Charge-Transfer-Controlled Phase Transition in a Molecular Conductor, (DMe-DCNQI)$_2$Cu—Doping Effect—

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Li$^+$-doping in the Cu salt of deuterated DMe-DCNQI-$d_1$ has shown drastic effects on electrical and magnetic properties. Undoped (DMe-DCNQI-$d_1$)$_2$Cu exhibits a first-order metal-insulator (M-I) transition at 80 K. A small amount of Li$^+$-doping suppresses the M-I transition. The M-I-M (reentrant) transition, which is similar to that in selectively deuterated (DMe-DCNQI)$_2$Cu, appears in a narrow region of Li content x. The x-T phase diagram under ambient pressure well reproduces the P-T phase diagram of the (DMe-DCNQI)$_2$Cu system. This doping effect is explained by the change in charge transfer amount from metal ions to DCNQI molecules. The effect of pressure or deuteration on the M-I transition in the DCNQI$_2$Cu system is generally understood from this viewpoint.

[DCNQI, copper, doping effect, molecular conductor, metal-insulator transition, deuterium, charge transfer, reentrant transition]

The interaction between organic $p\pi$ bands and $d$-level of the transition metal includes very attractive physical problems. A molecular conductor DCNQI$_2$Cu (DCNQI = N,N$'$:di-cyanooquinodimine) system has a characteristic architecture: uniform one-dimensional (1D) columns (parallel to the tetragonal c axis) of planar DCNQI molecules interconnected by tetrahedrally coordinated Cu ions.\(^1\)\(^-\)\(^3\)\) The Cu ion in the metallic phase is in a mixed-valence (valence-fluctuating) state (Cu$^{4+/3+}$).\(^4\)\(^,\)\(^5\)\) The electronic structure is characterized by the coexistence of $d$-like narrow three-dimensional (3D) bands and wider $2p\pi$ 1D bands near the Fermi level.\(^2\)\(^,\)\(^3\)\(^,\)\(^6\)\) The undeuterated (DMe-DCNQI)$_2$Cu (abbreviated as h system) is metallic down to very low temperature (Group I). This h system exhibits a sharp metal(M)-insulator(I) transition even under unusually low pressure ($\geq$ 250 bar),\(^7\) or due to introduction of deuterium atoms:\(^8\)\) Group II. One of the unique characters of the DCNQI$_2$Cu system is the M-I-M (reentrant) transition observed in the vicinity of the critical pressure,\(^7\) or in selectively deuterated systems:\(^9\)\) Group III. The insulating state in these systems is accompanied concurrently by charge density wave (CDW) with the 3c period on the DCNQI 1D columns and by spatial charge ordering at the Cu site (Cu$^{4+}$:Cu$^{2+}$ = 2:1). The role of the pressure and/or the deuteration in this system has been the question at issue. In this paper, we propose that one of the essential parameters is the degree of the charge transfer between Cu and DCNQI, on the basis of detailed studies of the Li-doped system (DMe-DCNQI-$d_1$)$_2$Cu$_{1-x}$Li$_x$, (x < 0.1).

The Group II salt (DMe-DCNQI-$d_1$)$_2$Cu (d$_1$ system) has a tetragonal unit cell with the space group I4$_1$/a, and the lattice parameters are $a = 21.615(2)$ Å, $c = 3.8776(4)$ Å and $V = 1811.7(6)$ Å$^3$. (DMe-DCNQI)$_2$Li is isostructural with (DMe-DCNQI)$_2$Cu, but shows no marked isotope effect.\(^10\) The Li salt is a typical 1D conductor with 1/4-filled 1D bands because Li$^+$ is a closed-shell ion. The lattice parameters of the Li salt are $a = 21.848(3)$ Å, $c = 3.8528(8)$ Å and $V = 1839.1(6)$ Å$^3$. The difference between the structural parameters of the Cu and Li salts is so small that (DMe-DCNQI-$d_1$)$_2$Cu$_{1-x}$Li$_x$ forms a good solid solution with satisfactory quality throughout all the examined concentrations (x < 0.1). The structural parameters of the alloy system well conform to Vegard's law, indicating homogeneity in the crystals.

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Figure 1 shows the temperature dependence of resistivity of \((\text{DMe-DCNQI}-d_1)_2 \text{Cu}_{1-x} \text{Li}_x\) \((x<0.06)\). The pure Cu salt \((x=0)\) shows a sharp M-I transition at 80 K. The doping of a small amount of Li\(^+\) \((x=0.03)\) to the Cu site lowers the transition temperature (TMI). In the concentration region of 0.038 < \(x<0.052\), the giant reentrant transition is observed as in Group III.\(^{7,9}\) The larger contents of Li\(^+\) \((x \geq 0.055)\) stabilize metallic state down to 4.2 K.

Figure 2 shows the temperature dependence of the static magnetic susceptibility \((\chi)\) of the alloy systems (randomly oriented single crystals). The susceptibility of the Li salt \((x=1)\) gradually decreases with decreasing temperature down to 55 K, where a rapid drop due to the \(2k_F\) instability occurs.\(^{11}\) In the high-temperature metallic \((M_R)\) state, all the alloy systems exhibit almost constant and similar \(\chi\) values. The alloy system with \(x=0.01\) shows a typical temperature dependence of \(\chi\) for Group II salts.\(^{12}\) The behavior of the alloy with \(x=0.04\) is very similar to that of Group III.\(^{13,14}\) The suppression of the Curie constant in the insulating state and the enhancement of the Pauli-like susceptibility in the reentrant metallic \((M_R)\) state would be caused by the overcooling through the first-order transition.\(^{13,14}\) For instance, the susceptibility in the \(M_R\) state was appreciably reduced by the overnight anneal at point A in Fig. 2. Almost temperature-independent \(\chi\) of the system with \(x=0.06\) is consistent with the metallic temperature dependence of the resistivity.

X-ray monochromatic Laue photographs were taken at 60 K \((M_0)\), 45 K \((I)\) and 10 K \((M_3)\) for the alloy with \(x=0.04\) (Fig. 3). The satellite reflections are observed only in the insulating state as in other Group III salts.\(^{13,15,16}\) It was recognized that the period of the lattice distortion in the insulating state is exactly 3c for not only this sample but also other Li-doped ones. The 3c periodicity implies that the charge of DCNQI is \(-2/3\) \((1/3\)-filled 1D band\), and the formal valence of Cu is +4/3 in the insulating state. When the formal valence of Cu is +4/3, the charge distribution is conducted as \(\cdots \text{Cu}^{2+} \text{Cu}^{+} \text{Cu}^{+} \cdots\) along the c axis. Therefore, the 3c periodicity is a special point where both the CDW and the charge ordering can appear with the same period.\(^{17}\) Such a situation yields a large energy gain due to the commensurability between the \(p\pi\) and \(d\)-systems. If the valence of Cu (DCNQI) exhibits a shift from +4/3 \((-2/3)\) in the M state, the redistribution of the charge is required for the M-I transition. Therefore, such a shift of valence should tend to lower \(T_{MI}\), which plays an important role in the subsequent discussion.

On the basis of the resistivity measurements, the \(x-T\) phase diagram shown in Fig. 4 is deduced. By taking \(\Delta P/\Delta x = -5.8 \times 10^3\) bar, this \(x-T\) phase diagram well agrees with
the $P$-$T$ phase diagram. Thus, the Li$^+$-doping corresponds to negative pressure.

The next useful information is the influence of the divalent-metal doping. Figure 5 shows the temperature dependence of resistances of Zn$^{2+}$-doped $d$ and $h$ systems. In the $d$ system (Group II), the Zn$^{2+}$-doping slightly raises $T_M$, while the Li$^+$-doping lowers it. In the $h$ system (Group I), the Li$^+$-doping does not affect the metallic state for causing an except increase in the residual resistance due to randomness. On the other hand, the weak re-entrant behavior is caused by the Zn$^{2+}$-doping. Thus, the Zn$^{2+}$-doping corresponds to positive pressure.

In order to explain all these doping effects in the (DMe-DCNQI)$_2$Cu$_{1-x}$X$_x$ (X=Li, Zn; $x<0.1$) system, we introduce two assumptions: i) In the M state of the pure Cu salt, the valence of DCNQI positively shifts from $-2/3$, and therefore the valence of Cu ($q_0$) is expressed as $q_0 = 4/3 - \delta$, where $\delta$ is a small positive number ($0 < \delta < 1/3$). ii) The valence of Cu is not affected by the doping and remains $q_0$. This assumption is not obvious. However, the valence of Cu would be governed by the local coordination, and this coordination for almost all the Cu sites would not be affected in the small $x$ region ($x<0.1$).

In the Li$^+$-doped system, the average valence of the metal site ($q$) is described as follows: $q = q_0 + x(1-x) + 1/3 x = 4/3 - \delta - (1/3-\delta) x$. In this case, since $\delta x$ can be negligible, $q = 4/3 - \delta - x/3$.

The valence of DCNQI molecule ($p$) is $p = - q/2$. Monovalent-metal doping enhances the shift of $q$ ($p$) from the special point $+4/3$ ($-2/3$), which stabilizes the metallic state (Fig. 4).

On the other hand, in the Zn$^{2+}$-doped system, the formal valence of the metal site is calculated in a similar way, $q = 4/3 - \delta + 2x/3$; (Cu$^{4/3-\delta}$(Zn$^{2+}$)$_x$). This indicates that divalent-metal doping raises $T_M$ because the $q$ ($p$) value shifts closer to $+4/3$ ($-2/3$).

The $x$-$T$ phase diagram is well explained in terms of the change in the charge transfer amount (Fig. 4). This result gives us a suggestion that the general $P$-$T$ phase diagram of the DCNQI$_2$Cu system can also be explained.

* The Zn$^{2+}$-doped crystals had poor quality, and we could not measure other properties. The Zn concentration in the crystal was determined by EMPA.
valent-metal doping. This would be a general interpretation of the “pressure”-induced M-I transition in the DCNQI$_2$Cu system.

In conclusion, the Li$^+$-doped alloy system (DME-DCNQI-$d_1$)$_2$Cu$_{1-x}$Li$_x$ has reproduced the low-pressure region of the P-T phase diagram. The degree of charge transfer from Cu to DCNQI molecule is proposed to be a fundamental factor which governs the stability of the metallic state.

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References

* It should be noted that the Li$^+$-doping tends to enlarge the distortion, which appears to contradict the above description. This is because in the low-$x$ region the shift $\delta$ is affected mainly by the Li contents ($x$) and not by the distortion of the Cu coordination.