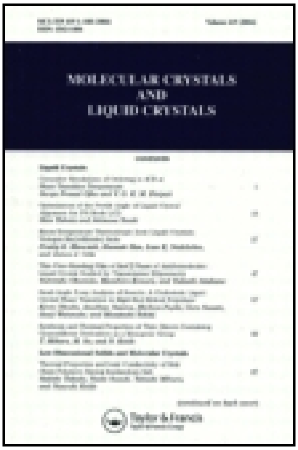

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pπ-d INTERACTION IN THE $(R_1,R_2\text{–DCNQI})_2Cu$ SYSTEM

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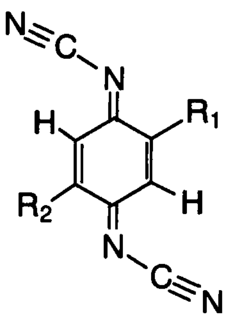
Abstract Pressure effects in the iodine-containing pπ-d system $(DCNQI)_2Cu$ are mainly described. Electrical and magnetic properties of $(R_1,R_2\text{-DCNQI})_2Cu$ are quite sensitive to the substituents R_1 and R_2. A variety of substituent effects would be generally understood in terms of the amount of charge transfer from Cu to DCNQI which is sensitive to the N–Cu–N coordination angle. In the iodine-containing DCNQI-Cu system, however, an inter–stack LUMO···LUMO interaction would also play an important role.

INTRODUCTION

An introduction of metal d electrons to the pπ-electron system would promise a variety of new phenomena. A series of π-acceptor molecules R_1,R_2-DCNQI (DCNQI=*N*,*N* '-dicyanoquinonediimine; R_1, R_2 = CH_3, CH_3O, Cl, Br, I) form isostructural 2:1 salts with Cu ion. These Cu salts exhibit very unique electronic states associated with an interaction between the one-dimensional pπ (LUMO) band of DCNQI and 3d (d_{xy}) orbital of Cu.[1] The valence of Cu in the metallic state is close to +4/3. The electronic structure of the Cu salts is characterized by a coexistence of one- and three-dimensional Fermi surfaces.[2] The application of pressure or the replacement of R_1 and R_2 with smaller substituents induces metal(M)-insulator(I) transition. We have proposed that the pressure and substituent effects can be understood in terms of the amount of charge transfer from Cu to DCNQI which is sensitive to the N–Cu–N coordination angle (α).[3]



R_1,R_2-DCNQI

	R_1	R_2
DI-	I	I
BrI-	Br	I
MeI-	CH_3	I
DMe-	CH_3	CH_3

In the course of studying $(DI\text{-DCNQI})_2Cu$ (DI-salt ; $R_1 = R_2 = I$) and other iodine-containing salts, however, we have noticed that there should be other factors that affect the electronic state of the DCNQI-Cu system. The iodine atom has the largest van der Waals radius in the (quasi) spherical substituents (Cl, Br, I, and CH_3). In the crystal, a very short inter-stack I···I distance is observed. And orbital coefficients of the LUMO indicate a small but significant contribution of iodine atoms. Therefore, there exists weak inter–stack LUMO···LUMO interaction, which can be neglected in other DCNQI-Cu salts.[4] In this paper, we describe new aspects of the pπ-d interaction in the iodine-containing DCNQI-Cu system.

RESULTS AND DISCUSSION

Crystal Structure

All the iodine-containing DCNQI-Cu salts are isostructural with other Cu salts of R_1,R_2-DCNQI. The crystal structure is characterized by the one-dimensional columns of planar R_1,R_2-DCNQI molecules (along the tetragonal *c* axis) which are interconnected to each other through the tetrahedrally coordinaed Cu ions (Fig. 1). The DCNQI molecule is on the inversion center. Therefore, the unsymmetrical DCNQI molecules (MeI- and BrI-) show an orientational disorter. Important structural parameters are listed in Table 1. The Cu ion is coordinated in a D_{2d} ditorted tetrahedral fashion to the N atoms. In the DCNQI columns, the DCNQI unit repeats by a unit translation c. The iodine substitution enhances the inclination of the DCNQI molecular plane with respect to the stacking axis (see ϕ values in Table 1), which is associated with a reduction of the D_{2d} distortion around the Cu ion (see α values in Table 1) and an enlargement of the overlap displacement in the direction parallel to the long molecular axis. It is well known that the smaller α values corresponds to the more stable metallic state (lower M-I transition temperature $T_{\mathrm{M\text{-}I}}$ or higher critical pressure $P_{\mathrm{M\text{-}I}}$).[3] Another singificant feature is a very short intercolumn I···I distance. For example, in the DI-salt, the observed I···I distance 3.654 Å is 15 % shorter than the van der Waals distance (4.30 Å).

Anomalous Metallic State under Ambient Pressure

All the iodine-containing DCNQI-Cu salts are metallic down to very low temperature under ambient pressure. The metallic state of the iodine-containing salts exhibits very unique behaviors in electrical and magnetic properties.[4,5] The magnetic susceptibilities of them are 2–3 times larger than that of other DCNQI-Cu salts. These susceptibilities exhibit a broad maximum around 100–200 K, which is different from the Pauli-like behavior in other DCNQI-Cu salts. The electronic specific heat coefficient γ of these salts ranges 40–70 mJ K^{-2} mol^{-1}, which indicates the enhancement of the density of states at the Fermi level and thus the narrowed band width.[6]

Complicated *P-T* Phase Diagram

The iodine-containing DCNQI-Cu salts exhibit very complicated pressure(*P*)-temperature (*T*) phase diagram. Figure 2 shows temperature dependence of the electrical resistivity of

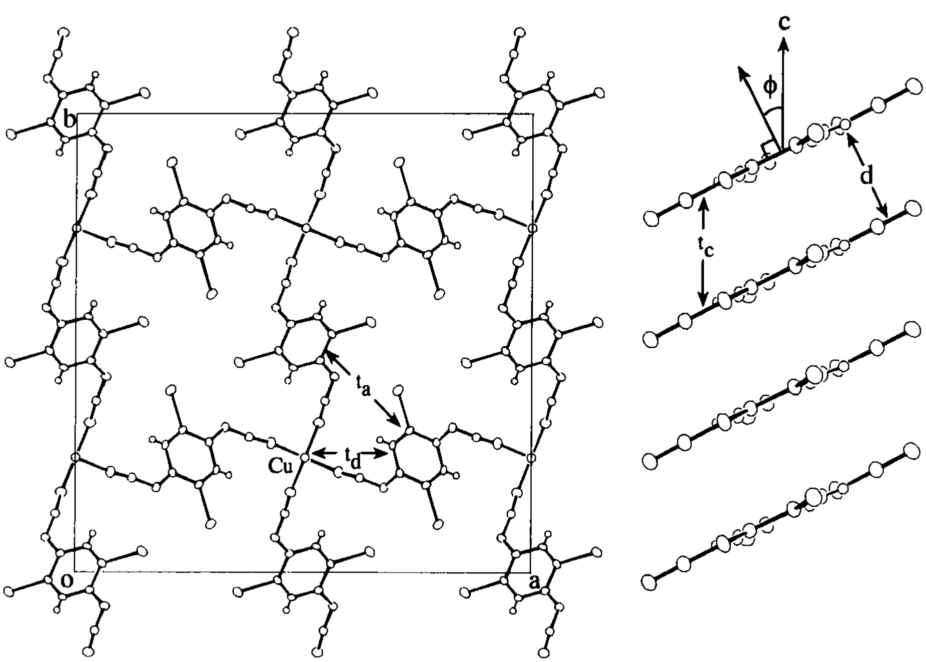
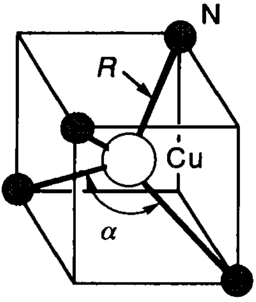


FIGURE 1 Crystal Structure of (R_1,R_2-DCNQI)$_2$Cu.

TABLE 1 Structural parameters, critical pressure, and intermolecular overlap integrals for (R_1,R_2-DCNQI)$_2$Cu.

	DMe–	MeI–	BrI–	DI–
R / Å	1.986(1)	2.001(6)	1.987(5)	1.997(3)
α / deg.	124.7 (1)	123.6 (4)	123.1(3)	122.3 (2)
ϕ / deg.	33.8	35.7	36.6	37.9
d / Å	3.18	3.24	3.22	3.23
$P_{M\text{-}I}$ / kbar	0.1	4	3	15
t_d (× 10^3)*	4.9	4.3	5.0	4.6
t_c (× 10^3)*	16.7	14.9	16.3	14.5
t_a (× 10^3)*	0.19	0.31	0.40	0.49
t_a / t_c	0.011	0.021	0.025	0.034

*for the MeI- and BrI-salts, averaged values assuming DCNQI molecules in the random orientation.



the DI-salt under pressure. In the low pressure region (< ca. 15 kbar), the DI-salt remains metallic down to very low temperature. The higher pressure induces a sharp M-I transition (Fig. 2a) with hysteresis, which is the common feature in the DCNQI-Cu salts. The critical pressure $P_{M\text{-}I}$ for the DI-salt is the highest in the DCNQI-Cu system. This corresponds to the smallest α value. This M-I transition, however, is suppressed above ca. 20 kbar. In this pressure region (ca. 20–22 kbar), the system remains metallic down to ca. 180 K, and shows resistivity maximum around 120 K followed by the reentrance to the metallic state (Fig. 2b). There is little hysteresis, which indicates the second order character of the transition. On the other hand, in the DMe-salt ($R_1=R_2=CH_3$), the high pressure up to 20 kbar only enhances the semiconductive behavior. The resistivity behavior of the DI-salt under pressure higher than ca. 25 kbar is more complicated. The M-I transition appears again around 25 kbar. This transition exhibits little hysteresis and is suppressed above ca. 35 kbar (Fig. 2b).

The BrI-salt (R_1=Br, R_2=I) also shows a complicated pressure effect similar to that in the DI-salt (Fig. 3). This system shows a clear M-I-M (reentrant) transition in the vicinity of $P_{M\text{-}I}$, as is often observed in other DCNQI-Cu salts. Although we have confirmed the pressure-induced M-I transition for the MeI-salt ($R_1=CH_3$, R_2=I), resistivity measurements under higher pressure (> 10 kbar) have been unsuccessful.

Electronic State under High-Pressure

The electronic structure of the DCNQI-Cu system (especially the DMe-salt) can be described by the semi-empirical tight-binding band calculation.[2] Unfortunately, we cannot obtain full band parameters for the DI-salt. Recently, first-principles band calculations based on LDA (Local Density Approximation) and GGA (Generalized Gradient Approximation) for the DCNQI-M (M= Cu, Li) salts. have been successfully performed.[7] The first-principles band calculation for the DI-salt indicates much narrower band width of the LUMO band, which would correspond to the reduced overlap integral along the stacking axis (t_c in Table 1). And the Fermi wave number k_F for the LUMO band is appreciably different from that for the DMe-salt ($k_F \approx \pm\pi/3c$).

The M-I transition of the DCNQI-Cu system is accompanied by the charge density wave (CDW) on the DCNQI column with $3c$ periodicity and the static charge ordering at the Cu sites ($\cdots Cu^{2+}Cu^{+}Cu^{+}\cdots$).[1] Theoretical studies have indicated that an interplay of the 3-fold periodic potential and the strong correlation leads to the first-order M-I transition followed by the large hysteresis and the localized spins.[8] It should be noted that the periods of the CDW and the static charge ordering at the Cu sites are functions of the amount of charge transfer and the 3-fold periodicity is a special point where both the CDW and the charge ordering have the same period (Fig. 4).[3] Such a situation yields a large energy gain due to the commensurability between the pπ- and d-systems. Therefore, the valence shift of Cu from +4/3 should require the redistribution of the

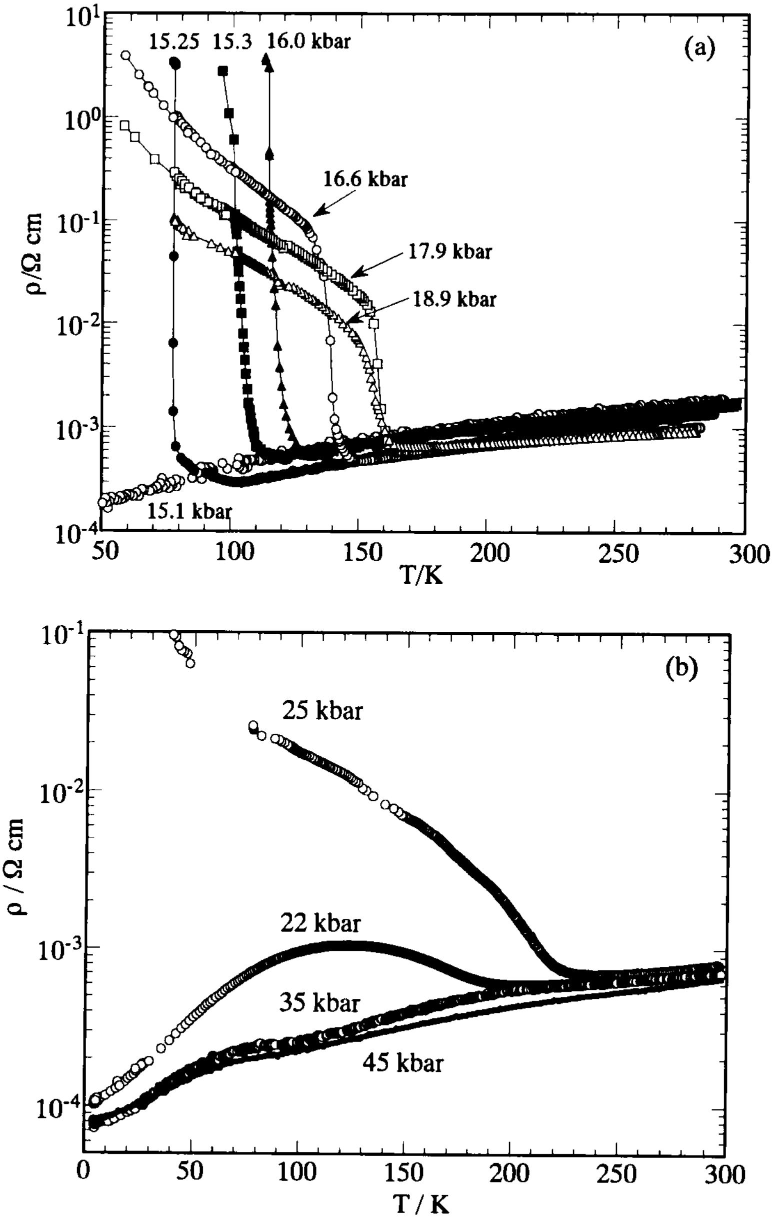


FIGURE 2 Temperature dependence of the electrical resistivity of the DI-salt under pressure.

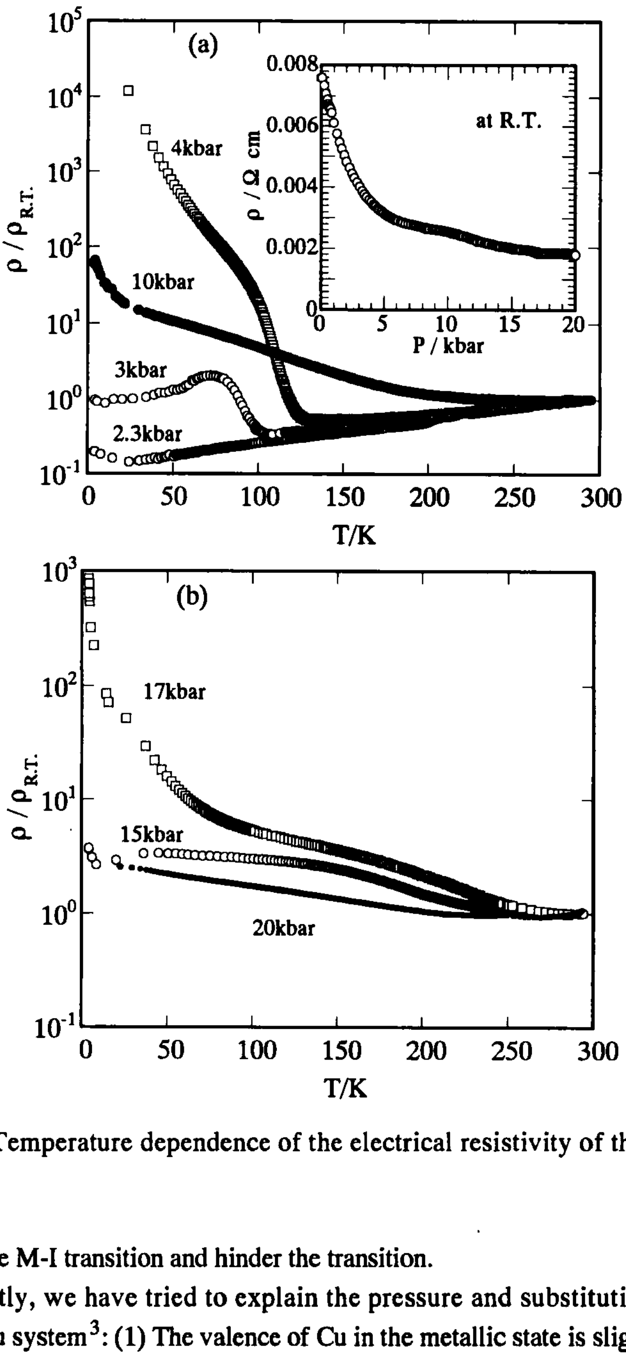


FIGURE 3 Temperature dependence of the electrical resistivity of the BrI-salt under pressure.

charge for the M-I transition and hinder the transition.

Recently, we have tried to explain the pressure and substitution effects in the (DCNQI)$_2$Cu system[3]: (1) The valence of Cu in the metallic state is slightly smaller than +4/3. This shift in the valence from +4/3 stabilizes the metallic state. (2) The application of pressure or the smaller substituent enhances the distortion of the coordination tetrahedron. (3) The distortion raises the highest-lying d_{xy} level and induces extra charge transfer from Cu to DCNQI. (4) The valence state of Cu closer to +4/3 provokes the

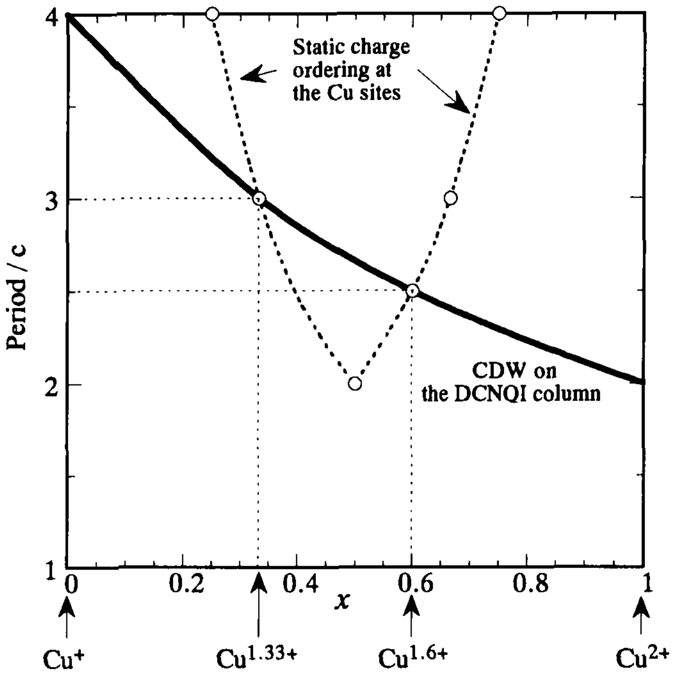


FIGURE 4 Relation between a mole fraction of Cu^{2+} in total Cu (x in $(DCNQI)_2(Cu^+)_{1-x}(Cu^{2+})_x$) and periods of the static charge ordering and CDW.

first-order M-I transition triggered by the CDW in the presence of the strong correlation.

This mechanism could be available to the M-I transition of the iodine-containing DCNQI-Cu salts in the lower-pressure region. The higher critical pressure (P_{M-I}) value should correspond to the smaller α value. In order to explain the high-pressure metallic phase, however, we must consider another factor. Compared with the DMe-salt, the iodine-containing DCNQI-Cu salts exhibit an enhancement of the inter-stack LUMO···LUMO interaction (t_a in Table 1). This is due to the very short I···I distance and the contribution of the iodine atom to the LUMO. The Fermi surface of the DCNQI-Cu salt includes a pair of planar sheets associated with the one-dimensional LUMO band. When t_a is negligible, the pair of planar sheets is doubly degenerate. This is the case, for example, with the DMe-salt. The CDW formation that triggers the M-I transition originates from the perfect nesting of this one-dimensional Fermi surface. Although the t_a value is rather small under ambient pressure, the application of pressure is expected to enlarge it. The enhancement of t_a removes the degeneracy and generates two pairs of corrugated sheets. In this case, the perfect nesting of the sheet-like Fermi surface becomes difficult. It is plausible that the best nesting vector is no longer $c^*/3$ and thus the CDW formation is not coupled to the charge ordering at the Cu sites. Such a situation will explain the resistivity peak and the low-temperature metallic behavior above 20 kbar. According to our picture, the transition above 20 kbar is a simple CDW transition with $2k_F \neq c^*/3$ and the three-dimensional Fermi surface (and a part of the corrugated sheets) survives down to the lowest temperature.

An origin of the complicated behaviors under higher pressure, especially the second M-I transition around 25 kbar, remains an open question. It seems a clue that the CDW and the charge ordering have the same period at another point where the valence of Cu is +1.6 (Fig. 4). If such a valence state is possible under very high pressure, the CDW formation will couple to the charge ordering and stabilize the insulating state. Even in this case, the inter-stack interaction will play an important role.

CONCLUSION

We have described very unique physical properties of the iodine-containing DCNQI-Cu salts and pointed out that the inter-stack LUMO···LUMO interaction can change the electronic state drastically. These systems indicate new aspects of the pπ-d interaction in the DCNQI-Cu system.

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