Cu NMR Study of Organic Conductor DCNQI-Cu System

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Abstract

The Cu NMR was performed to investigate an electronic property of a counterion site in (DMe-DCNQI)2Cu, (DMeO-DCNQI)2Cu, (DBr-DCNQI)2Cu, and partially deuterated (DMe-DCNQI-d2[1,1,0])2Cu. In these compounds, it is microscopically demonstrated that each metallic and insulating state possesses a similar electronic and magnetic properties and near the metal-insulator (M-I) boundary, any specific effect of electron correlation of d-electrons is not identified from a systematic measurements of the spin-lattice relaxation rate, (1/T1), of 63Cu.

1. INTRODUCTION

A new type of organic conductors (R1, R2-DCNQI)2Cu (R1, R2=CH3, CH3O, Cl, etc.) was synthesized. R1, R2-DCNQI are organic π-acceptor molecules which are uniformed stacked along the crystallographic c-axis in one dimensional column and Cu sites are coordinated by four DCNQI molecules. Among the DCNQI-Cu systems, it is well known that there are three groups despite of the close resemblance of the structure. Group-I compounds, to which (DMe-DCNQI)2Cu and (DMeO-DCNQI)2Cu belong, stay in the metallic state down to low-T. Group-II compounds such as (DBr-DCNQI)2 Cu show the sharp metal-insulator (M-I) transition accompanied by the structure changes. In the group-I compounds, whereas, the M-I transition is induced by pressure. Under the specific pressure, the group-I compound show M-I-M reentrant transition with decreasing T. Recently, Hüning et al. reported that the chemical pressure was produced by the substitution of 2D for 1H.[2] Partially deuterated (DMe-DCNQI-d2[1,1,0])2Cu shows the M-I-M transition under the ambient pressure.[3] The compounds showing M-I-M transition, such as (DMe-DCNQI-d2[1,1,0])2Cu and the group-I compounds under the specific pressure, are considered to be in Group-III.

In the previous paper,[4] we reported the Cu NMR measurements in (DMe-DCNQI)2Cu belonging to the group-I. We here deal with the T-dependence of 1/T1 in the group-II and III.

2. EXPERIMENTAL RESULTS AND DISCUSSION

The process of synthesis was described elsewhere.[1] The sample of (DBr-DCNQI)2Cu was crushed into powder for NMR measurements. In (DMe-DCNQI-d2[1,1,0])2Cu, single crystals were used to avoid crystal distortion and stress. 1/T1 was measured at Cu site by saturation-recovery method on (1/2 ↔ −1/2) transition of the quadrupole split spectrum in a magnetic field of 11T.

Figure 1: T-dependence of 1/T1 in (DBr-DCNQI)2Cu.

2.1 Group-II

Fig. 1 shows the T-dependence of 1/T1 in (DBr-DCNQI)2 Cu. In the metallic state, T1 obeys T1T=const. law roughly. The value of 1/T1T in (DBr-DCNQI)2Cu is twice larger than that in (DMe-DCNQI)2Cu, associated with a stronger electron correlation effect. At the temperature, (Tm) where the M-I transition occurs, the peak of NMR spectrum shifts discontinuously and the signal intensity decreases significantly. The NMR intensity in the insulating phase are decreased to two-third of that in the metallic one accompanied by a smaller shift. One third of Cu NMR signal is wiped
out because of much short relaxation time. Below $T_M$, the homogeneous mixed valence state with an average valence of $Cu^{1.33}$ is differentiated into two $Cu^{1+}$ and $Cu^{2+}$ ionic states with a concentration ratio of two to one as pointed out by XPS experiments. [5] Consistently to this result, the NMR for the $Cu^{2+}$ sites carrying local moments are out of observation, whereas that from nonmagnetic $Cu^{1+}$ with closed d-shell has been observed. Remarkably, the relaxation process for $Cu^{1+}$ nuclei is dominated by fluctuating $Cu^{2+}$ local moments in the paramagnetic state and below 15K, $1/T_1$ decreases and at the same time, the full-width at half maxium of $Cu$ NMR spectrum starts to increase, which provide evidences of the antiferromagnetic ordering of $Cu^{2+}$ moments below 15K.

2.2 Group-III

Fig. 2 shows the $Cu$ NMR spectrum for $(1/2 \leftrightarrow -1/2)$ transition. Fig. 3 shows the $T$-dependence of $1/T_1$ in (DMe-DNCQI-d$_2$(1,1:0))$_2$Cu. The NMR spectrum in the low-$T$ metallic state is the same as that in the high-$T$ metallic phase, and $1/T_1$ in the high- and low-$T$ metallic phases are on the same line showing a $T_1T=const$.law. This means that the electronic state in the metallic phases is the same. It is, furthermore, remarkable that the value of $1/T_1T$ is also the same as that in (DMe-DNCQI)$_2$Cu. In the insulating state, there present two $Cu$ NMR signals as shown in Fig.2. One is the same as that in the metallic phase. Another signal appears only in the insulating phase where $1/T_1$ is nearly $T$-independent with almost the same value as in the insulating phase for (DBr-DNCQI)$_2$Cu. Thus the insulating state in (DMe-DNCQI-d$_2$(1,1:0))$_2$Cu is shown to be almost the same as that in (DBr-DNCQI)$_2$Cu. In the former case, the metallic phase remains partially even in the insulating state below $T_M$ from a microscopic point of view.

3. SUMMARY

From the NMR measurements, the metallic and insulating phase in both (DBr-DNCQI)$_2$Cu and (DMe-DNCQI-d$_2$(1,1:0))$_2$Cu, which exhibit the M-I and M-I-M reentrant transition, possesses a same density of states at the Fermi level and magnetic nature, respectively. The M-I transition in these compounds occurs as first order transition and hence the electronic state changes discontinuously. Since the mass enhancement in the vicinity of the M-I transition, which was pointed out by the specific heat measurements, [6] has not been evidenced from the measurement of $T_1$, the usual Fermi liquid description is considered to be valid in these organic conductors.

References