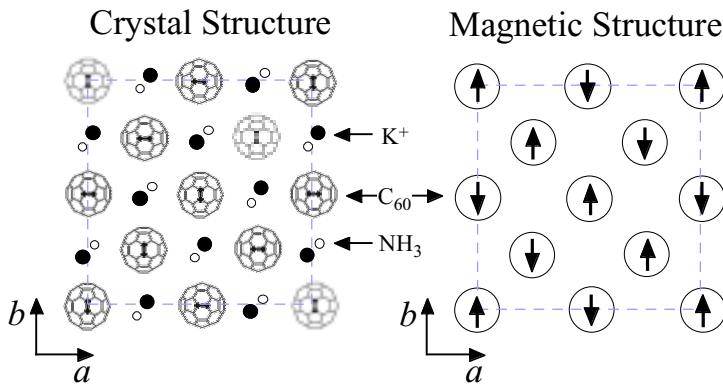


Figure 3. Crystal and Magnetic structure of  $\text{NH}_3\text{K}_3\text{C}_{60}$ .

neutron and x-ray powder diffraction data shows the molecular orientational ordering below the structural transition temperature at 150K (Figure 3). This is in a striking contrast with the molecular orientational disordering in the superconducting state of  $\text{K}_3\text{C}_{60}$ . An important and significantly new result is that the magnetic structure determined by an independent NMR experiment is strongly correlated with this orientational ordering (Figure 3). This is the first molecular magnet controlled by the molecular rotation.

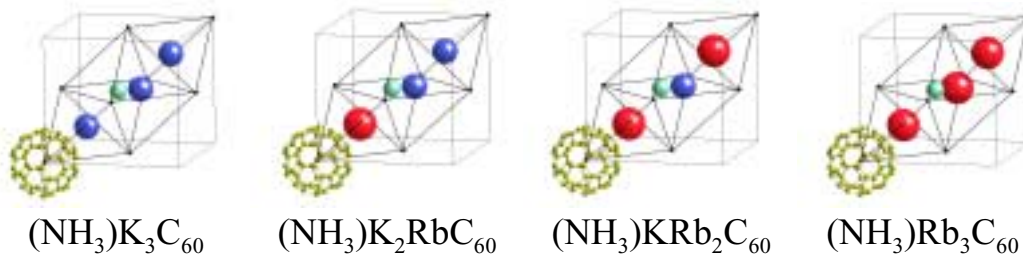


Figure 4. Schematic structures of  $(\text{NH}_3)\text{A}_3\text{C}_{60}$ .  $\text{C}_{60}$ s,  $\text{Rb}^+$  ions,  $\text{K}^+$  ions,  $\text{NH}_3$  molecules are represented as dots, big, middle, and small balls, respectively.

The other approach is the synthesis of new  $(\text{NH}_3)\text{K}_3\text{C}_{60}$  type compounds,  $(\text{NH}_3)\text{A}_3\text{C}_{60}$  ( $\text{A}=\text{K}$  or  $\text{Rb}$ ) (Figure 4). The author succeeded to synthesize these compounds despite the failure of competitors. ESR, SQUID, and SR experiments on this new series of compounds revealed that all materials are antiferromagnets. The  $T_N$  increased with lattice expansion from 40 K for  $(\text{NH}_3)\text{K}_3\text{C}_{60}$  to 76 K for  $(\text{NH}_3)\text{KRb}_2\text{C}_{60}$ , which is the highest magnetic transition temperature among molecular substances without magnetic elements (Figure 5).

Moreover, the author found that, in  $(\text{NH}_3)\text{KRb}_2\text{C}_{60}$ , the molecular orientational ordering is destroyed by quenching accompanied with a considerable reduction of  $T_N$ . These results also show a strong correlation between the molecular orientational ordering and magnetic states.

### 3. $\text{C}_{70}$ COMPOUNDS

In striking contrast with a variety of  $\text{C}_{60}$  compounds, the understanding of  $\text{C}_{70}$  intercalation compounds is quite poor. The most unique feature of  $\text{C}_{70}$  solid is the larger interstitial site than  $\text{C}_{60}$ , providing large space for intercalants. In fact, the number of intercalated metals in saturated phase

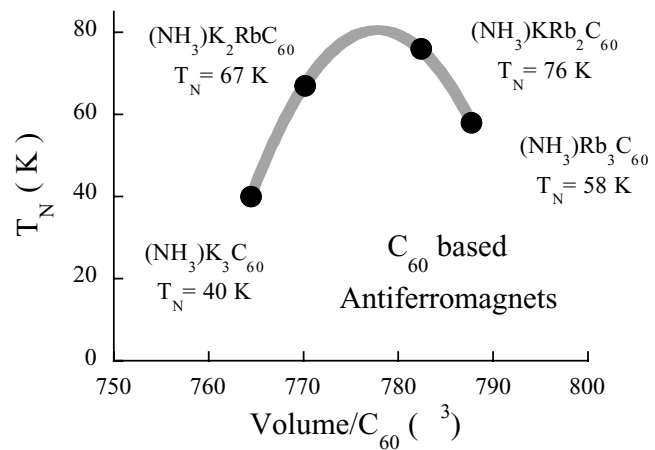


Figure 5.  $T_N$  v.s. volume per  $\text{C}_{60}$  in  $\text{NH}_3\text{A}_3\text{C}_{60}$ .

is nine metals per fullerene in  $C_{70}$ , while it is six in  $C_{60}$ . In this study, the author has first found  $C_{70}$  compounds with alkaline earth and rare earth metals. In contrast to monovalent alkali metals, alkaline earth metals ( $A$ ) supplies two electrons to each fullerene, producing a tremendously high reduction state  $(C_{70})^{18-}$  in  $A_9C_{70}$ . The author succeeded to synthesize  $Ba_xC_{70}$  and  $Sr_xC_{70}$  ( $x=3, 4, 6$ , and  $9$ ). The crystal structure was determined by structure analysis, and the highly reduced state is confirmed by Raman spectra. The former result indicates a similarity of structure sequence between  $C_{60}$  compounds and  $C_{70}$  compounds except for the  $M_9C_{70}$  phase ( $M=A, A$ ), which is specific to  $C_{70}$  compounds. The latter result suggests a possible application of higher fullerenes to battery materials, since a tremendously high reduction state  $(C_{70})^{18-}$  is available. This carbon/electron ratio is comparable to that for the carbon nanotube.

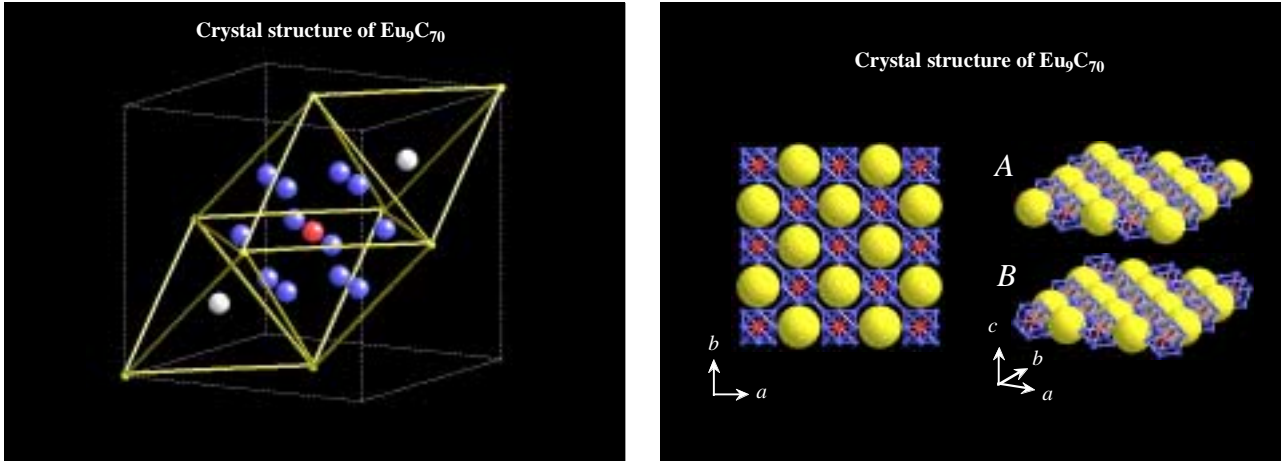


Figure 6. Schematic structure of  $Eu_9C_{70}$ . Left figure is the unit cell of  $Eu_9C_{70}$  crystal.  $C_{70}$ s and Eu ions are represented by dots and balls, respectively. Right figure is the large view of  $Eu_9C_{70}$  structure. Here,  $C_{70}$ s and Eu ions are represented by large and small balls, respectively.

Furthermore,  $Eu_xC_{70}$  was synthesized and,  $Eu_3C_{70}$  and  $Eu_9C_{70}$  were found to be the first  $C_{70}$  based ferromagnets. The crystal structure of  $Eu_9C_{70}$  is very unique and similar structure is expected in  $M_9C_{70}$  (Figure 6). Particularly, the Curie temperature of the latter compound reached 40K, which is also the highest among the fullerene based ferromagnets (Figure 7).

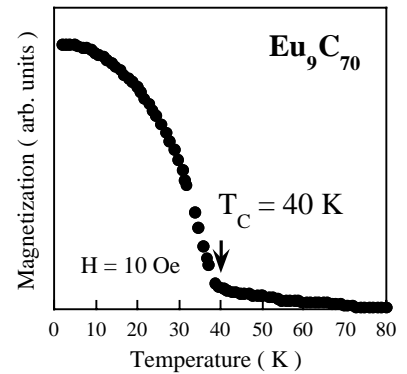


Figure 7. Ferromagnetic interaction in  $Eu_9C_{70}$ .

#### 4. SUMMARY

In  $C_{60}$  compounds, the author has synthesized new types of fullerene-based antiferromagnets with the highest Neel temperature ( $T_N$ ) among molecular materials. Moreover, we found that the orientational ordering of molecules controls the magnetic spin structure *via* molecular orbital. Experimental observation of molecular orbital ordering and clarification of relationship between superconductor and antiferromagnets are next issue.

For  $C_{70}$  fullerenes, several new intercalation compounds of alkaline earth metals and rare earth metals have been discovered, including the first  $C_{70}$  based ferromagnets with the highest Curie temperature among the fullerene based materials. These results reveal the unique properties and the possibilities of  $C_{70}$  compounds.