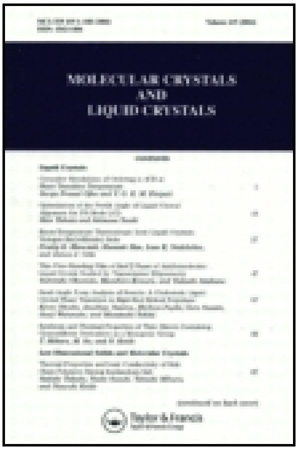

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Ground States of DCNQI-Metal Complexes, $(R_1,R_2\text{-DCNQI})_2M$; $(R_1,R_2 = CH_3, I, M = Ag, Cu, Li_{1-x}Cu_x)$

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GROUND STATES OF DCNQI-METAL COMPLEXES, $(R_1,R_2\text{-DCNQI})_2M$; $(R_1, R_2=CH_3, I, M=Ag, Cu, Li_{1-x}Cu_x)$

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Abstract The electrical resistance, magnetic susceptibility, ^{1}H- and ^{13}C-NMR measurements have been performed to investigate the ground states of the metal complexes of DCNQI, $(R_1,R_2\text{-DCNQI})_2M$, where $R_1(R_2)$ is CH_3 (Me) or iodine (I) and M is Ag, Cu or $Li_{1-x}Cu_x$. A new member of DCNQI-M complexes, $(\text{DI-DCNQI})_2Ag$, is nonmetallic below room temperature and shows a Bonner-Fisher type of susceptibility, of which the value is nealy the same as that of $(\text{DI-DCNQI})_2Cu$ at room temperature. An antiferromagnetic ordering was found at 5.5K in contrast to the spin-Peierls ground state in the isostructural $(\text{DMe-DCNQI})_2Ag$. The alloy systems, $(\text{DMe-DCNQI})_2Li_{1-x}Cu_x$, have been studied with an aim at control of the electronic state by the doping of Cu into the insulator, $(\text{DMe-DCNQI})_2Li$. For the Cu doping up to x=30%, the systems show the spin-Peierls transition while the system with x>50% are metallic down to low temperatures. The $(T_1T)^{-1}$ of ^{13}C-NMR shows systematic change with doping.

INTRODUCTION

A family of $(2,5\text{-}R_1,R_2\text{-DCNQI})_2M$ contain a variety of electronic phases. Planer DCNQI molecules are uniformly stacked in one-dimensional (1D) columns along the crystallographic *c*-axis and, at the same time, coordinate to the metal ion, M, tetrahedrally through the cyano group [1]. The Li and Ag salts of DMe-DCNQI ($R_1=R_2$=Me; M=Li or Ag), DMe-Li and DMe-Ag, behave metallic in high temperature region while, with decreasing temperature, the $4k_F$ charge density wave fluctuations associated with dimerization of DMe-DCNQI develop with appearance of nonmetalic resistive behavior and a spin-Peierls transition occurs at lower temperatures [2]. In this case, the metal ions do not contribute to the conduction band, which is constructed by the 1D π orbitals with quarter filling. On the other hand, in case of M=Cu (DMe-Cu), the 3d-orbitals of Cu ions are strongly hybridized with the π-band in the DMe-DCNQI columns [3, 4]. This salt remains metallic down to lower temperatures [5].

$(\text{DI-DCNQI})_2\text{Cu}$ (R_1,R_2=I; M=Cu), DI-Cu, is also metallic down to low temperatures [6]. DI-Cu is compared with DMe-Cu in the following respects; 1) anisotropy of resistivity, $\rho_\perp/\rho_\parallel \cong 3$, is less than that of DMe-Cu ($\rho_\perp/\rho_\parallel \cong 10$) [7]; 2) the pressure-temperature phase diagram of DI-Cu is curious in that the critical pressure of the metal-insulator transition (~15kbar) is much higher than the value of DMe-Cu (~0.3kbar), and a metallic state appears again in a high pressure region (>20kbar) [7]; 3) spin susceptibility of DI-Cu is about twice larger than DMe-Cu and forms a broad peak around 110K [8]. These characteristics of DI-Cu attract interest in the electronic state of the DI-DCNQI family.

In the present work, electrical resistance, R, magnetic susceptibility, χ, and ^{1}H- and ^{13}C-NMR measurements have been performed to investigate the ground states of a series of $(R_1,R_2\text{-DCNQI})_2\text{M}$. We see the effect of the functional group, R_1 and R_2, and filling and/or dimensionality of the electronic band possibly controlled by alloying of M; the valence of Li and Ag in the salts is +1 while that of the Cu salt is $+1+\delta$, so that the Cu doping to the Li or Ag salt is expected to cause some change in filling of the 1D π-band and/or generate 3D character through hybridization of the Cu 3d orbitals with the π orbitals. In addition, we have synthesized and characterized a new salt, $(\text{DI-DCNQI})_2\text{Ag}$, which is expected to be a purely π-electronic system analogous to DMe-Ag. In this paper, (i) the electronic state of DI-Ag is compared with DI-Cu and (ii) the doping effect on the insulating DMe-Li is examined.

The experiments in the present work were performed for powered samples. The ^{1}H- and ^{13}C-NMR measurements were made at frequencies of 85.3 and 61.5 MHz, respectively.

$(\text{DI-DCNQI})_2\text{M}$ [M=Ag, Cu]

The newly synthesized material, DI-Ag, is insulating below room temperature with a charge gap of ~490K, which was obtained by the temperature dependence of resistace. The χ follows a Curie-Weiss law in high temperature region and forms a broad peak around 30K. A sharp kink is observed around 10 K.

The ^{1}H-NMR shift, ^1K, and the spectral width determined by the second moment scale to the static susceptibility above ~50K, the second moment continuous to increase; this may be a manifestation of the short range ordering. From the slope of the K-χ plot and linewidth-χ plot, it is found that the isotropic term and the square root of the mean square of the anisotropic term of the hyperfine coupling tensor, **A**, are -230Oe/μ_B and 270Oe/μ_B, respectively.

At 5.5K, the ^{1}H relaxation rate, $^1T_1^{-1}$, forms a peak anomaly and the ^{1}H-NMR linewidth abruptly becomes broadened as shown in Fig.1. These evidence an antiferromagnetic ordering of the spins at this temperature. The value of the linewidth extraporated at 0 K is 260 kHz. The spectral width for a powdered sample with antiferromagnetic order is roughly given by (γ**A**$<\mu>$)/2π, where γ, **A** and $<\mu>$ are the gyromagnetic ratio of ^{1}H nuclei, hyperfine coupling constant and amplitude of the AF moment, respectively. In our case, the external field is larger than the spin flop field so that the anisotropic part of **A** is an only contribution to the line width. The formula gives a small amplitude of $<\mu>$ ~0.25μ_B/dimer, which may indicate reduction of the moment due to the zero point motion of spin waves, so-called spin contraction encountered in the low dimensional magnetic systems[9].

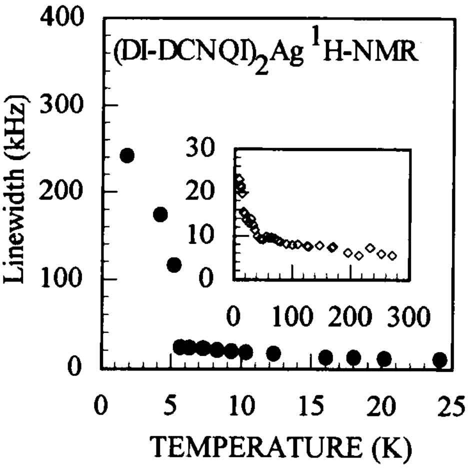

Fig.1 Temperature dependence of linewidth.

The DI-Ag is considered as a purely π-electron system like DMe-Ag and DMe-Li, of which the ground states are nonmagnetic spin-Peierls states associated with the 1D nature of the π-electron system. The DI-Ag salt is the first case in the DCNQI-M family that the π electrons are responsible for AF ground state. The difference of the ground states are attributable to the difference in the dimensionality of the electronic states [10]; according to the estimation of the transfer integral [7, 11], the DI-systems are more three dimensional than the DMe-systems.

Next, our attention is directed to DI-Cu. In Fig.2, the spectral shift of ^{13}C- and ^{1}H-NMR, ^{13}K and ^{1}K from the line position of TMS are shown in comparison with χ [12]. Both of ^{13}K and ^{1}K form broad peaks like that of χ. However, it should be noted that the peak temperature of ^{1}K is lower than that of χ while the peak temperature of ^{13}K is slightly higher than that. The overall temperature dependence of χ is in between the two profiles. Since K probes the local spin susceptibility, this fact is considered as a microscopic evidence that the electronic structure consists of several bands with different characters, which is believed to come from hybridization of the π and d orbitals; ^{1}H-NMR detects the electrons of π-band preferentially, while ^{13}C-NMR at the cyano group coordinated to the Cu ions can probe the d-electrons through the off-site core polarization as well as the π electrons [13].

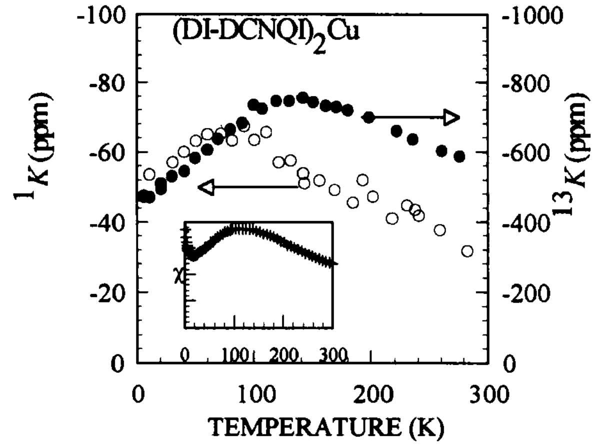

Fig.2 Temperature dependence of ^{1}H-shift, ^{1}K (open circles), and ^{13}C-shift, ^{13}K (closed circles). The shifts are measured from the line position of TMS. The χ is shown in the inset.

The ground state of DI-Ag salt is a magnetic insulator, while the isostructual DI-Cu salt is a paramagnetic metal with hybridization of the π orbitals with Cu 3d orbitals. The present result of DI-Ag shows an important role of π band in electron correlation manifesting itself in ,e.g. enhancement of spin susceptibility in the DI systems. The first principles electronic band calculations show that the π band in the DI system is narrower than in the DMe system [14].

(DMe-DCNQI)$_2$Li$_{1-x}$Cu$_x$

From the resistivity measurements of several alloy systems with different Cu contents, it was found that the systems up to x~30% undergo the metal-insulator transition while the systems with x>50% are metallic in the whole temperature range investigated. Figure 3 shows the temperature dependence of χ for typical alloy systems. A systematic change of behavior with the doping content is observed.

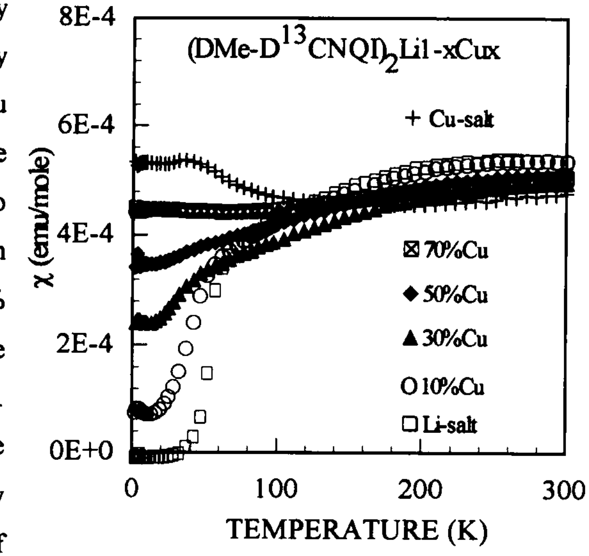

Fig.3 Temperature dependence of spin susceptibility.

The ^{13}C (in the cyano group) nuclear spin-lattice relaxation rate, $^{13}T_1{}^{-1}$, is shown in Fig.4. For x<30%, one can see abrupt decrease of $(^{13}T_1T)^{-1}$, which is associated with the spin-Peierls transition. The transition temperature slightly shifts with increasing x.

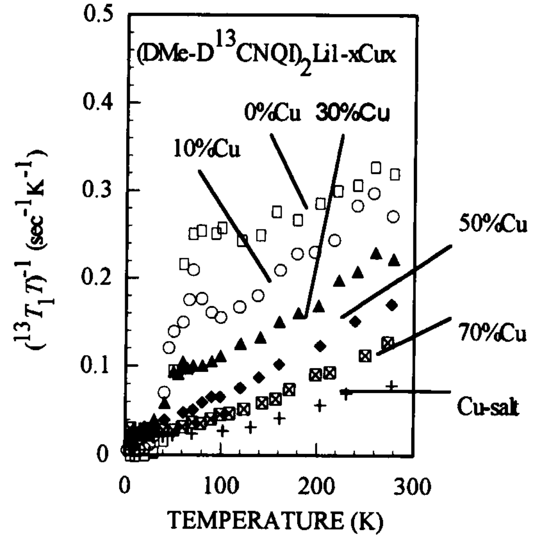

Fig.4 Temperature dependence of ^{13}C-NMR, $(^{13}T_1T)^{-1}$.

For the Cu-rich systems of x>50%, $(^{13}T_1T)^{-1}$ does not exhibit any anomaly but converges into about 0.03 sec^{-1}K^{-1} in the low-temperature limit. They show positive temperature dependence, which have a clear correlation with the doping content. This is an indication that the doping causes some change in the electronic states, particularly in excitation spectrum visualized in higher temperature region.

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