Magnetic and Structural Properties of Mixed-Valence Molecular Conductors (DMeDCNQI)$_2$Cu and (DMeODCNQI)$_2$Cu

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Temperature dependence of magnetic susceptibilities and lattice parameters is measured at ambient pressure in the title compounds, which are metallic down to the lowest temperature measured and have a mixed valence state of Cu. In (DMeDCNQI)$_2$Cu an anomalously large susceptibility having a thermal hysteresis is found in the range below 100 K. This result combined with the change in the lattice parameter tells that (DMeDCNQI)$_2$Cu is a marginal metal in which the number of stable Cu$^{2+}$ ions changes with temperature. It is pointed out that the reentrant behavior already found in the title compounds under respective pressure range has a close relation with the lattice-parameter change.

mixed-valence, valence fluctuation, molecular conductor, DCNQI, low dimensional conductor, heavy electron, charge ordering, magnetic susceptibility

§1. Introduction

Organic conductors provide unique electronic systems which are seldom found in conventional materials: Their best-known properties are electronic low-dimensionality, lattice softness, relatively strong Coulomb interaction between conduction electrons etc. Problems of charge-density and spin-density waves arise basically from these. Also the superconductivity and strong pressure dependence of its nature are presumably related to these properties.

In addition to the above characteristics the DCNQI*-Cu family, which the title compounds belong to, has unique properties as the followings: (1) The lattice is formed by parallel stacks of DCNQI molecules interconnected by copper ions as shown in Fig. 1.\(^{1,2}\) π-electrons of DCNQI molecules form a one-dimensional metallic band. This means that a possible Peierls instability of the one-dimen-

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* An abbreviation of N, N'-dicyanoquinonedi-imine.

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** Oppositions against this have been given claiming the average valence to be $+1$.\(^6\) However, the first by NMR\(^7\) employs too crude assumptions to derive the charge transfer rate from the NMR results. One of EPR measurements\(^8\) reveals rather the presence of Cu$^{2+}$ in the pressed samples.\(^9\) This is reasonably explained in our framework as discussed in §4. The third by XPS\(^7\) has been criticized by A. Fujimori (private communication). He points out that a correct analysis of XPS data tells the presence of both Cu$^{1+}$ and Cu$^{2+}$ in addition to some amount of Cu$^{2+}$ contaminated by oxygen, and that the content of the intrinsic Cu$^{1+}$ and Cu$^{2+}$ gives the average valence of 4/3. Hence in this paper we employ the picture of the mixed valence state of Cu$^{4/3+}$.\(^8\)
Fig. 1. The crystal structure of (DMeDCNQI)$_2$Cu and the configuration around a copper ion. All compounds belonging to DCNQI-Cu family are isostructural.

electrons. Actually heat capacity measurements claim an anomalous increase in the density-of-states of electrons in a certain alloy belonging to the present family.\textsuperscript{3,8} (3) In some compounds of this family the copper ions undergo a charge ordering of Cu$^{2+}$ and Cu$^{1+}$ giving rise to a metal-insulator transition.\textsuperscript{1,9}

One may regard this as a Peierls transition. However, also the nitrogen-copper-nitrogen bond angle is found to change abruptly there.\textsuperscript{20} A Jahn-Teller like mechanism is possibly participating in the transition. (4) When the metal-insulator transition occurs, localized magnetic moments ascribed to Cu$^{2+}$ emerge obeying the Curie-Weiss law. They undergo apparently an antiferromagnetic transition in the range 5–10 K in spite of the small content of Cu$^{2+}$ of only 1/3 of the total number of copper ions.\textsuperscript{10} Details of exchange interactions between spins are still unclear.

As described above the DCNQI-Cu family is expected to have a lot of physical aspects; a low-dimensional electron system, a Peierls instability, a valence mixing, heavy electrons, a charge ordering, a Jahn-Teller mechanism, a magnetic ordering etc, but not a superconductivity yet. Phenomenological investigations have already clarified some of these problems related especially to the metal-insulator transition.

It is still unclear, however, which roles the possible interaction between the $\pi$- and the d-electrons plays. We consider this must be one of most essential problems in this system. To attack this a key is a study of details of the metal-insulator transition in the vicinity of its transition point because many mechanisms involved in the transition are expected to compete there in energy or collaborate or both.

In order to investigate the above problem we study the title compounds, (DMeDCNQI)$_2$Cu\textsuperscript{**} and (DMeODCNQI)$_2$Cu,\textsuperscript{***} by magnetic and X-ray measurements at ambient pressure. Among many kinds of compounds belonging to the DCNQI-Cu family, they are only two that are electrically most investigated in the group which remains metallic at ambient pressure down to the lowest temperature.

Systematic studies have revealed that presumably all compounds in this family have qualitatively a common temperature-pressure phase diagram like that shown in Fig. 2. In a high-temperature-low-pressure regime they

\textsuperscript{**} 2,5-Dimethyl-DCNQI. C$_{18}$N$_4$H$_8$. Two methyl groups are bonded to a main frame of DCNQI.

\textsuperscript{***} 2,5-Dimethoxy-DCNQI. C$_{18}$N$_4$O$_2$H$_8$. Two methoxy groups are bonded to a main frame of DCNQI.

\textsuperscript{*} Y. Nishio: private communication.
are metallic, and become insulating in the other low-temperature-high-pressure regime. The title compounds remains metallic down to the lowest temperature measured, and the minimum pressure to enter the insulating state is found to be about 50 bar in (DMeDCNQI)$_2$ Cu$^{11)}$ and about 6 kbar* in (DMeODCNQI)$_2$ Cu.$^{12)}$ In addition a reentrant behavior with temperature as shown in Fig. 2 has been found in both compounds.

In a comparative study of these two compounds we expect to have an insight into the nature of the metal-insulator transition and the reentrant behavior. The critical pressure of (DMeDCNQI)$_2$ Cu is low enough to expect emergence of indications of the insulating state and the reentrant behavior even at ambient pressure.

In the following sections we will present the magnetic susceptibility and the lattice parameters as functions of temperature. When these results are combined with a current picture for the key role of the angle of nitrogen-copper-nitrogen bond in dominating electronic properties of this family of compounds, it is found that (DMeDCNQI)$_2$ Cu is actually a marginal metal close to an insulating state but (DMeODCNQI)$_2$ Cu is not.

* The critical pressure, 8 kbar, shown in ref. 12 is a nominal one measured at room temperature. A real pressure at low temperatures is estimated to be this.

In addition the reentrant phenomenon is found to involve largely a change in the lattice parameters, although we do not necessarily ascribe the reentrance only to a structural origin.

§2. Experiments

Sample crystals were synthesized by the method described by Aumuller et al.$^{13)}$ Typical size of samples is 2–3 mm in length and 0.05–0.1 mm in thickness and width. The needle axis is found to be parallel to the stacking axis of DCNQI molecules, which is the c-axis of the lattice. We measured electrical resistivity along the c-axis by conventional four-probe method. Gold wires of 25 μm dia. and gold paste were used to make electrical contacts.

For magnetic susceptibility measurements we used two types of SQUID susceptometer. Polycrystalline samples like cotton-wool were put in sample cells of plastics or gelatin. A background susceptibility of the gelatin cell was verified to be temperature independent down to the lowest temperature measured, 4.2 K. The plastic-tube cell did not contribute to the measured susceptibility because the tube was long enough to keep it always through two pick-up coils. We made measurements on (DMeDCNQI)$_2$ Cu samples from three different batches and on (DMeODCNQI)$_2$ Cu from two. Most of samples were measured in a SQUID susceptometer under magnetic fields up to 9 kOe. One of the (DMeDCNQI)$_2$ Cu samples was measured also in the other SQUID up to 50 kOe. The samples were cooled by flowing helium gas whose temperature was controlled.

We made X-ray diffraction on single crystals using CuKα radiation. Needle like crystals were glued by gold paste onto a sample holder in a chamber filled with helium gas. Lattice parameters were evaluated as functions of temperature by measuring the Bragg angles of both (hkl) and (hk0) reflections at each temperature. This method made it possible to obtain results free from movement of samples due to thermal contraction of the sample holder and the gold paste.

In the above experiments accuracy of temperature measurements was better than 0.5 K in the range below 100 K.
§3. Experimental Results

We verified that our samples showed simple metallic properties consistent with previous results.1,14,15) Also a transverse magneto-resistance at 4.2 K under the field of 120 kOe was found to be about 5% of the zero-field resistance in accordance with a previous result.16)

3.1 Magnetic Susceptibility

Figure 3 shows typical results of susceptibility measurements on (DMeDCNQI)$_2$Cu and (DMeODCNQI)$_2$Cu. It is apparent that the susceptibility is contributed by, at least, two origins: First one finds a nearly temperature independent susceptibility reminiscent of the Pauli paramagnetism of simple metals. (DMeDCNQI)$_2$Cu appears to be dominated only by this. The small increase below about 30 K is sample dependent and can be ascribed to impurity spins of 1/2 whose content is only about 2 $\times$ 10$^{-3}$/formula unit.

Another source of magnetic moments appear in (DMeDCNQI)$_2$Cu below about 100 K. It has two peculiar features as shown in Fig. 3; a hysteresis for temperature cycling and a kink at about 7 K. With decreasing temperature the susceptibility increases showing a plateau below about 25 K followed by a sudden drop below about 7 K. With increasing temperature again the susceptibility has no hysteresis up to 7 K, above which, however, it decreases without making a plateau. At about 50 K it comes back to the results obtained in the cooling process. As far as the results obtained in the heating process are concerned, they are found to be independent whether the sample is cooled in the magnetic field or the field is turned on after cooling the sample down to the lowest temperature.

The magnitude of the susceptibility is interpreted in two ways: First, from a view point of the Pauli paramagnetic susceptibility, the result above 100 K gives about 10 states/eV/formula unit/spin and that at 10 K about 22 states/eV/formula unit/spin. Here we took account of the core diamagnetism of about 0.8 $\times$ 10$^{-6}$/emu/g but not of other sources like the Landau diamagnetism. Second, from another view point of localized spins of 1/2 obeying the Curie law, the susceptibility below 100 K is explained in terms of varying number of moments. Its maximum reached at about 30 K is 10% of total number of copper ions. Qualitatively the same results have been obtained by electron-paramagnetic-resonance (EPR) measurements although the

![Fig. 3. Temperature dependence of the magnetic susceptibility of (DMeDCNQI)$_2$Cu and (DMeODCNQI)$_2$Cu. A diamagnetism due to core electrons (estimated to be about 0.8 $\times$ 10$^{-6}$/emu/g) is not taken into account. The arrows indicate directions of temperature change.](image-url)
maximum content of Cu\(^{2+}\) is evaluated as about 1% of the total number of copper ions.\(^{15}\) It is unclear at present, however, what this discrepancy implies. It is possible to obtain quantitatively different results between the static susceptibility and the EPR measurements depending on the spin dynamics. In addition we must keep another possibility of sample dependence between cotton-wool-like polycrystals used in the present study and single crystals in EPR. This point will be discussed in §4.

We found that the hysteresis loop was independent of applied fields of measurements, 350 Oe–50 kOe and did not shrink even when (1) we kept the sample temperature in the hysteresis regime for longer than 5 hr, and (2) we stopped cooling (or heating) at a certain temperature in the same regime and started heating (or cooling) back. This implies that some mechanisms of presumably structural origin are working to lock-in the physical state of this compound.

It is interesting to see that the above difference between (DMeDCNQI)\(_2\)Cu and (DMeODCNQI)\(_2\)Cu, and the hysteretic properties of the former compound are never found in the electrical resistance.

We found non-linear magnetic properties in only (DMeDCNQI)\(_2\)Cu again. The magnetizing process is sublinear with respect to the applied field in the range below about 10 kOe. Figure 4 shows the susceptibility evaluated as \(M/H\) under different applied fields, where \(M\) and \(H\) denote the magnetization and the magnetic field, respectively. We verified that the susceptibility is field-dependent only in the range below about 10 kOe and 100 K. It is hard to ascribe this to extrinsic origins because the anomaly is found in several samples from different batches, in both SQUID susceptometers, and, in addition, only in the range below 100 K. One may point out a possibility of mechanical rotation of cotton-wool-like samples due to a possible anisotropy in susceptibility. It is easy to see, however, that this mechanism should give a nonlinearity in the opposite sense.

3.2 Lattice parameters

In lattice parameters we found anomalous behavior which appears to be closely related to the magnetic anomaly described above. Figures 5 and 6 show temperature dependence of lattice parameters of (DMeDCNQI)\(_2\)Cu and (DMeODCNQI)\(_2\)Cu, respectively. We measured only the parameters \(a\) and \(c\) because the lattice was found to keep tetragonal symmetry at all temperatures measured. In both compounds the parameter \(c\), which denotes the unit-cell size along the stacking axis of DCNQI molecules, decreases with decreasing temperature as expected naively. The parameter \(a\), however, increases with lowering temperatures. These results suggest the followings: (1) One-dimensionality increases with

![Fig. 4. Details of the magnetic susceptibility of (DMeDCNQI)\(_2\)Cu under different fields. Above 10 kOe data points fall on nearly the same curve as at 10 kOe. The data were taken with increasing temperature.](image-url)
decreasing temperature because the interstack distance characterized by the parameter \( a \) increases while the intrastack distance, \( c \), between molecules decreases. (2) The nitrogen-copper-nitrogen bond angle \( \alpha \) shown in Fig. 1 is expected to increase with decreasing temperature. Although we did not make direct measurements of \( \alpha \), it is natural to expect this because in isostructural (MeBrDCNQI)$_2$-Cu the correlation between the angle \( \alpha \) and the ratio \( a/c \) has been verified directly.\(^2\)

It is to be noted that the parameter \( a \) of (DMeDCNQI)$_2$-Cu begins to decrease below about 30 K. Furthermore it shows hysteretic behavior as shown in Fig. 5 reminiscent of the hysteresis in the magnetic susceptibility shown in Fig. 3. On the other hand the parameter \( a \) of (DMeODCNQI)$_2$-Cu saturates below about 100 K. Here again one finds (DMeDCNQI)$_2$-Cu anomalous also in the structural properties.

§4. Discussion

The anomalous behavior in the magnetic and structural properties of (DMeDCNQI)$_2$-Cu is considered to be related to the low

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**Fig. 5.** Change of lattice parameters of (DMeDCNQI)$_2$-Cu relative to those at 140 K. The results were derived from the diffractions with indices (260), (260), (321) and (321). The arrows denote directions of temperature change. The curves are guides for the eye.

**Fig. 6.** Change of lattice parameters of (DMeODCNQI)$_2$-Cu relative to those at 140 K. The results were derived from the diffractions with indices (800), (800), (321) and (321). The curves are guides for the eye.
critical pressure of only about 50 bar to enter
the insulating state. One may expect either to
find some precursor effects of the insulating
state, or to have some volume fraction of a
sample being already in the insulating state
because of possible strains in it, or both.

Actually the results in (DMeDCNQI)$_2$Cu
are consistent with the current picture for
some DCNQI-Cu compounds that undergo a
metal-insulator transition. It is to be noted,
however, that the changes in the magnetic and
the structural properties are continuous with
temperature while those are abrupt in com-
ounds undergoing the metal-insulator transi-
tion. This difference is natural because the
change in (DMeDCNQI)$_2$Cu is considered to
be incomplete to enter the insulating state.

We propose the following picture for the
present compounds: The Cu ions have the
mixed valence state whose average valence is
about 4/3 presumably at all temperatures and
pressures measured. At high temperatures
the fluctuation between Cu$^{2+}$ and Cu$^{1+}$ is fast
enough to give metallic properties in not only
the electrical resistance but also magnetic sus-
ceptibility.

When the temperature is lowered, the ratio
of the lattice parameters, $a/c$ is expected to in-
crease given rise to the increase of the bond
angle $\alpha$. When this angle exceeds a threshold
value, the Cu$^{2+}$ ionic state begins to be stabil-
ized. The number of stabilized Cu$^{2+}$ ions will
increase with decreasing temperature resulting
in the anomalous increase in the susceptibility.
Below about 50 K the lattice parameter $a$
changes in the opposite sense as shown in Fig.
5 resulting in the saturation of the susceptibil-
ity.

We consider that the increase of the angle $\alpha$,
and hence the number of Cu$^{2+}$ ions is not
large enough to make the present system elec-
trically insulating. To make it insulating the
period of charge ordering must be such as to
open a gap at the Fermi level of the conduc-
tion electrons. This happens only when the Cu
ions have the average valence of 4/3 and all
ions order.

The pressure application above about 50
bar is considered to make the angle $\alpha$
sufficiently large to stabilize and order all
Cu$^{1+}$ and Cu$^{2+}$ ions below certain tempera-
tures. In this respect it is interesting to see the
conflict among EPR measurements$^{5,6,15}$ and
the present work in the presence of Cu$^{2+}$ and
the estimates of its content. We consider these
conflicts can be removed when we assume the
presence of sample dependence in an effective
pressure in samples. Actually the organic
superconductor (BEDT-TTF)$_2$Cu(NCN)$_2$Br
has the threshold pressure to enter the super-
conducting state ranging from 1 bar to 300–
400 bar. It depends on the sample preparation
condition.$^*$ We consider, hence, it is probable
that a small difference in the angle $\alpha$ among
samples brings about the difference in the con-
tent of Cu$^{2+}$ ions. This problem remains to be
solved in future studies of systematic pressure
dependence of physical properties.

It is unclear at the present stage whether or
not the average valence changes with tempera-
ture or pressure. The present study can tell
only that the stabilized Cu$^{2+}$ ions in the pre-
sent compounds at ambient pressure do not
form a ordering structure which opens a band
gap at the Fermi level.

In the light of this picture the reentrant
behavior is simply ascribed to the anomalous
change in the lattice parameter described
above. We point out that the reentrance in the
phase diagram will be removed when one
draws it against, instead of the pressure, the
ratio $a/c$ or the angle $\alpha$, which must be
physically more meaningful. We must keep a
possibility, however, that the lattice-
parameter change is only a result of the reen-
trance phenomenon but not its origin.

The hysteresis in both the susceptibility and
the lattice parameter is interpreted in terms of
a kind of pinning of the lattice-parameter
change. We consider that this mechanism
must be an origin of the hysteresis in
resistance observed in the reentrant regime.$^{11}$
However, the microscopic mechanism of the
pinning is still unclear.

It is difficult at the present stage to explain
the field dependence of the magnetic suscepti-
bility of (DMeDCNQI)$_2$Cu below about 100
K. As shown in Fig. 4 the susceptibility
decreases by 10% with increasing field only in
the range less than 10 kOe. In addition the

$^*$ I. F. Schegolev: private communication.
kink in the susceptibility vs temperature curve shifts from about 7 K up to about 9 K in the same field range. One can understand neither of these properties in terms of a naive picture of localized spin system. In the model of Pauli paramagnetism it is possible to have a field dependent susceptibility when a density of states near the Fermi level has an energy dependence other than the linear. In order for this, however, the thermal energy must be less than the Zeeman energy. The typical field strength we found, 10 kOe, and the temperature range of about 50 K can never be reconciled with this idea. We consider that the field dependent magnetic properties in the quite low-field range may be a key to clarify more the electronic properties of this family of compounds.

§5. Conclusion

In (DMeDCNQI)$_2$Cu and (DMeODCNQI)$_2$Cu we measured the temperature dependence of the magnetic susceptibility and lattice parameters, from which we evaluated the change in the angle of nitrogen-copper-nitrogen bond as a function of temperature. Both measurements suggest that the key role is played by the bond-angle also in these compounds as it has been experienced in similar compounds that undergo metal-insulator transitions.

(DMeDCNQI)$_2$Cu is considered to be a marginal metal close to the insulating state while (DMeODCNQI)$_2$Cu appears to be a simple one. Signs of the reentrant behavior observed in these compounds under pressure are already seen in the bond angle and the magnetic susceptibility in (DMeDCNQI)$_2$Cu at ambient pressure.

The magnetic susceptibility is found to be field dependent in the low-field range below about 1 T. In addition an anomaly in the susceptibility, which appears to be a sign of an antiferromagnetic transition, is also field dependent. Origins of these are remaining to be clarified in future studies.

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