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Reentrant Behavior of the Temperature Dependence of Resistivity of DCNQI-Cu Alloy System, $[(\mathrm{DMe})_{1-x}(\mathrm{MeBr})_x\text{-DCNQI}]_2\mathrm{Cu}$

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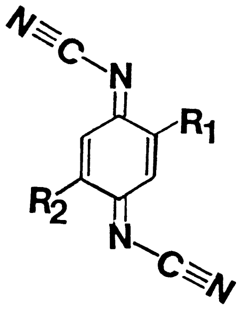
Reentrant resistivity behavior (metal→semiconductor→metal) is observed at ambient pressure in the alloy system of $[(\text{DMe-DCNQI})_{1-x}(\text{MeBr-DCNQI})_x]_2\mathrm{Cu}$ ($x<0.1$). Resistivity maximum appears around 60 K. The magnitude of the resistivity maximum is extremely sensitive to x. This anomaly resembles the anomalous pressure-induced reentrant resistivity behavior in $(\text{R,R-DCNQI})_2\mathrm{Cu}$ (R= CH_3, CH_3O).

Recent progress in the field of the molecular conductors has brought about a new interesting system, $(\mathrm{R_1,R_2\text{-}DCNQI})_2\mathrm{Cu}$($R_1$, R_2 = CH_3, CH_3O, Cl, Br, I; DCNQI =N,N'-dicyanoquinonediimine). The crystals are composed of the one-dimensional(1D) columns of R_1,R_2-DCNQI molecules interconnected through the tetrahedrally coordinated Cu cations.1-3) They have many exotic features: (1) 2pπ-d mixing in the formation of the conduction band (2) mixed-valency of Cu (Cu^+, Cu^{2+}) and antiferromagnetic interaction of Cu^{2+} spins via organic molecules and (3) pressure-induced resistivity anomaly. All these features are considered to be interrelated with each other. The DCNQI-Cu systems can be classified into two groups: (I) the system with stable metallic state down to at least 0.5 K (e.g. $(\text{DMe-DCNQI})_2\mathrm{Cu}$, $R_1=R_2=CH_3$) and (II) the system with sharp metal-insulator (MI) transition (e.g. $(\text{MeBr-DCNQI})_2\mathrm{Cu}$, ($R_1=CH_3$, R_2=Br) (T_{MI}= 156 K)). The group-I compound shows a pressure-induced metal instability above the critical pressure (Pc) and transforms to group-II compound at higher pressure.4-6) In the case of $(\text{DMe-DCNQI})_2\mathrm{Cu}$, Pc is extremely low (≈50 bar). In usual molecular conducting systems with one-dimensional (1D) nature, the MI transitions are originated from the nature of the electric susceptibility ($\chi(q,T)$) of 1D electron gas, which diverges at $q= 2k_F$ and T= 0 K. Since pressure tends to suppress this divergence, the metallic state becomes more stable under high pressure. Therefore, the pressure-induced metal instability observed in the DCNQI-Cu system with the stacking structure of planar π-molecules is not so trivial. In addition, this system exhibits a unique temperature dependence of resistivity (ρ) at high pressure (metal → semiconductor → metal).5,6) For



R_1,R_2-DCNQI

example, the metallic state of $(DMeO\text{-}DCNQI)_2Cu$ becomes unstable above 8 kbar and below ca. 100 K. The system reenters into the metallic phase below ca. 60 K. We have recently proposed that the DCNQI-Cu system is a possible candidate of the molecular metal which belongs to a family of so-called dense Kondo materials ever known in the metallic compounds of lanthanides and actinoides such as CeB_6 and UPt_3. The interaction between 2pπ conduction electrons and the magnetic ions (Cu^{2+}) is considered to be of central importance.[6)]

In this paper, we will report that similar "reentrant resistivity behavior" is also observable at ambient pressure in the alloy system, $[(DMe\text{-}DCNQI)_{1-x}(MeBr\text{-}DCNQI)_x]_2Cu$ (hereafter, $[(DMe\text{-}DCNQI)_{1-x}(MeBr\text{-}DCNQI)_x]_2Cu$ is abbreviated to $[(DMe)_{1-x}(MeBr)_x\text{-}DCNQI]_2Cu$).

The black needle crystals of $[(DMe)_{1-x}(MeBr)_x\text{-}DCNQI]_2Cu$ were prepared electrochemically from the acetonitrile solutions of DMe-DCNQI and MeBr-DCNQI with various mixing ratios. $[Cu(CH_3CN)_4]ClO_4$ was used as a supporting electrolyte. The values of x were determined on 13 crystals by the X-ray crystal structure refinements of the occupancy probability of the Br-site (or Me-site).[7)] The mixing ratio of DMe-DCNQI and MeBr-DCNQI in the acetonitrile solution was largely different from the DMe/MeBr ratio in the crystal. As shown in Fig. 1, MeBr-DCNQI tends to be highly concentrated in the solid. The electrical resistivities were measured by conventional four probe method over the temperature range of 4.2 - 300 K. Gold wires of 15 μm diameter were bonded to the crystals with gold paint and used as the electrical leads.

The lattice constants of $[(DMe)_{1-x}(MeBr)_x\text{-}DCNQI]_2Cu$, determined by a Rigaku automated X-ray four-circle diffractometer are not simple arithmetic means of the lattice constants of $(DMe\text{-}DCNQI)_2Cu$ and $(MeBr\text{-}DCNQI)_2Cu$. The cell volume takes a

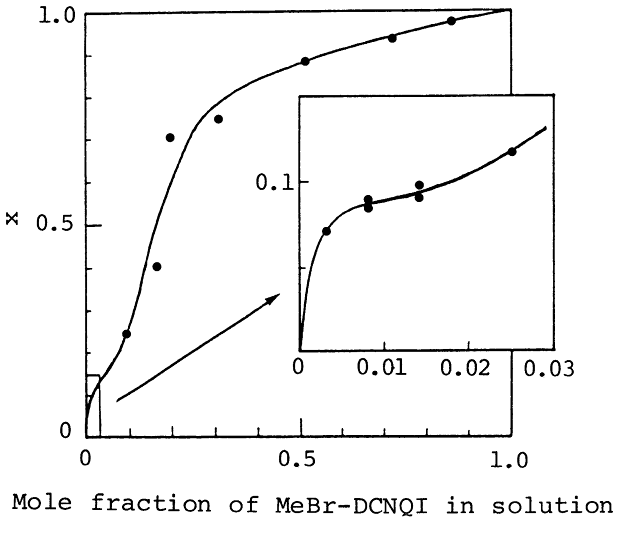


Fig. 1. Correlation diagram between x determined from X-ray crystal structure refinement and the mole fraction of MeBr-DCNQI in solution.

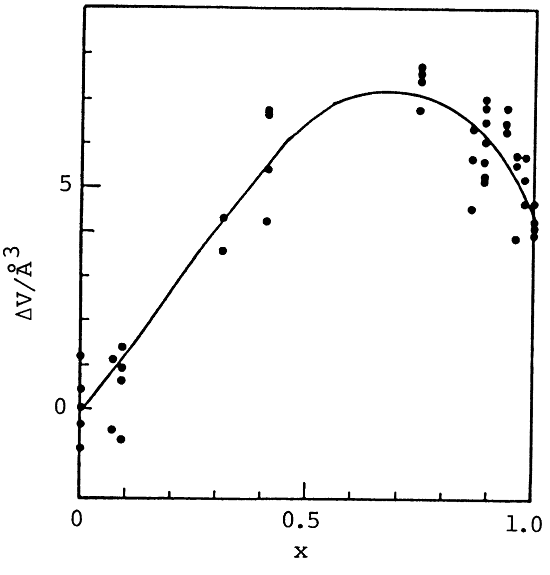


Fig. 2. Unit cell volume of $[(DMe)_{1-x}(MeBr)_x\text{-}DCNQI]_2Cu$ as a function of x. The cell volume of $(DMe\text{-}DCNQI)_2Cu$ is 1797.4 Å^3 (x=0.0).

maximum around x= 0.6-0.7 (Fig. 2). Similar non-additivity also appeared in the temperature dependence of the resistivity. Since $(DMe\text{-}DCNQI)_2Cu$ is metallic down to low temperature and $(MeBr\text{-}DCNQI)_2Cu$ undergoes a MI transition at 156 K, it might be imagined that the alloy system would exhibit a MI transition whose transition temperature decreases continuously with increasing x. However, the observed resistivity behavior was quite different. The modes of the temperature dependences of the resistivity changes can be classified into four types: (I) $x < 0.1$; a reentrant resistivity behavior (metal → semiconductor → metal) similar to that observed in the group-I compound at high pressure was observed (Fig. 3). The residual resistivity seems to increase rapidly with x, indicating the strong effect of the lattice disorder. The reentrant behavior is accompanied by the hysteresis. The possible existence of some kind of domain structures (or non-uniformity) of the alloy system might be responsible for it. (II) $0.1 < x < 0.6$; the T-ρ curve shows a large hysteresis. In the cooling cycle, the system is metallic down to ca. 90 K where ρ increases almost discontinuously, while the system remains to be low-conductive up to ca. 210 K in the warming cycle. (III) $x \approx 0.7$; the system shows semiconductive behavior for all over the temperature range, which may be ascribed to the electron localization due to the expected large lattice disorder. (IV) $x > 0.8$; the system shows a sharp MI transition around 155 K similar to that of pure $(MeBr\text{-}DCNQI)_2Cu$, where a small hysteresis was observed.

As mentioned above, the increase of ρ followed by the reentrance of the metallic phase has been already found in group-I compound at high pressure.

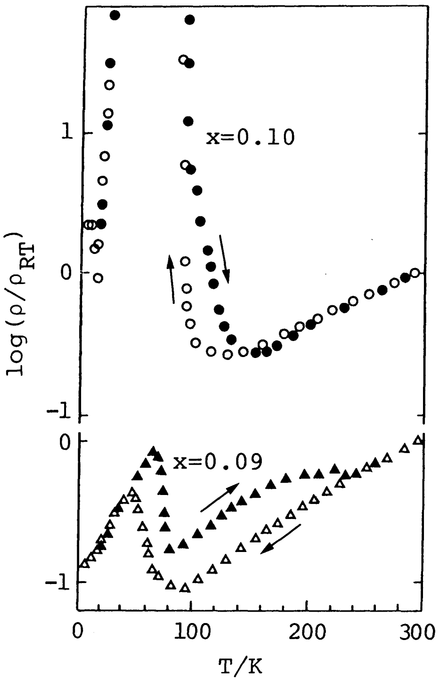


Fig. 3. Temperature dependence of the resistivity of $[(DMe)_{1-x}(MeBr)_x\text{-}DCNQI]_2Cu$. Room-temperature resistivities are ca. 10^{-3} Ω cm.

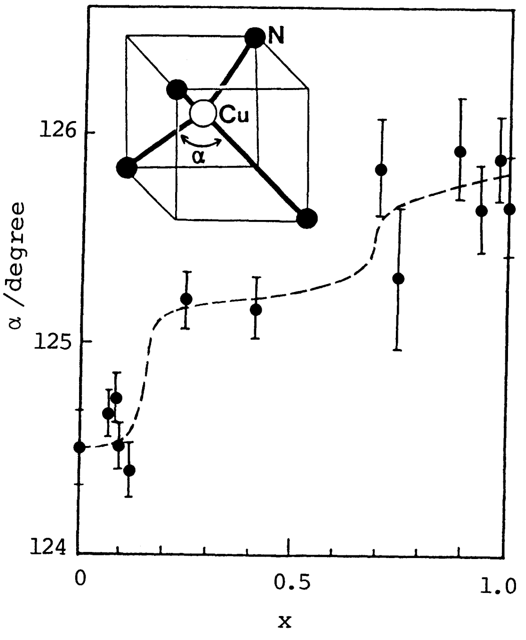


Fig. 4. The x dependence of α.

Therefore, the increase of x and the pressure might be considered to have similar effect on the crystal lattice. However, the situation is not so simple. Since the unit cell volume of $(DMe\text{-}DCNQI)_2Cu$ is smaller than that of $(MeBr\text{-}DCNQI)_2Cu$, the replacement of DMe-DCNQI by MeBr-DCNQI makes the cell volume large. This is contrary to the pressure effect. Therefore, the observation of the reentrant ρ behavior in the alloy system suggests that the reduction of the cell volume is not essential to induce the metal instability. As pointed out before, the magnitude of the $\bar{4}$ distortion of the coordination geometry around Cu seems to be essential for determining the stability of the metallic sate of the DCNQI-Cu system.[2,3] The angle α ($\angle$ N-Cu-N) can be regarded as a good measure of the magnitude of the crystal field splitting of 3d orbitals of Cu (see Fig. 4). The x dependence of α, determined by the X-ray crystal structure refinement, shows that α increases stepwise with increasing x. There are three regions: small-α region ($x<0.1$), intermediate α-region ($0.1<x<0.6$) and large-α region ($0.8<x$). The reentrant resistivity behavior was observed in the small-α region, where the coordination geometry is almost identical to that of pure $(DMe\text{-}DCNQI)_2Cu$. This is consistent with that Pc of $(DMe\text{-}DCNQI)_2Cu$ is extremely low ($\approx$50 bar).

In summary, we have observed the metal instability and the reentrant resistivity behavior in the DCNQI-Cu alloy system, $[(DMe)_{1-x}(MeBr)_x\text{-}DCNQI]_2Cu$ in the small x region. This observation opens a way to study the nature of the reentrant resistivity anomaly at ambient pressure. Detailed studies are now in progress.

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7) The X-ray intensity data were collected on a Rigaku automated diffractometer and corrected for absorption. The final R-values were 0.04-0.08 % (for 13 crystals). A good agreement between the x-value determined by X-ray structure refinement and that by X-ray microanalysis (XMA) has been confirmed in the similar alloy system $\beta\text{-}(BEDT\text{-}TTF)_2(I_3)_{1-x}(AuI_2)_x$ (A. Kobayashi et al. (to be published)). The details of the structure refinement will be published elsewhere.

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