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Study for Fulleren Superconductivity based on Alkali-ammonia Complex Fullerides

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Abstract

Low temperature synthesis in liquid ammonia yielded new superconductors, $(NH_3)_x NaA_2C_{60}$ ($0.5 < x < 1$, $A = $ K and Rb). These compounds retained the fcc cell with tunable lattice constant around $a = 14.37$Å and $a = 14.52$Å, for K and Rb compounds, respectively, by controlling the ammonia concentration x. T_c of both compounds decreases with increasing the lattice parameter, in a striking contrast with the empirical correlation. A Na-NH_3 cluster occupies the octahedral interstice and remaining K or Rb occupies the tetrahedral site. The Na ion is displaced by 0.4-0.6Å from the center of the octahedral site.

Magnetic susceptibility, electron spin resonance (ESR), ^{13}C-nuclear magnetic resonance (NMR), and muon spin relaxation(μSR) data on $NH_3K_3C_{60}$ reveal that $NH_3K_3C_{60}$ is a narrow band metal with a transition to an antiferromagnetic insulating ground state at 40K. This transition suppresses the superconductivity that is expected to occur at around 30K according to the simple empirical relation between T_c and the cell volume in alkali doped C_{60} superconductors.

Introduction

C_{60} is regarded as an element for constructing new solids of interesting properties. Among various kinds of intercalated C_{60} compounds, high T_c superconductivity is observed in alkali metal intercalated materials with C_{60} molecules.[1,2] While the observed superconductivity is well explained by the BCS weak coupling theory, a fundamental question remains to be solved; that is the conditions for the occurrence of superconductivity, in other words, structural and electronic constraint for superconductors. In alkali metal intercalated C_{60}, for instance, superconductivity appears only at the $3-$ reduction state and in face centered cubic (fcc) or simple cubic structures, although there exist various kinds of materials.[3] Meanwhile, superconductivity is observed at highly reduced states when alkali earth metals[4] or rare earth metals[5] are intercalated.

As to the alkali intercalated C_{60} superconductors, one of the current important issues is search for new materials with large lattice parameters and their electronic properties. This is motivated by the well-known correlation between T_c and cell dimensions;[6-8] T_c increases with lattice parameters, in accord with the BCS theory. Further expansion of lattice produces a new question: Whether T_c increases following the empirical relation or electrons are localized due to too much band narrowing. An effective method to expand the unit cell is the intercalation of neutral molecules, which was first demonstrated by Zhou, Rosseinsky and coworkers. Zhou et al. showed that ammoniation of Na_2CsC_{60} increased T_c from 10.5K to 29.6K forming $(NH_3)_4Na_2CsC_{60}$.[9] Reaction of K_3C_{60} with NH_3, on the other hands, resulted in a disappearance of superconductivity.[10] This compound was found to recover the superconductivity by application of high pressure.[11]

Here we report synthesis, structure and magnetic property of new superconductors, $(NH_3)_xNaK_2C_{60}$ and $(NH_3)_xNaRb_2C_{60}$ ($x \sim 0.5 - 1.0$), and also magnetic propaties of non-superconducting $NH_3K_3C_{60}$ at ambient pressure.

Experimental results

$(NH_3)_xNaK_2C_{60}$ and $(NH_3)_xNaRb_2C_{60}$ were synthesized by a reaction of stoichiometric amount of alkali metals and C_{60} powders in liquid ammonia.[12] NH_3 concentration x can be controlled from about 0.4 to 1.0 by synthesis conditions.

The data of XRD and the results of Rietveld refinement show that all new compounds $(NH_3)_xNaA_2C_60$(A=K,Rb : $0.4 < x < 1$) have fcc structure and a Na-NH_3 cluster occupies the octahedral interstice and this Na cation is displaced by $0.4-0.6$Å from the center of this site. The lattice constants increase with increasing anmmonia concentration x.

The mesurement of the temperature dependence of susceptibility at 10 Oe reveals all new compounds are superconductors. The T_c's are dramatically lower than the empirical relation and decrease with increasing lattice parameters in sharp contrast with the conventional relation.

To investigate the reason for the absence of superconductivity in $NH_3K_3C_{60}$, we performed the electron spin resonance (ESR), magnetic susceptibility, ^{13}C-nuclear magnetic resonance (NMR) measurements, and muon spin relaxation (μ^+SR) at ambient pressure.

$NH_3K_3C_{60}$ was prepared following the previous works.[10,11] Starting K_3C_{60} was synthesized by a direct reaction of K-vapor and C_{60} powders and following one-month anneal at 400°C. Thus obtained single phase K_3C_{60} powders (20-50mg) were loaded in a glass tube (5mm in diameter), evacuated to 10^{-3} torr and exposed to ammonia gas of 0.5 atom at room temperature for 20 minutes. After the reaction, the glass tube was sealed under 0.5 atom NH_3. The samples were annealed at 100°C for one month.

Magnetic susceptibility, electron spin resonance (ESR), ^{13}C-nuclear magnetic resonance (NMR), and muon spin relaxation(μSR) data on $NH_3K_3C_{60}$ reveal that $NH_3K_3C_{60}$ is a narrow band metal with a transition to an antiferromagnetic insulating ground state at 40K.

Summary

The low T_c materials having large fcc cells are suggestive about the mechanism of fulleren superconductibity. There are two common features in the three low T_c materials, $(NH_3)_xNaK_2C_{60}$, $(NH_3)_xNaRb_2C_{60}$, and $NH_3K_3C_{60}$: the ammonia composition is close to 1 and the presence of off-centered alkali cation in the octahedral site. Displacement of alkali metal ion from the center of the octahedral site makes the local potential on the C_{60} anion noncubic. Since the noncubic local field lifts the triple degenerancy of the t_{1u} orbital on the C_{60}, thus the electronic structures and superconductivity are significantly modified. The finding of low T_c materials indicates that the T_c of cubic fullerene superconductors are controlled not only by the sell size but also other parameters such as the position of alkali metals. On non cubic compound $NH_3K_3C_{60}$ the suppression of superconductivity has a magnetic origin, in analogy with the well-established results in high-T_c and organic superconductors.

In conclusion, alkali ammonia complex fullerides from a novel group of materials that exhibits unusual properties. These multinary systems are valuable for a full understanding of the superconductivity of fullerides.

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