Metal-Insulator Transition in C_{60} Fullerides

Y. Iwasa [a,1], T. Takenobu [a], H. Kitano [b] A. Maeda [b]

[a] *Institute for Materials Research, Tohoku University, Aoba-ku, Sendai 980-8577, Japan, and CREST, Japan Sceience and Technology Corporation, Kawaguchi 332-0012, Japan*

[b] *Department of Basic Science, The University of Tokyo, Meguro-ku Tokyo 153-8902, Japan*

Abstract

Intercalated fullerides A_3C_{60} (A =K and Rb) are well known BCS-type superconductors, but their superconductivity is easily destroyed by subtle chemical modification, resulting in the antiferromagnetically ordered states. This property is suggestive of the importance of electron correlation effect. Using microwave cavity perturbation technique, we found that the conductivity at 250K of the antiferromagnet compounds is already 3-4 orders of magnitude smaller than those of superconducting compounds. These results strongly suggest that the Mott-Hubbard transition in the A_3C_{60} systems is driven by a reduction of lattice symmetry.

Key words: fullerides; antiferromagnetic insulator; Mott-Jahn Teller system

Electronic properties of fullerenes have attracted much interest in this decade because of its superconductivity.[1] Recent report on superconductivity in the field effect ransistor structure [2] also invite particular attention to this class of materials. Fullerene superconductors are believed to be a textbook BCS superconductors, where the electronic states are understood within a band theory and Cooper pairing is mediated by the electron-phonon interaction.[1] However, a breakdown of the simple band picture are also known in the vicinity of the A_3C_{60} superconductors. One example is the even valent fullerides with chemical formulae of A_4C_{60} and Na_2C_{60}. The band theory predicts that both of these compounds are metallic because the conduction band derived from the triply degenerate molecular orbital is partially filled. These insulating compounds suggest that the Jahn Teller type electron-phonon interaction is considearbly strong in the alkali metal fullerides.

Another important example of particular interest is the antiferromagnetic ordering [3] observed in $(NH_3)K_3C_{60}$ [4] and their isostructural derivertives.[5] The compound is obtained by the intercalation of neutral ammonia molecules into fcc alkali metal fullerides A_3C_{60}, which are superconductors. $(NH_3)A_3C_{60}$ adopts an face centered orthorhombic (fco) structure which is slightly distorted from the cubic A_3C_{60}. In this paper, we report magnetic and conducting properties as investigated by electron spin resonance (ESR) and microwave conductivity experiments on the ammoniated alkali fullerides.

Compounds are synthesized by exposing preformed A_3C_{60} compounds with ammonia gas or by dissolving C_{60} and alkali metals in liquid ammonia. Sample characrterization was made by x-ray powder diffraction at the synchrotron radiation facility SPring-8 (beam line BL02B2). 9GHz ESR spectra have been recorded with the a JEOL ESR spectrometer equipped with an APD cryostat. Microwave conductivity measurement was performed with a cavity perturbation technique at 10.7GHz with a small amount of powder samples ($\sim$1mg) sealed in Pyrex capillaries.

Figure 1 displays temperature dependence of spin susceptibility and linewidth for $(NH_3)KRb_2C_{60}$.[5] The anomaly at T_S = 150K is attributed to the structuraltransition that is related to the freezing of rotation C_{60} molecules and K-NH_3 groups.[6] The

[1] Corresponding author, E-mail: iwasa@imr.edu, FAX: +81-22-215-2031

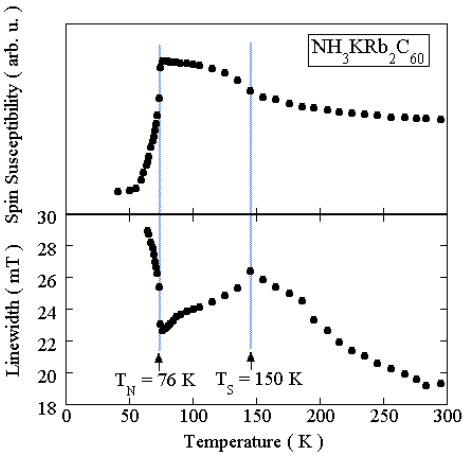

Fig. 1. Temperature dependence of supin susceptibility derived from theintensity of ESR intensity (top) and the linewidth (bottom) for $(NH_3)KRb_2C_{60}$.

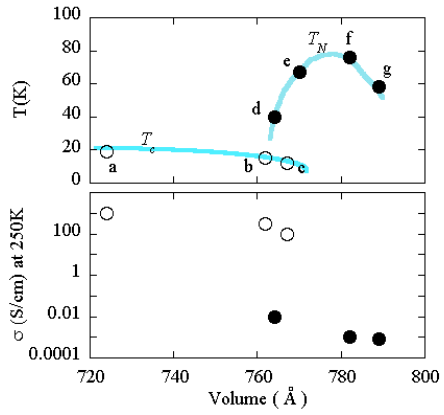

Fig. 2. A phase diagram of alkali ammonia fulleride superconductors and antiferromagnets (top). The horizontal axis represents volume per C_{60}, which is closely correlated with the interfullerene spacing. Open and closed circles show superconductors and antiferromagnts, respectively. The chemical formulae are a: K_3C_{60}, b: $(NH_3)_{0.8}NaRb_2C_{60}$, c: $(NH_3)_{0.9}NaRb_2C_{60}$, d:$(NH_3)K_3C_{60}$, e:$(NH_3)K_2RbC_{60}$, f:$(NH_3)KRb_2C_{60}$, g:$(NH_3)Rb_3C_{60}$

susceptibility drop at 76K is a sign of magnetic transition. The abrupt increase of the linewidth across 76K is strongly indicative of antiferromagnetic ordering. In fact, μSR and NMR provides convincing evidence for the antiferromagnetic ground states with a S=1/2 moment on each ball.[5] This result on ammoniated fullerides indicates that the on-ball Coulomb interaction is strong enough to destroy the superconductivity in $(NH_3)A_3C_{60}$ where metallic states are anticipated in terms of the band theory. The Neel temperatures (T_N) for investigated ammoniated fullerides are plotted in Fig. 2.

The next issue to be investigated is the conducting properties of the compounds. The conductivity experiments on the ammoniated fullerides have not been performed so far because samples are obtained only in powder form, in which reliable measurement of conductivity has been extremely difficult. 10.7GHz conductivity (σ) values at 250K are plotted for several superconducting and antiferromagnetic compounds are summarized in Fig. 2.[7]

The high conductivity of some ammoniated superconductors indicates that the ammoniation is not necesssarily fatal for the metallicity. In contrast, the conductivity of fco $(NH_3)A_3C_{60}$ is about three orders of magnitude smaller than the cubic fulleride superconductors. Also, this conductivity is recorded at 250K, which is higher than not only T_N but also T_S, indicating that the metal-insulator transition is not caused either by the magnetic ordering or by the structural transitions which is associated with the cell doubling. Thus,the unexpectedly low conductivity in the fco ammoniated fullerides should beattributed to the reduction of the crystal symmetry.

Though fullerene superconducotrs have been believe to be a typical band metal, both electron-phonon and Coulomb interactions are strong enough to destroy metallic states and thus superconductivity. These features indicate that the two interactions and the band width in fullerides are competing with each other. Hence, intercalated fullerides should be understood in terms of Mott-Jahn teller system. In this sense, the stable metallic state in A_3C_{60} compounds may be regardes as a quite accidental state, in which the interactions balances with each other. Several particular perturbations, such as a small change of the electron number per C_{60} molecule and a slight distortion of the lattice, could destroy the balance, causing the metal-insulator transition. According to a recent theory, just a small amount of splitting of the degenerate levels is sufficient to drive the metal-insulator transition.[8]

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