

Mixed valency of Cu, electron-mass enhancement, and three-dimensional arrangement of magnetic sites in the organic conductors
 $(R_1, R_2-N, N'$ -dicyanoquinonediimine) $_2$ Cu
(where $R_1, R_2 = CH_3, CH_3O, Cl, Br$)

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(Received 7 July 1992; revised manuscript received 13 October 1992)

The unique molecular conductors with $p\pi$ - d mixing band structures $(R_1, R_2-N, N'$ -dicyanoquinonediimine) $_2$ Cu [$(R_1, R_2$ -DCNQI) $_2$ Cu] ($R_1, R_2 = CH_3, CH_3O, Cl, Br$) were examined. General features of the phase diagram of the DCNQI-Cu system were depicted. A region that is related to the existence of anomalously heavy-metal electrons has been found. The T^2 dependence of the low-temperature resistivity of the alloyed system $(DMe_{1-x}MeBr_x$ -DCNQI) $_2$ Cu (where $Me = CH_3$) suggests a large enhancement of the electron mass at the critical situation where the system begins to exhibit a characteristic metal instability. The mixed valency of Cu ($Cu^{+1.3}$) in $(DMe$ -DCNQI) $_2$ Cu was confirmed by ir experiments performed on neutral DMe-DCNQI crystals and $(DMe$ -DCNQI) $_2M$ ($M = Li, Ba, Cu$). The same conclusion was also derived from a low-temperature x-ray-diffraction experiment. The gradual temperature dependences of the ir absorption intensities of totally symmetric modes of $(DMe$ -DCNQI) $_2$ Cu observed below the metal-insulator transition temperature (T_{MI}) are in contrast with the discontinuous resistivity and susceptibility changes at T_{MI} . This may be attributable to the existence of two driving forces characterizing the M - I transition. One is the sharp charge ordering in Cu sites and the other is the continuous development of charge-density waves on DCNQI stacks. The arrangement of Cu^{2+} and Cu^+ below T_{MI} was determined by an x-ray crystal-structure analysis of the threefold insulating phase of $(MeBr$ -DCNQI) $_2$ Cu at 110 K. The nearest-neighbor Cu^{2+} ions interact with each other via two DCNQI molecules. A plausible spin structure of the antiferromagnetic ground state was proposed. According to this spin-structure model, the magnetic moments of Cu^{2+} along the crystallographic c axis will be arranged ferromagnetically.

I. INTRODUCTION

In 1986, Aumüller *et al.* reported a molecular metal containing Cu atoms, $(DMe$ -DCNQI) $_2$ Cu (DMe -DCNQI = 2,5-dimethyl- N, N' -dicyanoquinonediimine) (Fig. 1).¹ Judging from the mode of molecular arrangement of DCNQI, it seemed mysterious that this system does not exhibit metal instability down to very low temperatures. The system must therefore have a non-one-dimensional (non-1D) electronic structure. But if the Cu cation is a closed-shell cation, there seems almost no possibility to obtain a non-1D electronic structure. In the course of our research on the DCNQI-Cu system, we have pointed out that the main interest of this system stems from the mixed valency of Cu, which means that the highest Cu 3d level is nearly equal to the Fermi level of the $2p\pi$ metal band of DCNQI.² In such a situation, even a weak interaction between the Cu 3d orbital and the frontier

molecular orbital of DCNQI can change the shape of Fermi surfaces or in other words, the nature of the metallic state.

Many DCNQI-Cu systems with various substituents analogous to $(DMe$ -DCNQI) $_2$ Cu have been examined.²⁻⁷ All the DCNQI-Cu systems are isomorphous and have tetragonal unit cells ($a = 21.5-22.5$, $c = 3.82-3.90$ Å) and space group $I4_1/a$. Planar DCNQI molecules are on the centers of symmetry and are stacked along the crystallographic c axis to form a 1D regular column. The Cu atom is coordinated by the terminal N atoms of surrounding DCNQI molecules in a D_{2d} distorted tetrahedral fashion ($\angle N$ -Cu-N $\approx 125^\circ$ and r (Cu-N) ≈ 1.97 Å).^{2,5} Despite the close resemblance of these structures, there are two groups in the DCNQI-Cu systems. Group-I compounds, to which $(DMe$ -DCNQI) $_2$ Cu and $(DMeO$ -DCNQI) $_2$ Cu belong, have stable metallic states down to very low temperatures (~ 50 mK), whereas

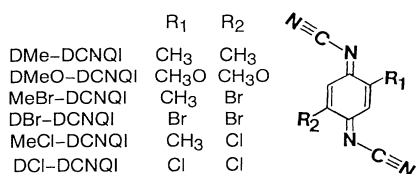


FIG. 1. Molecular structures and their abbreviations of 2,5- R_1, R_2 -DCNQI molecules.

group-II compounds, such as (MeBr-DCNQI)₂Cu and (DBr-DCNQI)₂Cu exhibit sharp metal-insulator ($M-I$) transitions accompanied by structural changes. Despite the orientational disorder of DCNQI molecules, very sharp $M-I$ transitions were observed even for systems composed of asymmetric DCNQI molecules [e.g., (MeBr-DCNQI)₂Cu], where Me=CH₃.

When x-ray-diffraction experiments revealed the development of the threefold structure below T_{MI} , it was noticed that the DCNQI-Cu system cannot be a simple monocation salt.² In fact, some Li and Ag salts with isomorphous structures were found to transform to fourfold structures ($c \rightarrow 4c$) at low temperatures.^{8,9} The fourfold structure corresponds to the $2k_F$ structure of the 2:1 monocation salt. In contrast, the threefold structure of the Cu salt and its 2:1 stoichiometry suggest a formal charge for Cu of +1.3. That is, Cu is in a mixed-valence state, which has recently been confirmed by x-ray photoemission spectroscopy (XPS) of (DMe-DCNQI)₂Cu [Cu(2p), N(1s)].¹⁰ The asymmetry of the XPS peaks [Cu(2p)] and the hump in the spectra were reasonably explained by a line-shape analysis. The valence of Cu fluctuates between that of Cu⁺ and Cu²⁺. The [Cu⁺]/[Cu²⁺] ratio is 2:1, which agrees with the prediction on the mixed valency of Cu based on an x-ray-diffraction experiment.²

In this paper, the ir evidence of the mixed valence of Cu, the general features of the phase diagram of DCNQI-Cu systems, the T^2 temperature dependence of the resistivity in the "low-temperature reentrant metallic state," and the x-ray crystal-structure analysis of the three-dimensional arrangement of Cu²⁺ and Cu⁺ below T_{MI} will be reported. A brief comment on the antiferromagnetic spin arrangement will be also made.

II. EXPERIMENT

Crystals of (R_1, R_2 -DCNQI)₂Cu and the alloy systems [(DMe-DCNQI)_{1-x}(MeBr-DCNQI)_x]₂Cu [abbreviated as (DMe_{1-x}MeBr_x-DCNQI)₂Cu] and [(DMe-DCNQI)_{1-x}(DBr-DCNQI)_x]₂Cu [abbreviated as (DMe_{1-x}DBr_x-DCNQI)₂Cu] were prepared electrochemically. The x values of 15 crystals were determined by x-ray crystal-structure analyses in which the occupancy probabilities of the atom of the Br sites (or Me sites) were refined. The x values thus determined must be considered to be the averaged ones because the mixing ratio of DMe-DCNQI and MeBr-DCNQI was found to be very inhomogeneous so that the distribution of x values in a crystal had to be determined by EPMA (electron probe microanalysis). The nine crystals were chosen

from three batches of the crystals. The [Cu]/[Br] ratio was determined on about 50 different data points per crystal.

The ir spectra of the KBr disks of R_1, R_2 -DCNQI and (R_1, R_2 -DCNQI)₂ M ($R_1, R_2 = \text{CH}_3, \text{Br}$; $M = \text{Cu, Li, Ba}$) were examined by using a Fourier-transform infrared (FTIR) spectrometer (Shimadzu FTIR-4000 and JEOL JIR-100) in the temperature range 300–25 K.

The electron spin resonances (ESR) were made on powdered samples of (MeBr-DCNQI)₂Cu by using JES FE1X and JESRE3X spectrometers over the temperature range 300–4.2 K. The g values were determined by simulating the spectra.

The electrical resistivities were measured by use of the four-probe method between 300 and 1.6 K. $15 = \mu\text{m}\phi$ -cross sectional-diameter gold wires were bonded to the crystal with gold paint and used as leads. The high-pressure resistivities were measured by using clamp-type high-pressure cells. Silicon oil (Idemitsu Daphne No. 7373) was used as pressure medium. The resistivities reported in this paper are those measured along the needle axis. The ratio of the resistivity of (DMe-DCNQI)₂Cu along the needle (c) axis (ρ_{\parallel}) and that perpendicular to it (ρ_{\perp}) was about 30 at room temperature. The room-temperature resistivity (ρ_{\parallel}) was 500–200 S cm⁻¹.

The low-temperature crystal-structure analysis of (MeBr-DCNQI)₂Cu was performed. Because of the weak intensities of the x-ray superlattice spots of the salts (DBr-DCNQI)₂Cu and (DCI-DCNQI)₂Cu, which were grown as thin needles, they were inappropriate for the x-ray data collection. After several trials, the x-ray intensity data were collected on a Rigaku automated diffractometer and a MAC rotary x-ray generator (18 kW, Mo $K\alpha$) at 115 K. The crystal was cooled by putting it in a stream of cold N₂ gas. The x-ray experiments were also made in the temperature range 300–20 K by using a T-2000 Cryo Controller (TRI Research, Inc.). Monochromatic Laue photographs were taken with Mo $K\alpha$ radiation.

III. EVIDENCE ON THE MIXED VALENCY OF Cu

As mentioned above, the indication of the mixed valency of Cu was first obtained from the x-ray observation of the development of the threefold structure below T_{MI} of (MeCl-DCNQI)₂Cu.² We have recently reported the ir evidence of the mixed valency of Cu in (MeBr-DCNQI)₂Cu.¹¹ The electron transferred form Cu to DCNQI occupies the lowest vacant molecular orbital of DCNQI, which has antibonding nature on the C=N(imine) and C=C bonds, so that the strength of the C=N(imine) and C=C bonds is reduced and their stretching frequencies are lowered with increasing magnitude of the charge transfer. The ir spectra of MeBr-DCNQI salts revealed that the absorption at 1540 cm⁻¹ of neutral MeBr-DCNQI assigned to the C=N(imine) stretching vibration frequency (ν) shows a large shift in Li (1500 cm⁻¹) and Cu (1488 cm⁻¹) salts, indicating a linear dependence on the charge (δ) of MeBr-DCNQI [$\delta=0$ (neutral molecule), 0.5 (Li salt), 0.66 (Cu salt)]:

$\nu=1540-79\delta$. This relation gave an evidence of the mixed valency of Cu ($+4/3$).¹¹

In order to obtain further ir evidence of the mixed valency of Cu for both group-I and group-II compounds, the ir spectra of DMe-DCNQI, DBr-DCNQI, (DBr-DCNQI)₂M, and (DMe-DCNQI)₂M ($M=Li, Cu, Ba$) were examined. The neutral molecule, Li salt, and Ba salt were used as standard materials showing the vibration frequency at $\delta=0$ (neutral molecule), 0.5 (Li salt), and 1.0 (Ba salt). The good correlation between δ and the ir frequency (ν) was obtained for various vibration modes including the C=N(imine) stretching mode.¹² Figure 2 shows the linear dependence of ν on δ in DMe-DCNQI systems at room temperature. A similar relation was also obtained for DBr-DCNQI systems. From the relation between δ and ν , the δ value of Cu salt was estimated to be about $2/3$. Therefore the charge of Cu must be $+4/3$. Since every Cu site is crystallographically equivalent in the metallic phase, the valence of Cu can be fixed in neither Cu⁺ nor Cu²⁺ but takes the intermediate state. Thus the ir spectra gave clear evidence of the average Cu valence in (DMe-DCNQI)₂Cu to be +1.3, which agrees with the XPS results.¹⁰ In contrast to the XPS spectra, which distinguish between Cu⁺ and Cu²⁺ and also between N atoms bonding to Cu⁺ and those bonding to Cu²⁺, the ir spectra show every DMe-DCNQI to be equivalent. This suggests the upper and lower limits of the lifetime of the valence fluctuation in the DCNQI-Cu system.

At low temperature, the ir bands of (DBr-DCNQI)₂Cu were split (Fig. 3), indicating the freezing of the charge-density wave (CDW) on DBr-DCNQI stacks. The magnitude of the splitting of the ir band at 25 K suggests that δ takes the values between 0.5 and 1.0. The details will be reported elsewhere.¹² The totally symmetric modes (869, 1220, 1312, 1566, 2135 cm⁻¹), which were also observed in the Raman spectra of neutral DCNQI, become ir active below T_{MI} (~ 155 K).¹³ The temperature dependence of the absorption intensities (Fig. 4) indicates the gradual structural change of DCNQI stacks, which is consistent with the gradual development of the split bands. As reported before, the $M-I$ transition of

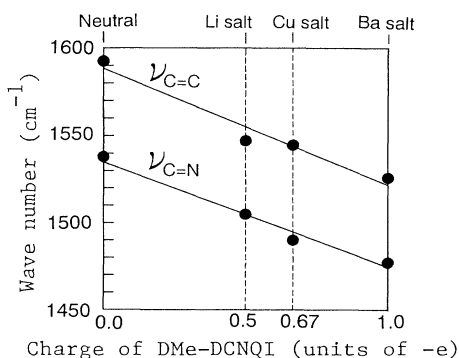


FIG. 2. Plot of C=N(imine) and C=C stretching frequencies of DMe-DCNQI molecules in neutral and (DMe-DCNQI)₂M ($M=Li, Ba, Cu$) against charge of DMe-DCNQI.

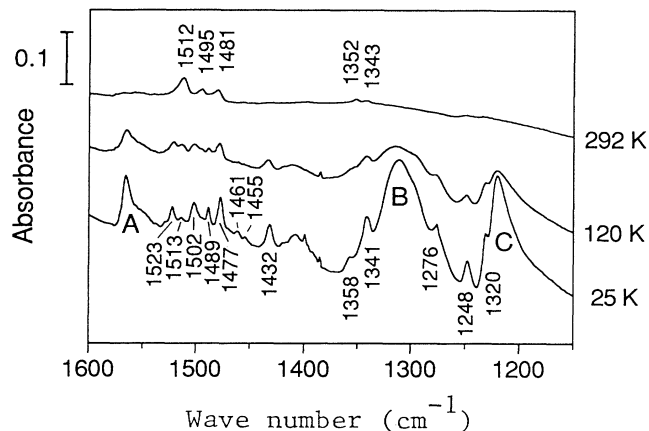


FIG. 3. The ir spectra of (DBr-DCNQI)₂Cu, showing the splitting of the peaks and the development of totally symmetric modes around 1200, 1300, and 1550 cm⁻¹ below T_{MI} ($T_{MI}=155$ K).

DCNQI-Cu systems cannot be regarded as a simple CDW transition but is considered to be induced by the cooperation of the distortion of the coordination tetrahedra, indicating the ordering of Cu⁺ and Cu²⁺ in the cation sites and the development of CDW on DCNQI stacks.^{2,5,14} The valence of Cu is considered to be fixed at T_{MI} , where a small jump of the susceptibility is observed.¹³ On the other hand, the present ir experiments seem to show that the temperature dependence of the development of the CDW on DCNQI stacks is more moderate. Therefore the sharp $M-I$ transition is considered to be triggered mainly by the charge ordering in the Cu sites, which is followed by the gradual development of the CDW on DCNQI stacks.

IV. PHASE DIAGRAM OF THE DCNQI-Cu SYSTEM

It is well known that the metallic state of group-I compounds becomes unstable under high pressure.¹⁵⁻¹⁷ The

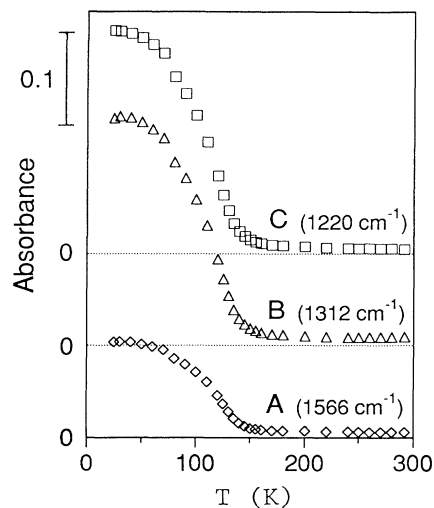


FIG. 4. Temperature dependence of ir intensities of totally symmetric modes.

critical pressure (P_c) of $(\text{DMe-DCNQi})_2\text{Cu}$, where the metal instability begins to appear, has been reported to be about only 10^2 bars.¹⁶ That of $(\text{DMeO-DCNQi})_2\text{Cu}$ is 6 kbar.¹⁸ Tomić *et al.* have reported an anomalous reentrant resistivity behavior of $(\text{DMe-DCNQi})_2\text{Cu}$ (metal \rightarrow semiconductor \rightarrow metal), observed in a small range of pressures above P_c . In the case of $(\text{DMeO-DCNQi})_2\text{Cu}$, a similar reentrant resistivity behavior was observed in the pressure range 6–7.5 kbar. At higher pressures the transition became sharp and the reappearance of the metallic phase could not be observed. The resistivity behavior at the higher-pressure region resembles those of group-II compounds. So, roughly speaking, a group-I compound is changed to a group-II compound at high pressure.¹⁷ In most group-II compounds, the system exhibits a M - I transition in the temperature range of 150–230 K and transforms to the antiferromagnetic state around 10 K: $(X,\text{Br-DCNQi})_2\text{Cu}$ ($X=\text{CH}_3,\text{Br}$), $T_{MI} \sim 155$ K, $T_{AF} \sim 12$ K; $(X,\text{Cl-DCNQi})_2\text{Cu}$ ($X=\text{CH}_3,\text{Cl}$), $T_{MI} \sim 210$ K, $T_{AF} \sim 9$ K.^{4,13}

In order to reconfirm the temperature dependence of the magnetic properties of group-II compounds, ESR spectra of $(\text{MeBr-DCNQi})_2\text{Cu}$ were examined and analyzed by simulating the spectra. The ESR signal due to Cu^{2+} could be observed over the entire temperature range 4–300 K. The peak-to-peak linewidth (H_{pp}) is about 230 G at room temperature and slowly decreases down to 160 K [$H_{pp}(160\text{ K})=205$ G]. A small jump of H_{pp} showing a change of the line shape was observed around 155 K, where the signal intensity begins to increase. The g values of the weak signal obtained above T_{MI} and below 10 K are different from those of the spectra taken between 150 K ($\sim T_{MI}$) and 12 K ($\sim T_{AF}$). This indicates the existence of Cu^{2+} ions probably produced by grinding the crystals into powder. The ESR spectra were simulated by use of the following parameters: g values (g_{\parallel} and g_{\perp}), hyperfine coupling constants (A_{\parallel} and A_{\perp}), and linewidth ($\Delta H_{1/2}$). An example of the comparison of the observed and simulated spectra is inserted in Fig. 5. The g values ($g_{\parallel}=2.40$, $g_{\perp}=2.06$) of the spectra observed below T_{MI} are characteristic of the g values of the Cu^{2+} ion in tetrahedral coordination and are in good agreement with those of $(\text{DMe-DCNQi})_2\text{Cu}$ obtained from single-crystal ESR experiments (Fig. 5).^{4,19} There was no change of the coordination structure between 150 and 12 K. The temperature dependence of the intensity ($20\text{ K} < T < 100\text{ K}$) suggests antiferromagnetic interaction between Cu^{2+} ions.⁴ The sharp drop of the intensity below 12 K corresponds to the onset of the magnetic transition. The dominant signals below 10 K, which probably originated from the extrinsic Cu^{2+} , gave g values of 2.17 and 2.04, indicating that the coordination structure of the extrinsic Cu^{2+} ion is different from that of the intrinsic one.

The antiferromagnetic transition suggested by the ESR and χ measurements^{4,13} has also been confirmed by NMR. Takahashi *et al.* have recently observed a sudden increase of $T^{-1}(H)$ of $(\text{DBr-DCNQi})_2\text{Cu}$ at T_{MI} and a sharp drop of $T^{-1}(H)$ around T_{AF} , which indicate the appearance of Cu^{2+} and the antiferromagnetic ordering

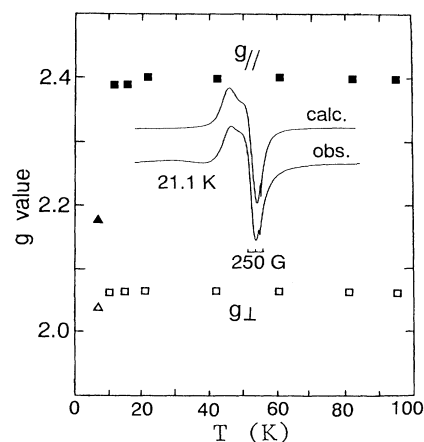


FIG. 5. The g values of Cu^{2+} signals obtained by simulation of the spectra. The triangles below 10 K indicate the g values of the signal of the extrinsic Cu^{2+} probably produced by grinding the sample to powder.

of the magnetic moments, respectively.²⁰ They have observed a similar NMR behavior in $(\text{DMe-DCNQi})_2\text{Cu}$ at high pressure,²⁰ which is consistent with the proposal that a group-I compound can be considered to transform to a group-II compound at high pressures.¹⁷

Contrary to the case of the usual molecular metals, the metallic state of the DCNQi-Cu system tends to become unstable with increasing pressure. In order to develop a better understanding of this anomalous property, we have measured the high-pressure resistivities of $(\text{MeBr-DCNQi})_2\text{Cu}$, which exhibits a M - I transition at 155 K at ambient pressure. As shown in Fig. 6, T_{MI} increases with increasing pressure. The room-temperature resistivity also increases above 2 kbar. A similar pressure dependence of T_{MI} has already been found in $(\text{MeCl-DCNQi})_2\text{Cu}$.²¹ The transition became broad and slug-

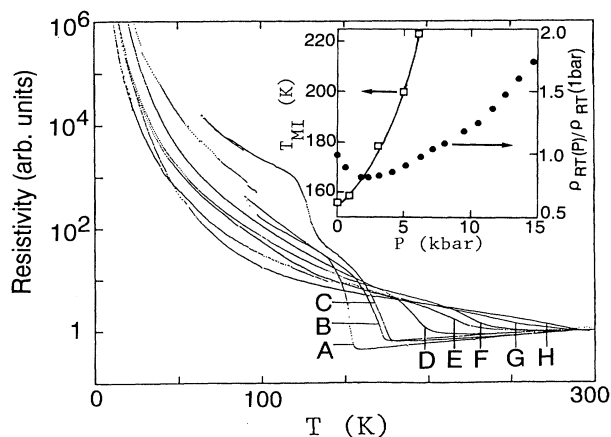


FIG. 6. Resistivities of $(\text{MeBr-DCNQi})_2\text{Cu}$ at high pressure: A = 1 kbar; B = 3 kbar (cooling cycle); C = 3 kbar (heating cycle); D = 4 kbar; E = 6 kbar (cooling cycle); F = 6 kbar (heating cycle); G = 10 kbar; H = 15 kbar. The inset is the pressure dependence of the metal-insulator transition temperature and pressure change of room-temperature resistivity [ρ (1 bar) = $3 \times 10^{-3} \Omega \text{ cm}^{-1}$].

gish at high pressures. No clear transition could be observed above 10 kbar. Around 3 kbar, stepwise M - I transitions with hysteresis were observed but it could not be determined whether or not it represents an intrinsic effect. The temperature dependence of the resistivity below T_{MI} cannot be fitted by a simple activation plot but seems to be linearly dependent on $\exp(T^{-1/4})$.

In summarizing the information on the electric, magnetic, and structural properties known, general features of the phase diagram of DCNQI-Cu systems have been depicted in Fig. 7. The abscissa (P) is the "effective pressure" whose origin is chosen tentatively as the P_c of $(\text{DMe-DCNQI})_2\text{Cu}$. Characteristic stepwise M - I transitions have been observed in $(\text{DMe-DCNQI})_2\text{Cu}$ between 3 and 7.5 kbar.¹⁶ The location of four DCNQI-Cu systems at ambient pressure is indicated by arrows. There are three characteristic regions in the phase diagram: (1) For $P < 0$, the system behaves as a "normal metal" down to low temperatures. $(\text{DMeO-DCNQI})_2\text{Cu}$ exhibits a constant Pauli paramagnetic susceptibility down to low temperatures.²² A low-temperature specific-heat measurement showed that the γ value of electronic specific heat ($\sim 9 \text{ mJ mol}^{-1}\text{K}^{-2}$) is almost equal to that of a typical organic metal (e.g., a Bechgaard salt).²³ (2) For $P > \Delta P$ [$\Delta P \sim 0.1 \text{ kbar}$ [$(\text{DMe-DCNQI})_2\text{Cu}$], $\sim 1.5 \text{ kbar}$ [$(\text{DMeO-DCNQI})_2\text{Cu}$]], the system shows a sharp M - I transition at T_{MI} ($> 60 \text{ K}$). Below T_{MI} , Cu^+ and Cu^{2+} are arranged in a threefold structure in which the magnetic moments of Cu^{2+} interact antiferromagnetically. At low temperatures, the system transforms to an antiferromagnetic state ($T_{AF} \sim 10 \text{ K}$). The antiferromagnetic transition temperature seems to become large with decreasing T_{MI} ,⁴ which is consistent with the high-pressure $T^{-1}(H)$ studies on $(\text{DMe-DCNQI})_2\text{Cu}$ by Takahashi *et al.*²⁰ The coexistence of CDW and spin structure has

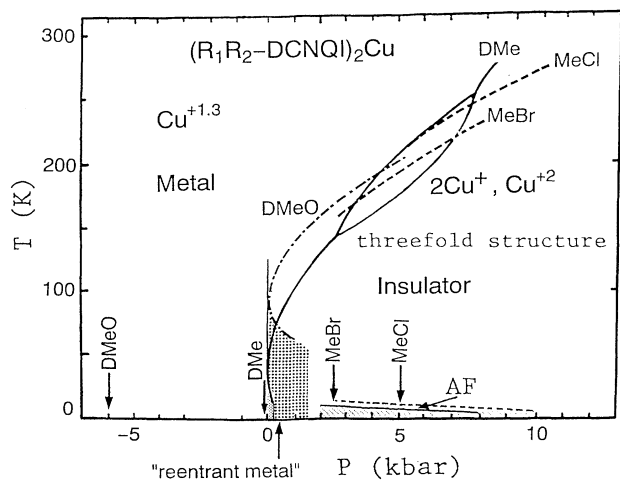


FIG. 7. The P - T phase diagram of $(R_1, R_2\text{-DCNQI})_2\text{Cu}$. The origin of "effective pressure (abscissa)" is tentatively chosen as the critical pressure of $(\text{DMe-DCNQI})_2\text{Cu}$ ($\sim 10^2$ bars). The arrows indicate the location of four DCNQI-Cu systems at atmospheric pressure. The shaded areas correspond to the area of the "reentrant metal" region and that of the antiferromagnetic phase.

also been suggested by recent theoretical work.²⁴ (3) At the intermediate-pressure region ($0 \leq x \leq \Delta P$), the system exhibits a reentrant resistivity behavior (metal \rightarrow semiconductor \rightarrow metal). As will be mentioned below, the effective mass of the metal electron in the low-temperature "reentrant-metal region" seems to be anomalously enhanced. The reason for the reappearance of the metallic state has been clarified by the recent theoretical study by Nakano, Kato, and Yamada.²⁵

In the case of group-II compounds, the development of a threefold superstructure could be detected by x-ray-diffraction experiments below T_{MI} . But in the case of group-I compounds, there has been no x-ray evidence. In order to confirm the threefold structure of $(\text{DMe-DCNQI})_2\text{Cu}$ below T_{MI} , the resistivities and x-ray-diffraction patterns of the "doped" system [$(\text{DMe}_{1-x}\text{DBr}_x\text{-DCNQI})_2\text{Cu}$] were examined. As shown in Fig. 8 $(\text{DMe}_{1-x}\text{DBr}_x\text{-DCNQI})_2\text{Cu}$ shows a metal instability around 60 K at $x \sim 0.05$ – 0.1 , which is quite similar to the metal instability of group-I compounds induced by pressure.^{16,17} After the resistivity measurements, x values were determined by x-ray structure refinements of the occupancy probabilities of Br (or Me) sites. The x-ray-diffraction patterns at 20 K (Fig. 9) showed that the crystal exhibiting an extremely sharp M - I transition around 70 K (sample *A* in Fig. 8) gave new Bragg reflections indicating the development of a threefold superstructure (Fig. 9). Sample *B* (Fig. 8), showing a more moderate resistivity jump around 60 K, also gave threefold Bragg reflections but new x-ray spots were rather faint and broad. No x-ray evidence of the structure change could be obtained in sample *C*, which showed reentrant resistivity behavior (Fig. 8). The threefold x-ray superlattice spots in Fig. 9 demonstrates that the threefold structure is common to the insulating state of the DCNQI-Cu system. Needless to say, this is an x-ray evidence of the mixed valency of Cu in group-I compounds.

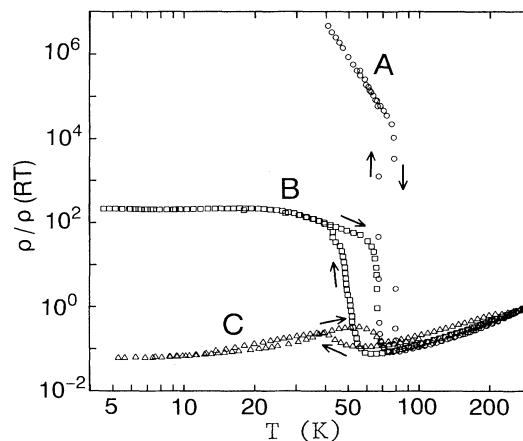


FIG. 8. Electrical resistivity of $(\text{DMe}_{1-x}\text{DBr}_x\text{-DCNQI})_2\text{Cu}$. The x values were roughly estimated from the population refinements by x-ray crystal-structure refinements: $x(A) \sim 0.1$, $x(B) \sim 0.08$, $x(C) \sim 0.05$.

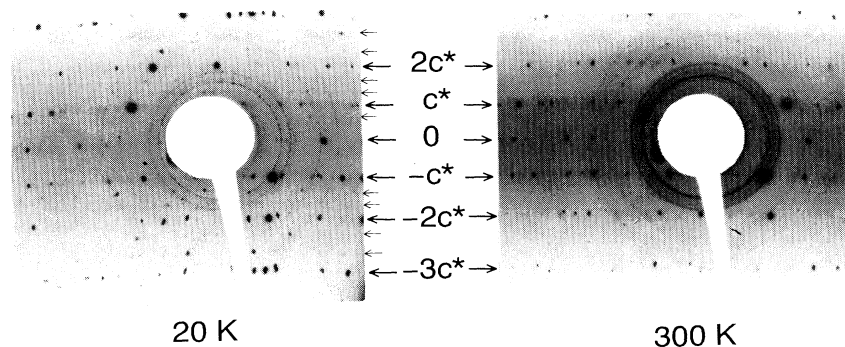


FIG. 9. X-ray-diffraction photographs of $(\text{DMe}_{0.9}\text{DBr}_{0.1}\text{-DCNQI})_2\text{Cu}$ at 300 and 20 K taken after the resistivity measurement [see the resistivity curve *A* in Fig. 8 ($T_{M1} \sim 60$ K)]. Small arrows indicate the layers of superlattice spots.

V. T^2 DEPENDENCE OF THE RESISTIVITIES AND ELECTRON-MASS ENHANCEMENT

As pointed out above, the mixed valency of Cu will mean that the highest Cu $3d$ orbital is located near the Fermi level of the $1\text{D } 2p\pi$ metal band of DCNQI, forming a $p\pi$ - d mixing band.^{2,5} The resistivity anomaly around P_c and the reentrance of the metallic state is reminiscent of the heavy-metal electron system, which is an interesting aspect in the study of molecular conducting systems.¹⁷ Of course, there may be other plausible models to explain the resistivity anomaly. A partial nesting of the planelike Fermi surfaces will give a possible interpretation of the recovery of the metallic conductivity at low temperature.⁵ In the usual CDW transition, the pressure tends to suppress the nesting of the Fermi surface, which is contrary to the case of the DCNQI-Cu system. Nevertheless, if the metallic behavior at low temperatures is due to surviving Fermi surfaces, the Fermi surfaces of the low-temperature metallic phase must be smaller than that of the high-temperature one. Then the magnetic susceptibility and electronic specific heat will both decrease.

In order to examine this possibility, the electrical resistivities and specific heat of the alloy system $(\text{DMe}_{1-x}\text{MeBr}_x\text{-DCNQI})_2\text{Cu}$ were examined. The result of specific-heat measurements has been already reported.²³ The measurements of the resistivity were very difficult because of the occurrence of resistivity jumps due probably to the inhomogeneity of alloyed crystals, so the measurements were made repeatedly to obtain reliable data. The inhomogeneity of the mixing of DMe-DCNQI and MeBr-DCNQI will be mainly originated from the fact that MeBr-DCNQI is a polar molecule. In the oscillation x-ray photograph of $(\text{MeBr-DCNQI})_2\text{Cu}$ around the c axis, very broad diffuse scattering could be observed in between strong spots on the layer lines, which indicates that in spite of the apparent random arrangement required from the symmetry of the space group $I4_1/a$, the dipole moments of MeBr-DCNQI molecules tend to arrange alternatively along the molecular stacking direction. In the case of $(\text{MeCl-DCNQI})_2\text{Cu}$, the diffuse scattering was weak, because of the relatively weak x-ray scattering power of Cl atom. This tendency on the arrangement of DCNQI molecules makes it very difficult to prepare the homogeneously alloyed crystals.

Figure 10 shows the resistivity behavior of the alloy system. The resistivity anomaly similar to the pressure-induced one can be observed below 80 K in the small- x region ($x < 0.06$). Roughly speaking, an increase in x corresponds to an increase in pressure. When the concentration of MeBr-DCNQI becomes larger than about 7%, the sharp M - I transition appears.

Nishio *et al.*²³ have measured the low-temperature specific heat of the alloy systems by thermal relaxation methods in the temperature range 1.0–4.2 K and found a strong indication of the extremely large enhancement of the state density. The γ value is $45 \text{ mJ K}^{-2} \text{ mol}^{-1}$ at $x=0$ [$(\text{DMe-DCNQI})_2\text{Cu}$, see Fig. 11].^{19,23} Around $x=5\%$, γ becomes very large ($\sim 75 \text{ mJ K}^{-2} \text{ mol}^{-1}$). The maximum value is almost one order of magnitude larger than the γ value of $(\text{DMeO-DCNQI})_2\text{Cu}$ ($=9 \text{ mJ K}^{-2} \text{ mol}^{-1}$),²³ which is nearly equal to that of a typical organic conductor, such as $(\text{TMTSF})_2\text{ClO}_4$ ($10 \text{ mJ K}^{-2} \text{ mol}^{-1}$). The decrease of γ at $x > 0.05$ is consistent with the fact that the system transforms to an insulating state for large x . In order to examine the inhomogeneity of the alloyed crystals, EPMA was made on nine crystals chosen mainly from the batches of the crystals whose specific-heat measurements had been finished (Fig. 12). The measurements were made on three batches. The number of datum points per crystal was

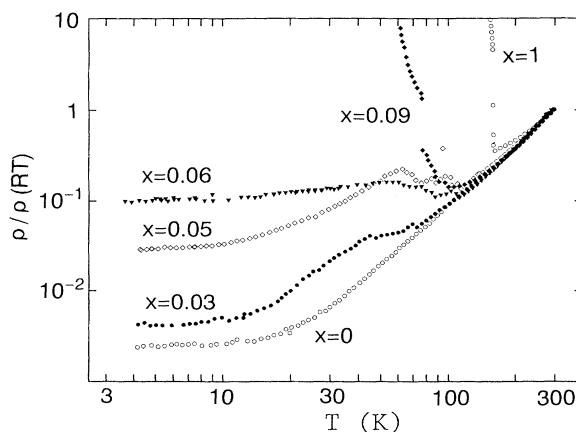


FIG. 10. Electrical resistivity of $(\text{DMe}_{1-x}\text{MeBr}_x\text{-DCNQI})_2\text{Cu}$.

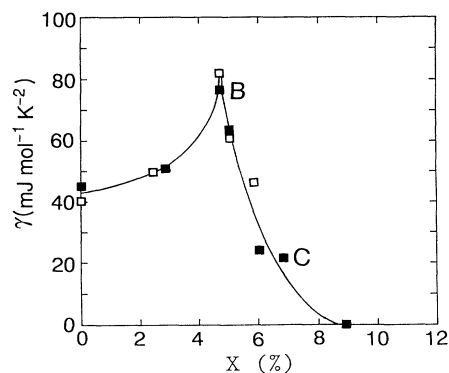


FIG. 11. The comparison between the γ values obtained by specific-heat measurements (solid squares) (Ref. 23) and those deduced from the ρ vs T^2 relation (open squares) (see Fig. 13). The data from Ref. 23 are slightly modified because of the reexamination of x values. The data B and C were obtained from the samples which gave the x distribution B and C shown in Fig. 12.

about 50. The x value was different largely on every datum point. As seen from Fig. 12, the distribution of x was very broad. Accordingly, the γ value obtained from the specific-heat measurement must be regarded as the average value. If the samples with very small x distribution were obtained, γ would become larger than $100 \text{ mJ K}^{-2} \text{ mol}^{-1}$ around $x \sim 0.05$. The large increase in γ seems to be difficult to be explained in terms of the CDW mechanism accompanied by the disappearance of the Fermi surfaces.

Considering the distribution of x , the observed γ can

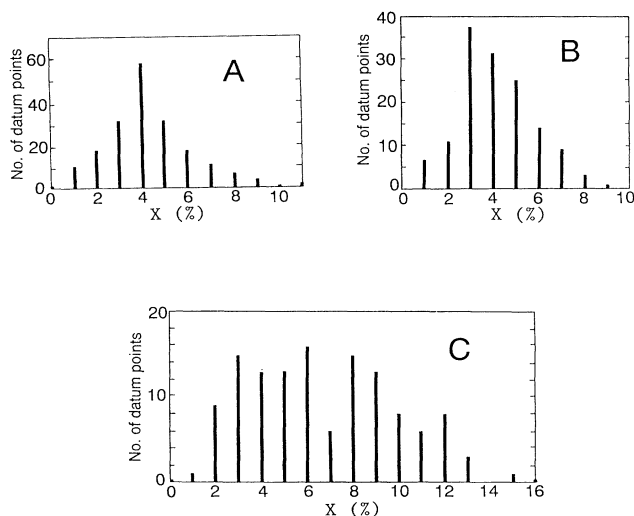


FIG. 12. The distribution of the x values determined by EPMA. The sample crystals were selected arbitrarily from three batches of the sample crystals whose mean x values are 0.041 (A), 0.044 (B), and 0.065 (C) (see Fig. 11). The samples of B and C were selected from the batches of the crystals whose specific-heat measurements had been made.

be expressed as $\gamma(x) = \int \gamma_0(y)g(x-y)dy$, where $\gamma_0(x)$ is γ of the “ideally alloyed crystal” without inhomogeneity of x and $g(x-y)$ [$\int g(x-y)dx = 1$] is the distribution of x of the sample with the mean x value of y . Since g depends on x and y (see Fig. 12), it is difficult to obtain γ_0 from the deconvolution of $\gamma(x)$. In order to estimate roughly the maximum value of γ_0 , the following simple assumption was made: $\gamma_0(x) = Ax^2 + 45$ at $x < 5$ (%) and $\gamma(x) = 0$ at $x > 5$ (%). Then the parameter A was estimated by referring the experimental γ values around $x = 4\text{--}5$ (%) ($\sim 60\text{--}75 \text{ mJ K}^{-2} \text{ mol}^{-1}$) and the x distribution obtained by simply averaging the data A and B of Fig. 12. The maximum γ_0 value calculated from the obtained parameter A ($=3.8$) was $140 \text{ mJ K}^{-2} \text{ mol}^{-1}$ at $x = 5$ (%). Thus even this rough estimation gave an indication of the extremely large enhancement of γ .

Since the specific heat was independent of the applied magnetic field ($H < 6 \text{ T}$),²⁶ the extremely large enhancement of γ seems to be hardly ascribed to the localized spins. The unique crystal and electronic structures of the DCNQI-Cu system, which permits the mixing of $2p\pi$ metal electrons of organic molecules and $3d$ electrons of mixed-valence Cu cations, will allow the possibility that the DCNQI-Cu takes an anomalous metallic state around the phase boundary between group-I and group-II compounds.

As mentioned above, all the Cu sites are crystallographically equivalent and the valence of Cu fluctuates between Cu^{2+} and Cu^+ with a lifetime longer than the time scale of XPS whereas, in the insulating state, the valence of Cu is fixed either in Cu^+ or Cu^{2+} with three-fold cation ordering ($a \times b \times 3c$). Thus the lifetime of the valence fluctuation seems to be a key factor with which to distinguish between the metallic and insulating states. Since the stability of the metallic state is sensitive to the pressure (or x value), the lifetime will become longer with increasing pressure. If the lifetime of Cu^+ (Cu^{2+}) becomes long enough to deform the lattice around Cu, it will be possible to form a three-dimensional ordered lattice of Cu^+ and Cu^{2+} . The coupling of the charge ordering and CDW is considered to be loose even in the system showing a sharp M - I transition, because the low-temperature ir spectra indicate the gradual development of CDW on DCNQI stacks, which is in contrast to the discontinuous development of charge ordering in the cation sites. Therefore there might be some special condition around the phase boundary between a “group-I state” and “group-II state” where the charge ordering in the Cu sites is almost independent of the development of CDW on DCNQI stacks. In such a situation, the metallic π electrons and the ordered arrangement of Cu^{2+} and Cu^+ might coexist. Such a situation will be analogous to that of the heavy-metal electron system.

In order to help clarify the possibility of a “molecular heavy (or quasiheavy) electron system,” the low-temperature resistivities were analyzed according to the following relation commonly observed in heavy electron compounds: $\rho = AT^2 + \rho_0$ and $A/\gamma^2 = 10^{-5} \mu\Omega \text{ cm mol}^2 \text{ K}^2 \text{ mJ}^{-2}$.²⁷ The γ value was estimated from the A value obtained by the least-squares fitting of the T^2 dependence of the low-temperature resistivity of the alloy

system (Fig. 13). The calculated γ values are in good agreement with those obtained by specific-heat measurements by Nishio *et al.*²³ (Fig. 11). This result supports the proposal that the DCNQI-Cu system can be regarded as a system related to heavy (or quasi-heavy) -metal electron systems. In the case of $(\text{DMe}_{1-x}\text{DBr}_x\text{-DCNQI})_2\text{Cu}$ ($x \sim 0.06$) system [Fig. 13(c)], which will be expected to be a better alloyed system with small x distribution, a much larger γ value ($200 \text{ mJ K}^{-2} \text{ mol}^{-1}$) was obtained from the same analysis.

VI. THREEFOLD STRUCTURE AND ARRANGEMENT OF Cu^{2+}

As mentioned above, the valence of Cu becomes fixed in either Cu^+ or Cu^{2+} at T_{MI} and a threefold arrangement of Cu^{2+} and Cu^+ appears. The c axis is abruptly shortened and the distortion of the coordination tetrahedron around Cu is enhanced.^{2,5} Since the spins of Cu^{2+} are considered to be arranged antiferromagnetically in the insulating ground state, the determination of the arrangement of Cu^{2+} is highly desired. But the intensities of the threefold x-ray superlattice reflections were found to be very weak and the usual procedure of the crystal-structure determination could not be used. The distribution of the x-ray-diffraction intensity of $(\text{MeBr-DCNQI})_2\text{Cu}$ around typical superlattice reflections has revealed that the lattice periods along the a and b axes are not changed at T_{MI} . The discontinuous increase of the x-ray intensity of the threefold reflection and the sharp change of the lattice constants^{2,5} indicates the first-order phase transition at T_{MI} , which is consistent with the theoretical analysis.²⁴ The indices (hkl) of almost all the superlattice reflections satisfy the characteristic extinction rule: the superlattice spots vanish if $h+k+l \neq 2n+1$ and $l=3n+1$. Since the $M-I$ transition temperature of $(\text{MeBr-DCNQI})_2\text{Cu}$ is 155 K, the x-ray intensity data were collected at 115 K. Only 150 significant superlattice reflections were obtained.

Considering the threefold lattice, lower crystal symmetry, and the small number of superlattice reflections, the conventional crystal-structure analysis is impossible. However, we have recently noticed that the arrangement of Cu^{2+} and Cu^+ can be derived from the average structure, obtained from the usual structure analysis on the basis of the main spots. The average structure without threefold lattice modulation is essentially the same as the room-temperature structure. As shown in Fig. 14, every DCNQI molecule is on the center of inversion and crystallographically equivalent. The Cu sites are on the fourfold improper rotation axes ($\bar{4}$). The difference of the z coordinates of Cu ions bonded by two terminal N atoms (e.g., A and B) of DCNQI [$Q(1)$] is $-\frac{1}{4}$ (see Fig. 15). Therefore, when we go down one cycle along this fourfold spiral step [$A \rightarrow Q(1) \rightarrow B \rightarrow Q(2) \rightarrow C \rightarrow Q(3) \rightarrow D \rightarrow Q(4) \rightarrow E$] (Fig. 15), we arrive at the position $-7c$ (E) lower than the starting point (A). If two Cu ions in the threefold structure (e.g., A and B) bonded by two terminal nitrogen atoms of DCNQI [e.g., $Q(1)$] are both Cu^{2+} , Cu^{2+} must appear at $-7c$. But this structure is not consistent with a threefold structure, where Cu^{2+}

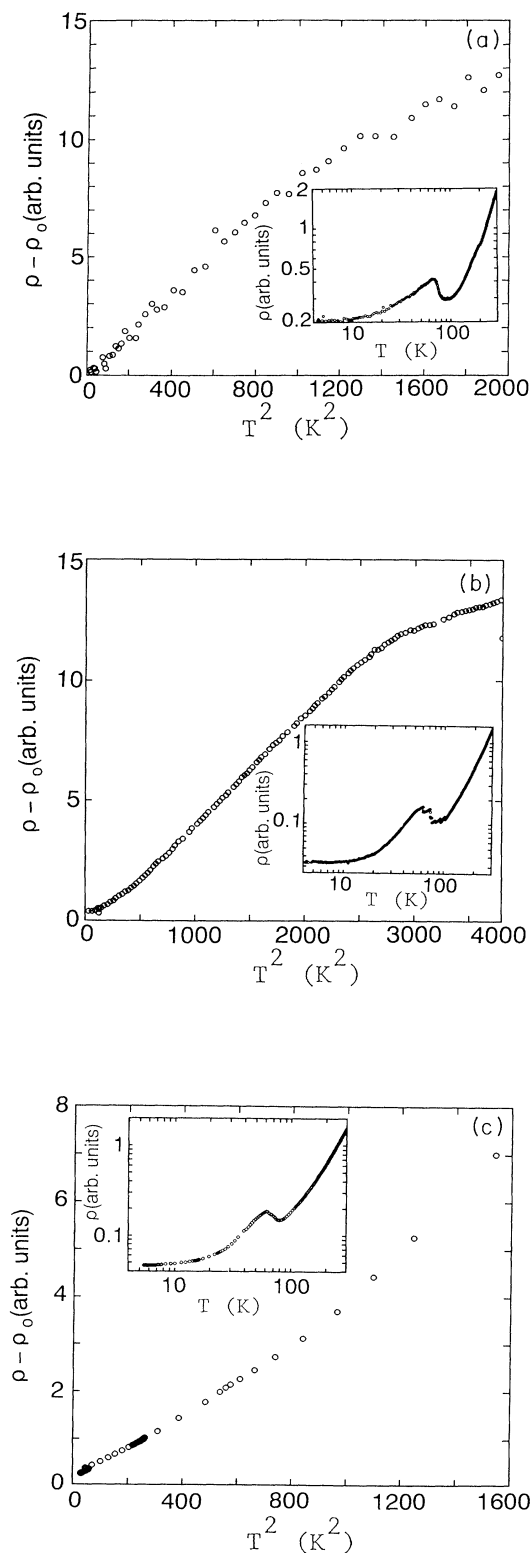


FIG. 13. The ρ vs T^2 relation of some alloy systems: (a) $(\text{DMe}_{1-x}\text{MeBr}_x\text{-DCNQI})_2\text{Cu}$ ($x \sim 0.045$), $A = 6.54 \times 10^{-2} \mu\Omega \text{ cm/K}^2$ ($\gamma = 80 \text{ mJ mol}^{-1} \text{ K}^{-2}$); (b) $(\text{DMe}_{1-x}\text{MeBr}_x\text{-DCNQI})_2\text{Cu}$ ($x \sim 0.052$), $A = 3.95 \times 10^{-2} \mu\Omega \text{ cm/K}^2$ ($\gamma = 60 \text{ mJ mol}^{-1} \text{ K}^{-2}$); (c) $(\text{DMe}_{1-x}\text{DBr}_x\text{-DCNQI})_2\text{Cu}$ ($x \sim 0.06$), $A = 0.34 \mu\Omega \text{ cm/K}^2$ ($\gamma = 200 \text{ mJ mol}^{-1} \text{ K}^{-2}$).

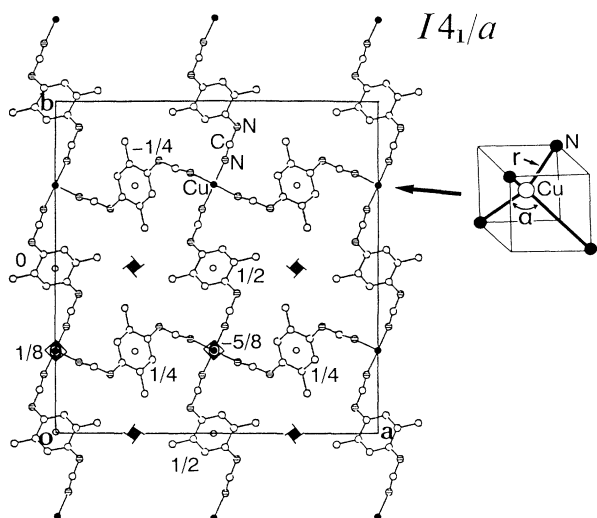


FIG. 14. The average structure of $(\text{MeBr-DCNQI})_2\text{Cu}$. The figures beside Cu atoms and DCNQI molecules are their z coordinates based on the lattice $a \times b \times c$.

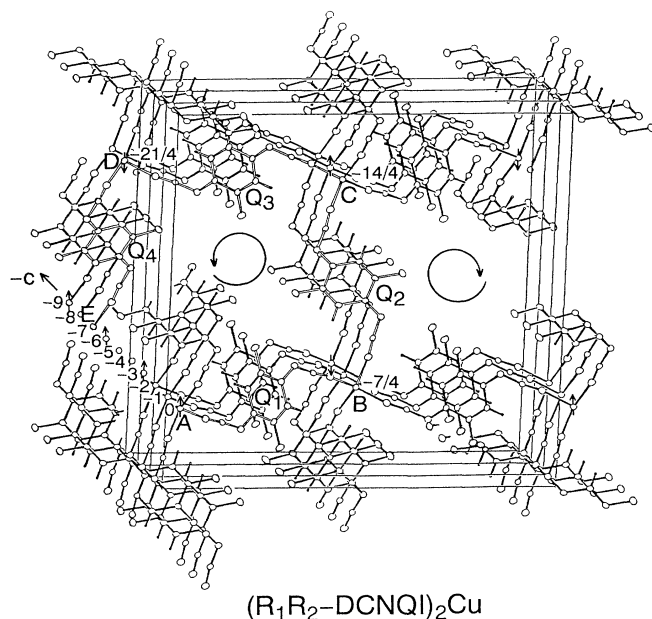


FIG. 15. Architecture of the DCNQI-Cu lattice. The Cu atoms A and B are coordinated by two terminal nitrogen atoms of DCNQI molecule $Q(1)$. Similarly, the Cu atoms B and C are connected by DCNQI molecule $Q(2)$. The large arrows indicate the downward spiral steps formed from Cu atoms and DCNQI molecules connected through the Cu-N coordination bonds. The figures beside the Cu atoms are the z coordinates based on the $a \times b \times c$ structure (average structure). The small arrows indicate the positions of Cu^{2+} , whose directions correspond to the “up” and “down” spins of Cu^{2+} ions in a possible antiferromagnetic spin-structure model. The Cu atoms without arrows are Cu^+ .

must appear every three Cu sites. If the Cu ion one period above the ion $\text{Cu}(B)$ is Cu^{2+} , the Cu ions two periods ($2c$) above C , three periods ($3c$) above D , and four periods ($4c$) above E must be Cu^{2+} . Thus the Cu^{2+} ion will appear at the position $-3c$ below A , which is consistent with the threefold structure. There remains another possibility, where the Cu ion one period below the position B is Cu^{2+} . Then the ion at $-11c$ ($= -7c - 4c$) below the starting position must be Cu^{2+} , which is again inconsistent with a threefold structure because 11 cannot be divided by 3. Thus we could determine almost uniquely the distribution of Cu^{2+} . The Cu^{2+} and Cu^+ positions are shown in Fig. 15. This threefold arrangement of Cu^{2+} has recently been confirmed independently by NMR studies by Takahashi.²⁸

As reported earlier,⁵ the low-temperature average structure is almost identical to the room-temperature structure. The N-Cu-N angle (α) [the bisecting axis of the N-Cu-N angle is parallel to the c axis (Fig. 14)], however, exhibits a significant change ($\Delta\alpha = 2^\circ$) around T_{MI} , which is consistent with the discontinuous shortening of the c axis at T_{MI} . This structural change can be regarded as the increase of the Jahn-Teller-like distortion around Cu cations¹⁴ and is ascribed mainly to the shift of Cu and DCNQI along the c axis. The longitudinal lattice modulation of the average structure below T_{MI} was also suggested from the distribution of the relatively strong superlattice reflections (hkl), which have higher l indices ($l = 3n \pm 1$).

The extinction rule of the superlattice reflections ($h+k+l=2n+1$) implies that the threefold structure does not have a body-centered lattice and there must be Cu atoms (and/or DCNQI molecules) interrelated by body-centered translational symmetry, whose positions are modulated in the antiphase fashion. Then the x-ray-diffraction intensity from these Cu atoms (and/or DCNQI molecules) interrelated by the body-centered symmetry is expressed as

$$\begin{aligned}
 F(hkl) &= (f + \Delta f) \exp\{2\pi i(hx + ky + lz)\} \\
 &\quad + (f - \Delta f) \exp[2\pi i\{hx + ky + lz \\
 &\quad\quad\quad + (h+k+l)/2\}] \\
 &= 2f \exp\{2\pi i(hx + ky + lz)\} \quad \text{for } h+k+l=2n \\
 &= 2\Delta f \exp\{2\pi i(hx + ky + lz)\} \\
 &\quad\quad\quad \text{for } h+k+l=2n+1,
 \end{aligned}$$

where Δf represents the variation of x-ray scattering factor due to the structure modulation. The strong reflections will appear at the positions whose indexes (hkl) satisfy the extinction rule of the body-centered lattice and the weak reflections appear at positions which break the body-centered lattice symmetry.

Of the possible maximal nonisomorphic subgroups with primitive lattice derived from $I4_1/a$ ($P\bar{4}$ and $P4_1$), $P\bar{4}$ was chosen because of the requirement of the “antiphase modulation” (Fig. 16). In the case of the space

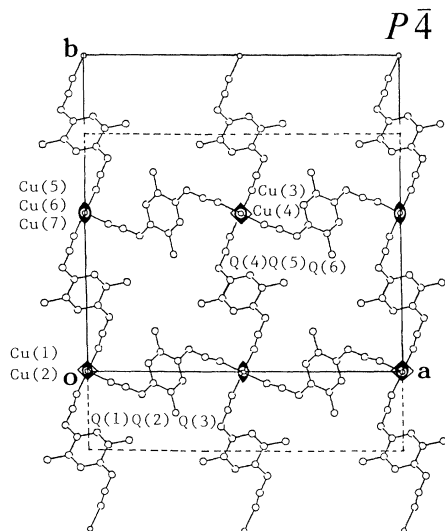


FIG. 16. The projection of the adopted $P\bar{4}$ structure. Seven Cu atoms [Cu(1)–Cu(7)] and six DCNQI molecules [Q(1)–Q(6)] are crystallographically independent.

group $P4_1$, the z components of the shifts of Cu atoms interrelated by the body-centered symmetry of the average structure must be the same, which is not consistent with the antiphase modulation. In the first step, we included only seven independent Cu atoms, which are on the 4 or 2 axes [Cu(1)–Cu(7) (Fig. 16)]. The Cu atoms on the inversion centers of $\bar{4}$ [Cu(1), Cu(3)] must be taken as Cu^{2+} owing to the requirement of the threefold arrangement of Cu^+ , Cu^+ , Cu^{2+} , This enabled us to determine the structural model. The x and y coordinates of all the Cu atoms are fixed as shown in Fig. 16. The R factor which is equal to

$$\frac{\sum \omega(hkl) \{ ||F_{\text{obs}}(hkl)| - |F_{\text{calc}}(hkl)| \}^2}{\sum \omega(hkl) |F_{\text{obs}}(hkl)|^2},$$

was decreased to 25%. Then six DCNQI molecules [Q(1)–Q(6)] on general positions are refined by assuming that DCNQI molecules are rigid bodies, because the number of reflection data is too small to refine the atomic parameters independently. The isotropic thermal parameters were used. The obtained R value was 17%, which will be satisfactory because the anomalous weighting scheme was adopted in order to obtain the structure strongly reflecting the information on the superlattice reflections, which are very weak and inaccurate: $w = 1.0$ for strong main reflections and $w = 10.0$ for weak threefold superlattice reflections. The z coordinates of the three Cu^{2+} ions are fixed: Cu(1), 0; Cu(3), $\frac{1}{2}$; Cu(6), 0.233. Those of the four Cu^+ ions determined by the least-squares refinements are Cu(2), 0.340; Cu(4), 0.154; Cu(5), 0.590; Cu(7), 0.902. The obtained $\text{Cu}^{2+} \cdots \text{Cu}^+$ distances are 3.77–3.93 Å, which are longer than the $\text{Cu}^+ \cdots \text{Cu}^+$ distances (3.56–3.74 Å). This may be reasonable in view of the Coulombic repulsion between cations. However, the information on the distortion of

the coordination structure around Cu could not be determined accurately, because of the assumption of the rigid body of DCNQI molecules.

As seen from Fig. 17, neighboring Cu^{+2} ions (A, B) are connected via two DCNQI molecules [Q(1), Q(2)]. Since the spins are interacting antiferromagnetically, two antiparallel spins will be on these cations sites. Then we can derive a simple model of the 3D spin arrangement by setting “up” and “down” spins alternately along the route of interaction. If this is the case, the magnetic moments along the c axis will be parallel, as indicated in Figs. 15 and 17.

VII. CONCLUSION

Based on the studies on the structural, electrical, and magnetic properties of DCNQI-Cu systems, we have proposed the possible presence of heavy electrons in a molecular conducting system. The mixed valency of $\text{Cu}(\text{Cu}^{1,3+})$ in $(\text{DMe-DCNQI})_2\text{Cu}$ was reconfirmed by a comparison of the ir frequencies of molecular vibrations of DMe-DCNQI molecules in the neutral DMe-DCNQI crystal and the salts of $(\text{DMe-DCNQI})_2M$ ($M = \text{Li}, \text{Ba}, \text{Cu}$). The same conclusion was also derived from the low-temperature x-ray-diffraction experiment on doped $(\text{DMe-DCNQI})_2\text{Cu}$ systems. The continuous temperature dependence of the ir absorption intensities of the totally symmetric modes observed below T_{MI} of $(\text{DBr-DCNQI})_2\text{Cu}$ is in sharp contrast to the almost discontinuous resistivity and susceptibility increases at T_{MI} . This may be attributable to the existence of two driving forces which characterize the $M-I$ transition. One is the sharp charge ordering in Cu sites and the other is the

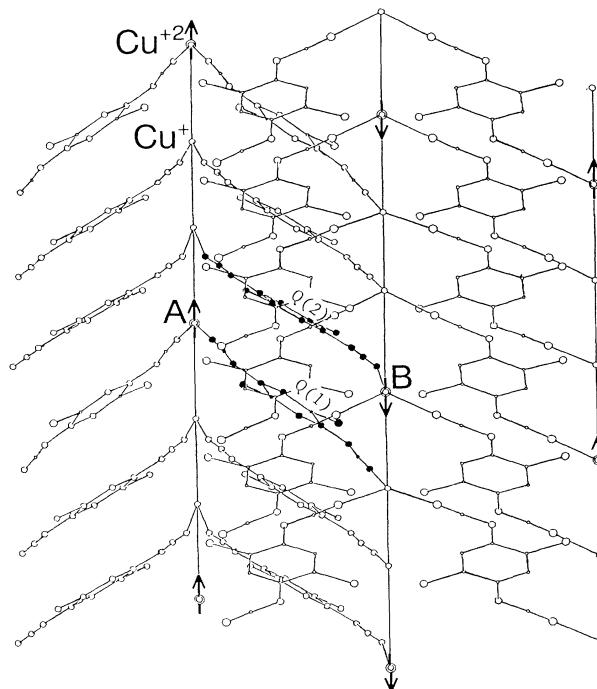


FIG. 17. Side view of the structure of $(\text{MeBr-DCNQI})_2\text{Cu}$. The arrows represent the Cu^{2+} ions with “up” and “down” spins in a antiferromagnetic spin-structure model. The Cu atoms without arrows are Cu^+ .

continuous development of the CDW lattice distortion along the DCNQI stacks. On the basis of all existing experimental results, the general features of the phase diagram of the DCNQI-Cu system have been illustrated. There are three regions in the phase diagram. When the "effective pressure" is lower than the critical pressure, the system behaves as a normal metal. At the higher "effective pressure" region, the system undergoes a $M-I$ transition ($T_{MI} > 50$ K) and antiferromagnetic transition ($T_{AF} \sim 10$ K). Around the critical pressure, the system exhibits a characteristic "reentrant resistivity behavior." The effective mass of the metal electron estimated from the T^2 relation of the low-temperature resistivity seems to become anomalously large, which is consistent with the previous proposal on the possibility of the "molecular heavy electron" state in this characteristic $p\pi-d$ mixing band system. The arrangement of Cu^{2+} and Cu^+ below T_{MI} was determined from x-ray crystal-structure analysis of the threefold insulating phase of $(\text{MeBr-DCNQI})_2\text{Cu}$ at 115 K. The nearest-neighbor Cu^{2+} ions interact with each other via two DCNQI molecules. If the directions of the magnetic moments of these two Cu^{2+} ions are antiparallel to each other, the model of 3D spin structure of

the antiferromagnetic ground state can be derived. In this case, the magnetic moments along the crystallographic c direction will be ordered ferromagnetically. The experimental determination of the magnetic structure of the antiferromagnetic phase of DCNQI-Cu systems is an important problem which remains to be solved.

ACKNOWLEDGMENTS

The authors thank Professor Y. Nishio, Professor K. Kajita, Professor A. Fujimori, Professor K. Kanoda, Professor T. Takahashi, Professor S. Kagoshima, and Professor Y. Suzumura for many helpful discussions and valuable information. They are also grateful to Professor H. Fukuyama and Professor W. Sasaki for their interest and encouragement. The x-ray structure refinements were made by using the group refinement program ANYBLK written by Dr. H. Imoto and the ESR experiments below 80 K were made by using the facilities of ESR Group Application Laboratory of JEOL Ltd. made available by Dr. M. Kohno and Dr. K. Mitsuta, to whom the authors are also grateful.

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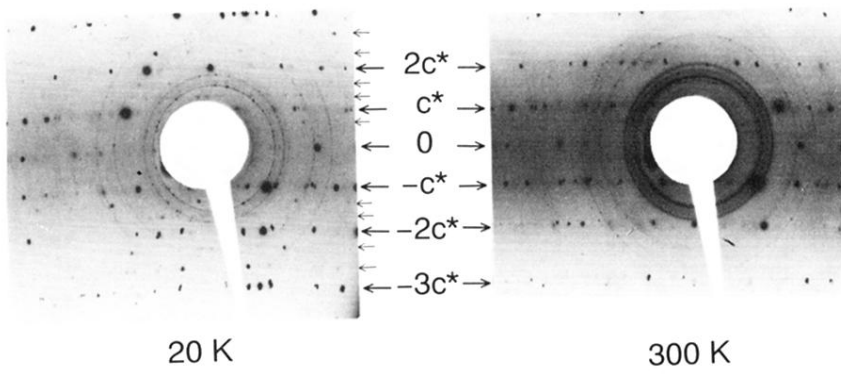


FIG. 9. X-ray-diffraction photographs of $(DMe_{0.9}DBr_{0.1}-DCNQI)_2Cu$ at 300 and 20 K taken after the resistivity measurement [see the resistivity curve *A* in Fig. 8 ($T_{M1} \sim 60$ K)]. Small arrows indicate the layers of superlattice spots.