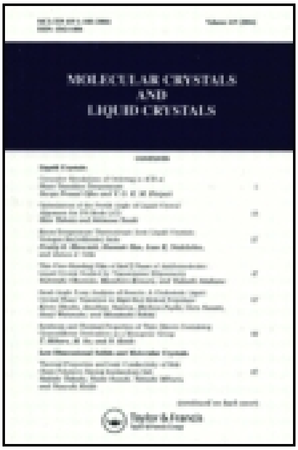

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CORRELATION BETWEEN THE THERMAL AND MAGNETIC PROPERTIES OF $(DCNQI)_2Cu$

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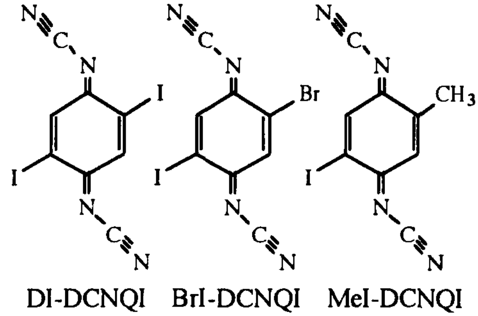
Abstract Low temperature electronic specific heat, C, was measured for three iodine-containing $(DCNQI)_2Cu$. The temperature coefficient γ has been found to correlate with the temperature dependence of magnetic susceptibility, χ. This supports the interpretation of the anomalous magnetism of these salts on the basis of itinerant electron magnetism.

INTRODUCTION

The pπ-d interactions in a series of Cu-based molecular conductors, $(R^1,R^2\text{-DCNQI})_2Cu$, where DCNQI is 2,5-disubstituted-*N,N'*-dicyanoquinonediimine, have been shown to play a significant role in stabilizing the metallic states of the systems.[1-3] Sufficient hybridization between the Cu-3d states and the one-dimensional π-band of DCNQI columns is believed to afford the three-dimensional metallic behavior at low temperature. For $(DMe\text{-DCNQI})_2Cu$ and its deuterated series, ordinary Fermi liquid behavior has been established by the studies of the magnetic susceptibility,[4] the de Haas-van Alphen oscillations,[5] and the specific heat.[6]

Application of pressure or decrease in the size of the substituents (chemical pressurization) induces a metal-insulator transition. This can be explained in terms of the change in degree of the charge transfer associated with distortion of the tetrahedral coordination around the Cu ions.[1,2,7] The origin of the M-I transition is the interplay between the one-dimensionality of the conduction π-



DI-DCNQI BrI-DCNQI MeI-DCNQI

Scheme 1. Chemical formulas of the three DCNQIs studied in this work.

electrons and the charge ordering on the Cu ions. The commensurability between them results in the specific valence of Cu in the insulating phase, $Cu^+ : Cu^{2+} = 2 : 1$. The spins on Cu^{2+} are completely localized and undergo an antiferromagnetic transition below about 10 K.[1,8]

The system undergoes M-I-M reentrant transitions in a certain (chemical) pressure region.[9,10] The origin of this peculiar reentrant transitions has been a subject of considerable investigations.[1] The magnetic susceptibility[11] and the de Haas-van Alphen[5] studies of selectively deuterated $(DMe\text{-}DCNQI)_2Cu$ samples showed that the low temperature reentrant metallic phase has the same ordinary Fermi liquid character as well as the other metallic region. It is not possible to find any anomaly unique to the low temperature metallic state which can explain the appearance of the reentrant transitions.

It has been pointed out that the appearance of the reentrant transitions can be phenomenologically explained by a thermodynamic treatment of a first-order transition, in which only the contribution of the Cu^{2+} spin degrees of freedom in the insulating phase and that of the conduction electrons in the metallic phase is considered.[12] However, for quantitative agreement with the experiments, the temperature coefficient of the electronic specific heat, γ, should amount to 40-50 K^{-2} mol^{-1}, which is about twice as large as the experimental value. According to our recent measurement of specific heat of the deuterated series of $(DMe\text{-}DCNQI)_2Cu$ over 20-100 K, the lattice specific heat in this temperature range shows approximately linear temperature dependence both in the metallic and insulating phases.[13] This means that the contradiction between the phenomenological theory and the experimental phase diagram can be removed by taking account of the difference in lattice contribution to the free energy between the metallic and insulating phases. In this way, the physical characters of the metallic phase can be understood without considering any anomalous situation such as strong correlation and mass enhancement.

Unlike the convensional $(DCNQI)_2Cu$, iodine-substituted systems exhibit quite unusual behavior as a molecular metal.[14] Three types of iodine-containing $(DCNQI)_2Cu$, the Cu salts of 2,5-diiodo-DCNQI (DI-DCNQI), 2-iodo-5-methyl-DCNQI (MeI-DCNQI) and 2-bromo-5-iodo-DCNQI (BrI-DCNQI), have been investigated until now. All these salts are metallic down to the lowest temperature under ambient pressure. Outstanding is the magnetic properties of these systems.[15,16] The susceptibility of $(DI\text{-}DCNQI)_2Cu$ is 2-3 times as large as that of the convensional $(DCNQI)_2Cu$ such as $(DMe\text{-}DCNQI)_2Cu$. Moreover, the susceptibility of these salts exhibits a broad maximum at 100-200 K, which evidently deviates from the magnetic behavior of ordinary metals. These features are in remarkable contrast to the convensional $(DCNQI)_2Cu$ in a metalic state. Thus, the iodine-substituted $(DCNQI)_2Cu$ has provided a new physical scope.

We have attributed these anomalies to itinerant electron magnetism, and pointed out the possibility of the exchange-enhanced mechanism in a narrow band.[15,16] However, only by the magnetic measurement, it is difficult to exclude the possibility of other mechanism. Since the band structures of the iodine-substituted salts have not been established yet, another explanation of the temperature dependence of susceptibility, such as that based on low-dimensional local spins, cannot be completely ruled out. Therefore, another kind of experiment to probe the behavior of the conduction electrons is desired. For this purpose, we have carried out low-temperature specific heat measurements of the crystals of (DI-DCNQI)$_2$Cu, (MeI-DCNQI)$_2$Cu and (BrI-DCNQI)$_2$Cu.

RESULTS AND DISCUSSION

The specific heat of about 1 mg of polycrystalline samples of the three iodine-containing (DCNQI)$_2$Cu was measured in the temperature range, 1-5 K, by the thermal relaxation method. Figure 1 shows the plot of C/T against T^2 for these samples. It follows from this that the temperature dependence of C of these salts is well described by the formula, $C = \gamma T + \beta T^3$, where the first and second terms stand for the electronic and lattice contributions, respectively. The intercepts obtained by linear extrapolation to $T^2 = 0$ give the estimation of values of the temperature coefficient, γ, while the slopes, beta, are related to the Debye temperatures. The γ values thus obtained from the plots are listed in Table I, together with that of (DMe-DCNQI)$_2$Cu. It is clear that the γ values of the three iodine-containing (DCNQI)$_2$Cu are enhanced in comparison with that of (DMe-DCNQI)$_2$Cu. Among them, γ of (DI-DCNQI)$_2$Cu, 70 mJ K^{-2} mol^{-1} is about three times as large as that of (DMe-DCNQI)$_2$Cu, 25±3 mJ K^{-2} mol^{-1}. The anomalous behavior of the conduction electron systems in the iodine-containing (DCNQI)$_2$Cu, which has been pointed out by the magnetic experiments, is thus supported by the thermal measurements, because the linear temperature dependence of specific heat is characteristic of the conduction electrons.

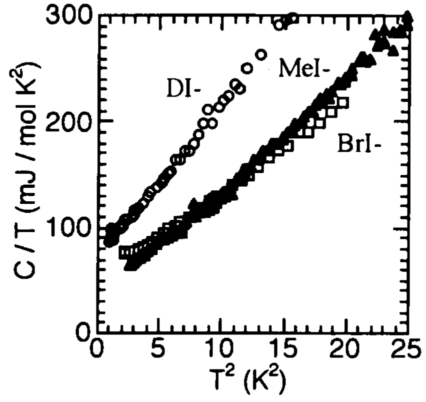


FIGURE 1. Plot of C/T vs. T^2.

Figures 2 shows the temperature dependence of these salts, where χ is corrected for diamagnetic contributions. Sizable Curie-like upturn of χ was observed for (MeI-DCNQI)$_2$Cu and (BrI-DCNQI)$_2$Cu at low temperatures, which is attributable to defects in the samples.[16] The present data for the two salts were corrected for this contributions as well as possible. The temperature dependence of χ can be characterized by two parameters, χ_0 and T_{max}, the susceptibility at absolute zero and the temperature where the susceptibility maximum appears, respectively. The parameters obtained from the data

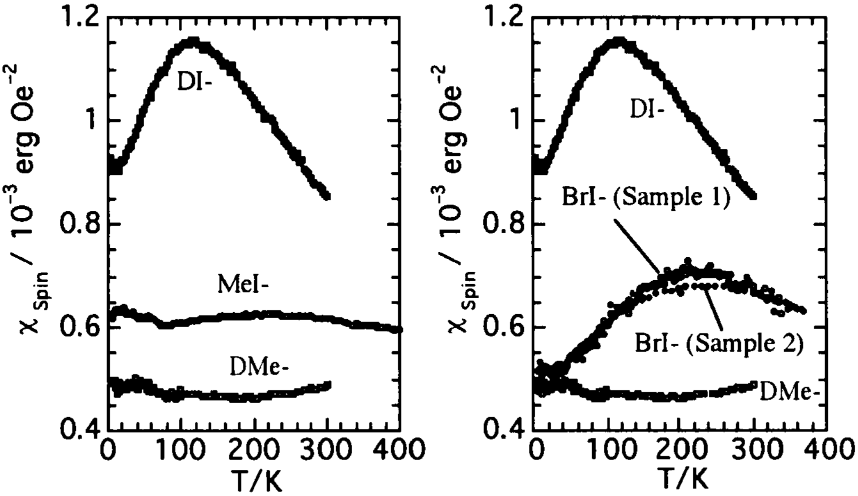


FIGURE 2. Comparison of the temperature dependence of spin susceptibility of the three iodine-containing $(DCNQI)_2Cu$ and $(DMe\text{-}DCNQI)_2Cu$.

are given in Table I. The χ_0 values for $(MeI\text{-}DCNQI)_2Cu$ and $(BrI\text{-}DCNQI)_2Cu$ have some ambiguity due to the low temperature upturn. The T_{max} values of $(MeI\text{-}DCNQI)_2Cu$ and $(BrI\text{-}DCNQI)_2Cu$ are about twice as high as that of $(DI\text{-}DCNQI)_2Cu$, and the χ_0 values of the two salts are about half of that of the latter.

TABLE I. Thermal and magnetic parameters of the iodine-containing $(DCNQI)_2Cu$ and $(DMe\text{-}DCNQI)_2Cu$.

	γ / mJ K^{-2}mol^{-1}	χ_0 / 10^{-3}emu mol^{-1}	T_{max} / K
DI-	70	0.9	110
MeI-	30-40	0.6	~ 200
BrI-	50-60	0.5	~ 200
DMe-	22-28	0.43	—

It is worth while comparing the thermal and magnetic properties summarized in Table I. It seems that increase in γ yields increase in χ_0 and decrease in T_{max}. The thermal and magnetic properties are correlating with each other. The correlation between γ and χ_0 can be interpreted in terms of the theory of Fermi liquid; the Wilson ratio[17] close to 1, $R_W = (\chi_0/2\mu_B^2)/(3\gamma/2\pi^2k_B^2) = 0.94$, is obtained from the data for $(DI\text{-}DCNQI)_2Cu$. The series of iodine-substituted $(DCNQI)_2Cu$ is thus characterized as a Fermi liquid system with enhanced mass and density of states.

As pointed out in our previous paper,[15, 16] T_{max} can be related to the characteristic temperature of spin fluctuation in the light of a phenomenological theory of itinerant electron magnetism.[18] In this framework, T_{max} is proportional to $1/\chi_0$, which seems to be satisfied by the present results. If the spin fluctuation mechanism is operative on these systems, T_{max} is a measure of effective pπ-d hybridization determining the width of peak structure of a narrow band near the Fermi level. It follows from this that the iodine-substitution results in reduction of effective pπ-d hybridization. Such a situation has not been known in any other molecular conductor. Therefore, the iodine-substitued $(DCNQI)_2Cu$ is identified as a new category of materials with exchange enhanced magnetism of itinerant electrons in a narrow band. On the other hand, it is still difficult to explain the small difference between $(BrI\text{-}DCNQI)_2Cu$ and $(MeI\text{-}DCNQI)_2Cu$, as noted by the difference in the curvature and slope of the susceptibility curves.

It should be noted that the peculiar behavior of the electron system in the iodine-substituted $(DCNQI)_2Cu$ is approached by weakening the effective interactions between the Cu 3d- and DCNQI π-orbitals. In the convensional $(DCNQI)_2Cu$ such as $(DMe\text{-}DCNQI)_2Cu$, the pπ-d hybridization is so large that the 3d electrons are well delocalized in the metallic state over the whole temperature range examined; T_{max} of $(DMe\text{-}DCNQI)_2Cu$ is too large to be estimated from the almost temperature independent susceptibility data below room temperature. This situation is consistent with the absence of additional mass enhancement.[5] The appearance of the M-I transitions is another thing. The stability of the insulating phase with localized Cu^{2+} spins is prescribed by the valence of the Cu ions; the role of pπ-d exchange interactions is a secondary one. In contrast to this, the enhanced γ and the temperature dependent susceptibility of the iodine-containing systems should be closely related to the interplay between the 3d-like electrons and π-electrons in the metallic state. The Kondo lattice (heavy electron) picture[1] may be still alive in the iodine-containing systems. It is required to do further experiments on the iodine-containing systems to elucidate detailed mechanism of the temperature dependennce of χ and enhancement of χ and γ; for example, microscopic site-selective information provided by magnetic resonance study is most appreciated.

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