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Suppression of the Metal Instability and Continuous Change of the Carrier Density in $(\mathrm{MeBr\text{-}DCNQI})_2\mathrm{Cu}_{1-x}\mathrm{Li}_x$

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Electrical resistivities and IR spectra of new mixed cation (Cu/Li)-DCNQI systems were examined. $(\mathrm{MeBr\text{-}DCNQI})_2\mathrm{Cu}_{1-x}\mathrm{Li}_x$ $(0.25<x<0.5)$ remains in the metallic state down to 4 K. The stretching frequency of C=N(imine) of DCNQI shows a linear dependence on the charge of DCNQI, which is consistent with the mixed valency of Cu $(\mathrm{Cu}^{+1.3})$.

Recently, an increasing interest has been focused on the electronic properties of DCNQI-Cu compounds (DCNQI=dicyanoquinonediimine).1) The DCNQI-Cu system has been first synthesized by Aumüller et al.2) The main interest in the DCNQI-Cu systems arises from the formation of the $p\pi$- d mixing band. The first indication of the possibility of the existence of such a unique metallic state has been obtained by X-ray diffraction experiments on $(\mathrm{MeCl\text{-}DCNQI})_2\mathrm{Cu}$.3) The development of a three-fold superstructure (axbx3c) below the MI transition temperature (T_{MI}) was thought to show the mixed-valency of Cu.3,4) In addition, the high-pressure resistivity experiments of $(\mathrm{DMeO\text{-}DCNQI})_2\mathrm{Cu}$ suggested that the system can take a peculiar metallic state analogous to that of so-called "heavy Fermion system" just above the pressure where the pressure-induced metal instability begins to appear.1,5) Similar metal instability can be observed in the alloy system, $[(\mathrm{DMe})_{1-x}(\mathrm{MeBr})_x\text{-}\mathrm{DCNQI}]_2\mathrm{Cu}$, where a large enhancement of the effective mass of the metal electron was observed.1,6)

Until recently, there was some controversy about the valency of Cu. One opinion denied the essential role of the mixed valency of Cu.7) However, re-examination of X-ray photoelectron spectra of Cu and N of

$(DMe\text{-}DCNQI)_2Cu$ by Fujimori et al., clearly showed the mixed-valency of Cu.[8] The Cu^+/Cu^{2+} ratio of 2 is completely consistent with our earlier conjecture.[3]

In this paper, we will report on the suppression of the metal instability and the continuous change of the carrier density in the mixed-cation (Cu/Li)-DCNQI systems.

Black needles of $(MeBr\text{-}DCNQI)_2Cu_{1-x}Li_x$ were obtained electrochemically from an CH_3CN solution of MeBr-DCNQI and $LiClO_4/CuBr_2$. The ratio of Li/Cu in the crystal was determined by X-ray structure analysis, where the occupancy probability of the cation site was refined. Most of the crystals used for the X-ray structure refinements were selected from crystals whose temperature dependence of the resistivity had been determined. The x-value of the crystal is very different from the mole ratio of the Li and Cu atoms in the solution (Fig. 1). When the Li/Cu ratio is less than 10, the x-values were scattered widely, even when their preparation conditions were almost the same.

Crystals with $x \approx 0.25$-0.50 are metallic down to 4 K (Fig. 2). This is not a trivial result, because both $(MeBr\text{-}DCNQI)_2Cu$ ($T<155$ K) and $(MeBr\text{-}DCNQI)_2Li$ ($T<300$ K) are semiconductive. It should be recalled that despite of the orientational disorder of MeBr-DCNQI, $(MeBr\text{-}DCNQI)_2Cu$ undergoes an extremely sharp MI transition at 155 K, below which the 3-fold structure develops. In the small-x region ($x<0.2$), the MI transition temperature decreases rapidly with increasing x: T_{MI} = 110 K - 130 K, at $x \approx 0.1$. As pointed out before,[3,4,9] the MI transition of (MeBr-

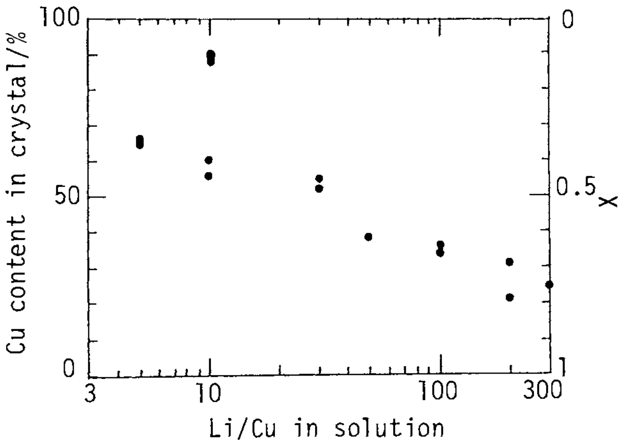

Fig. 1. Cu content in crystals vs. Li/Cu ratio added into solvent as supporting electrolyte.

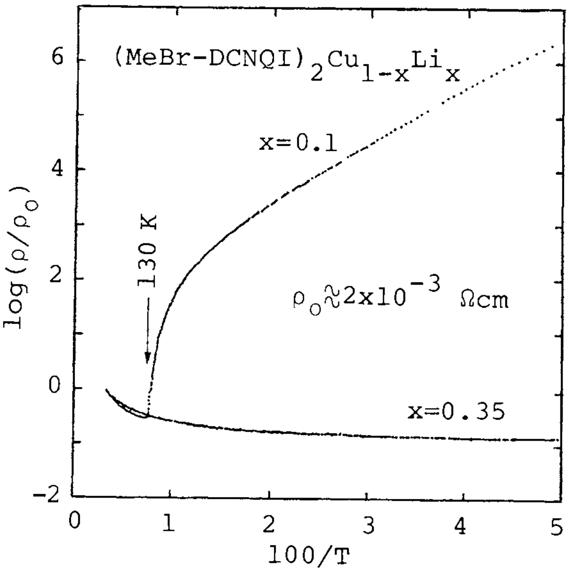

Fig. 2. Resistivity vs. temperature.

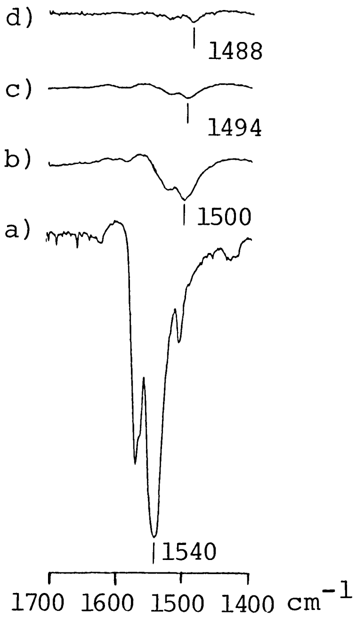

Fig. 3. FT-IR spectra of a) neutral MeBr-DCNQI and b) x=1, c) x ≈ 0.5, d) x=0 of $(\text{MeBr-DCNQI})_2\text{Cu}_{1-x}\text{Li}_x$.

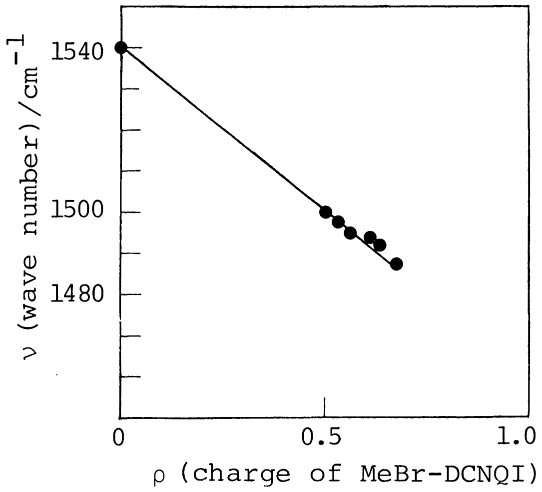

Fig. 4. Plot of C=N (imine)stretching frequencies of $(\text{MeBr-DCNQI})_2\text{Cu}_{1-x}\text{Li}_x$ vs. charge of MeBr-DCNQI estimated from the ratio of Li/Cu in crystals based on the results in Fig. 1. Average valence of Cu is assumed to be +1.3.

$\text{DCNQI})_2\text{Cu}$ is not considered to be a simple CDW transition. The 3-fold periodical lattice distortion is accompanied by the distortion of the coordination structure around Cu, which will be related to the 3-fold charge ordering in the cation sites. The increase of the Li content prevents the cation ordering. Therefore, it would be very natural for the depression of T_{MI} and subsequent suppression of the MI transition to take place with increasing x. At higher x-values, the system becomes semiconductive throughout the temperature range examined (4 K - 300 K).

Needless to say, the determination of the x-value does not determine the charge on DCNQI. It is well known that the stretching frequency of C=C(quinoid) bond of TCNQ is fairly well correlated with the degree of charge transfer of the TCNQ radical anion salt.$^{10)}$ We also investigated the IR spectra of $(\text{MeBr-DCNQI})_2\text{Cu}_{1-x}\text{Li}_x$ by FT-IR spectroscopy (Shimadzu FTIR-4000; resolution 1 cm^{-1}) to see whether the corresponding C=N(imine) stretching frequency of DCNQI of the mixed-metal (Cu/Li) system can be used as a measure of the charge on DCNQI. Measurements were made on the KBr disk. The absorption at 1540 cm^{-1} of neutral MeBr-DCNQI assigned to C=N (imine) shows a large shift in Li(1500 cm^{-1}) and Cu(1488 cm^{-1}) salts (Fig. 3), indicating a linear dependence against ρ (charge of MeBr-DCNQI = 0.5 (Li), 0.66 (Cu)): $\nu(\text{cm}^{-1})=1540-79\rho$ (Fig. 4). This linear ν-ρ

relation, which is quite similar to that observed for TCNQ salts (ν=1544-60ρ),[10] gives additional evidence of the mixed-valency of Cu(+4/3). Moreover, the C=N(imine) stretching frequency of the mixed-cation (Cu/Li) system takes an intermediate value between those of the Li- and Cu-salts. This implies that the charge of the MeBr-DCNQI molecule can be changed continuously by changing x. Since the average charge of the cation sites decreases with an increase of x, the number of Cu^{2+} ions ($T<T_{MI}$) will become insufficient to develop the insulating 3-fold superstructure. Besides the disorder effect mentioned above, this seems to contribute to the suppression of metal instability by introducing Li^+ cations.

In conclusion, we have presented a mixed-metal (Cu/Li)-DCNQI system with a stable metallic state, whose IR spectra gave evidence that the charge density of DCNQI is variable between -1/2 and -2/3.

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