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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 Novel Prize was awarded for the discovery of the succor 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 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.

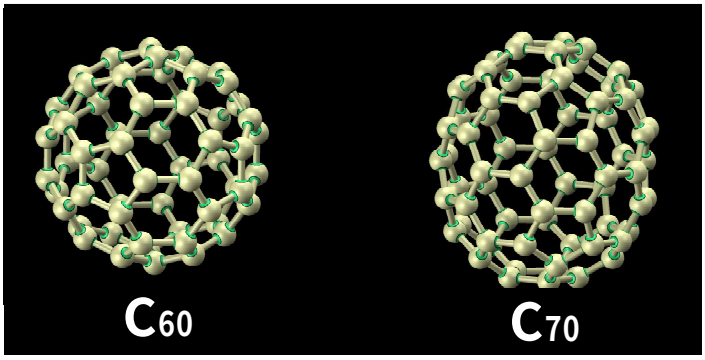

Figure 1. Molecular structures of C_{60} and C_{70}.

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 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

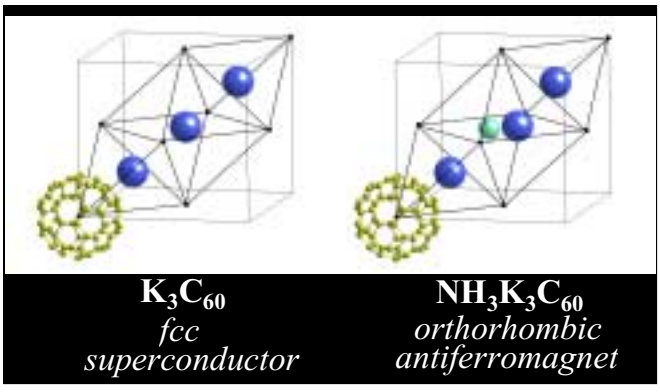

Figure 2. Schematic structures of K_3C_{60} and $NH_3K_3C_{60}$. C_{60}s, K^+ ions, NH_3 molecule are represented as dots, big and small balls, respectively.

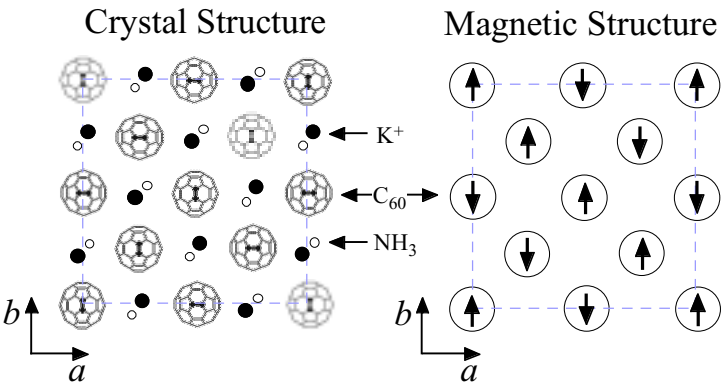

Figure 3. Crystal and Magnetic structure of $NH_3K_3C_{60}$.

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 K_3C_{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.

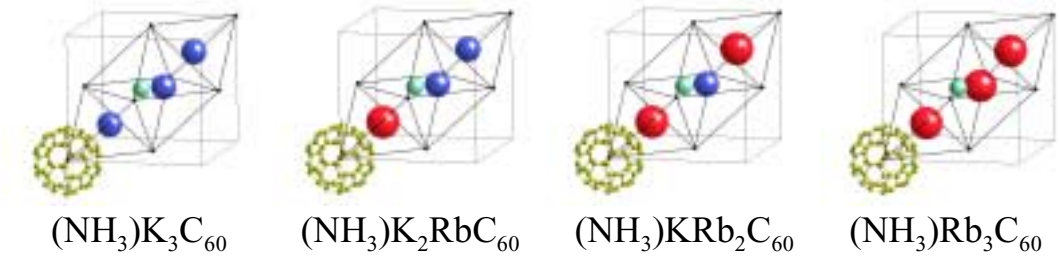

Figure 4. Schematic structures of $(NH_3)A_3C_{60}$. C_{60}s, Rb^+ ions, K^+ ions, NH_3 molecules are represented as dots, big, middle, and small balls, respectively.

The other approach is the synthesis of new $(NH_3)K_3C_{60}$ type compounds, $(NH_3)A_3C_{60}$ (A=K or 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 $(NH_3)K_3C_{60}$ to 76 K for $(NH_3)KRb_2C_{60}$, which is the highest magnetic transition temperature among molecular substances without magnetic elements (Figure 5). Moreover, the author found that, in $(NH_3)KRb_2C_{60}$, 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.

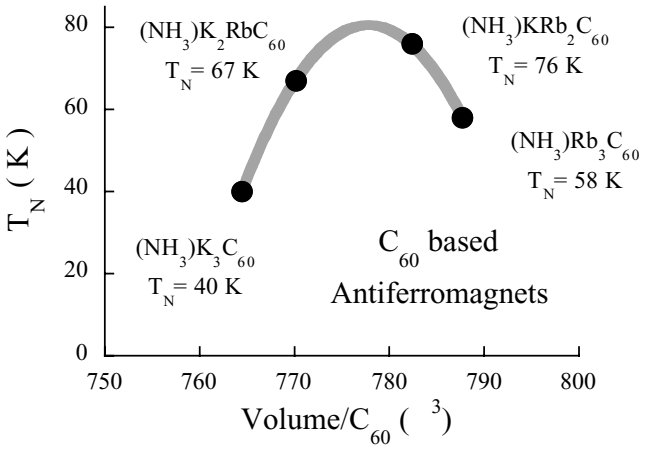

Figure 5. T_N v.s. volume per C_{60} in $NH_3A_3C_{60}$.

3. C_{70} COMPOUNDS

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

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.

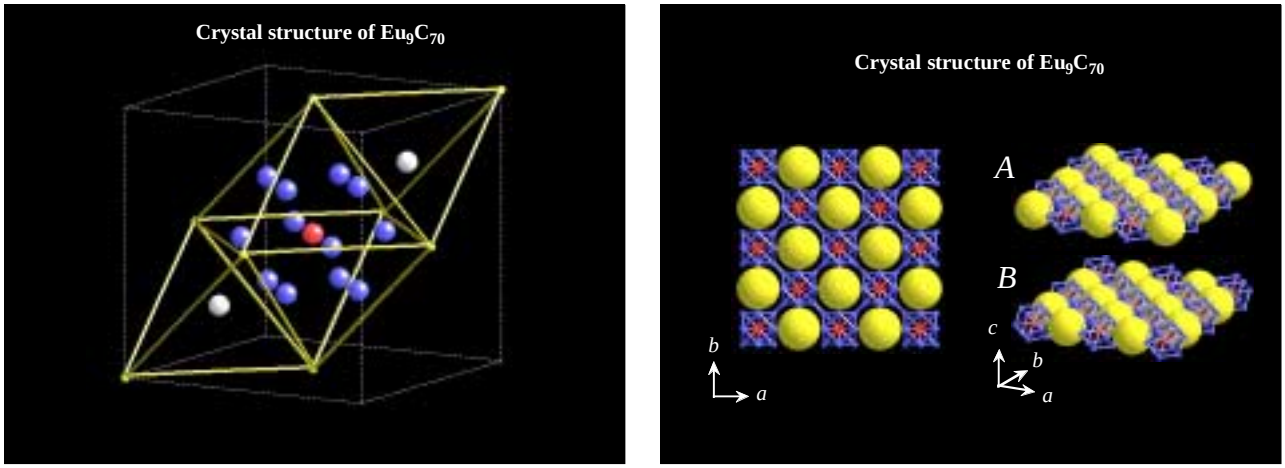

Figure 6. Schematic structure of Eu_9C_{70}. Left figure is the unit cell of Eu_9C_{70} crystal. C_{70}s and Eu ions are represented by dots and balls, respectively. Right figure is the large view of Eu_9C_{70} structure. Here, C_{70}s and Eu ions are represented by large and small balls, respectively.

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).

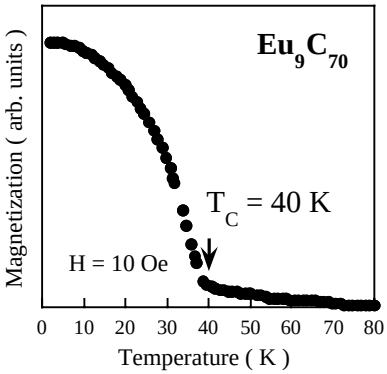

Figure 7. Ferromagnetic interaction in Eu_9C_{70}.

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.