Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006.

To cite this article: Masafumi Tamura , Hiroshi Sawa , Yoshiaki Kashimura , Shuji Aonuma , Reizo Kato & Minoru Kinoshita (1995): $(DCNQI)_2Cu$: Variety of Magnetism Arising from pπ-d Interactions, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 271:1, 13-18

To link to this article: http://dx.doi.org/10.1080/10587259508034034

Mol. Cryst. Liq. Cryst., 1995, Vol. 271, pp. 13–18
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$(DCNQI)_2Cu$: VARIETY OF MAGNETISM ARISING FROM $p\pi$-d INTERACTIONS

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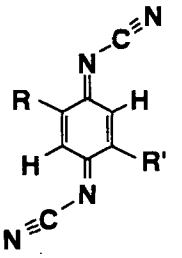
Abstract Recent advances of our study of magnetic properties of a series of molecular conductors, Cu salts of DCNQIs, are presented. First, we have found weak ferromagnetism in the antiferromagnetically ordered state of Cu spins in the insulating phase. Second, the metal-insulator (M-I) transitions of these systems have been characterized by the abrupt change of Cu 3d spins from the itinerant state to the completely localized state, even in the metal-insulator-metal (M-I-M) reentrant system, $(DMe\text{-}DCNQI\text{-}\alpha,\alpha'\text{-}d_2)_2Cu$. Finally, $(DI\text{-}DCNQI)_2Cu$ is found to exhibit enhanced and temperature dependent susceptibility, suggesting the effect of spin fluctuations of itinerant electrons in a Cu 3d narrow band.

INTRODUCTION

The peculiar electronic structure of a series of molecular conductors, $(DCNQI)_2Cu$, where DCNQI is *N,N'*-dicyanoquinonediimine, has attracted much attention.[1-3] In the crystals of $(DCNQI)_2Cu$, DCNQIs stack along the tetragonal *c*-axis to form one-dimensional columns, which are interconnected by Cu ions in a mixed-valence state[1] close to $Cu^{1.3+}$. $(DMe\text{-}DCNQI)_2Cu$ (DMe salt, where DMe-DCNQI is 2,5-dimethyl-DCNQI) is metallic down to low temperature, in spite of the one-dimensional character of the DCNQI columns. The stability of the metallic state has been believed to be governed by the $p\pi$-d interactions between DCNQIs and Cu ions. The carriers are delocalized over Cu ions and DCNQIs, so as to form a three-dimensional Fermi liquid system[4] with small constant susceptibility (χ).



RR'-DCNQI
DR-DCNQI (R = R')

FORMULA 1 Chemical formula of DCNQI.

Deuteration of $(DMe\text{-}DCNQI)_2Cu$ causes instability of the metallic state; a M-I transition or M-I-M reentrant transitions appears depending on the number and the site of deuteration.[5,6] The M-I transition appears also in other salts such as $(DBr\text{-}DCNQI)_2Cu$ (DBr-DCNQI is 2,5-dibromo-DCNQI). The M-I transition is first-order. The insulating phase is characterized by Curie-Weiss-like χ of the local spins on 1/3 of Cu ions and by the three-fold super-lattice along the DCNQI columns.[1] The spins undergo an antifer-

romagnetic transition at about 10 K. Therefore, it is obvious that the d-electrons are strongly correlating in the insulating state.

The M-I-M reentrance is one of the most peculiar features of the system. It has been in question whether the low temperature metallic (M_L) phase has the same character as that of the high temperature (M_H) metallic phase, because the M_L phase appears nearby the strongly correlating insulating phase. Or, more generally, the problem is whether there is any effect of the narrow 3d band character in the metallic state. The study of magnetic properties is an efficient way to detect the difference between the metallic phases and the trace of the Cu 3d character in the metallic state.

In this paper, we describe the magnetic structure in the antiferromagnetic ordered state of deuterated (DMe-DCNQI)$_2$Cu and (DBr-DCNQI)$_2$Cu first. Weak ferromagnetism, which is ascribed to canting of the spins, has been found in this state. Second, the magnetic characterization of the M-I-M reentrant behavior is presented. Finally, a novel magnetism of the metallic states of (DI-DCNQI)$_2$Cu and the related materials, enhanced susceptibility with maximum, is reported. This temperature dependence of χ is interpreted as the exchange-enhanced paramagnetism of itinerant electrons with spin fluctuations. A phenomenological analysis is applied and the characteristic temperature of spin fluctuations, which is a measure of the pπ–d interaction, is estimated.

RESULTS AND DISCUSSION

Antiferromagnetism and Weak Ferromagnetism in the Insulating State[7,8]

The fully deuterated (DMe-DCNQI)$_2$Cu (d_8 salt) is the most suitable example to study the magnetic properties of the antiferromagnetic state, since it affords satisfactory large single crystals. This salt undergoes the M-I transition at 80 K. Below this temperature, χ follows the Curie-Weiss law down to about 30 K. The Curie constant indicates that 1/3 of Cu ions possess local spins. The antiferromagnetic ordering occurs around 8 K. In the ordered state, the Cu spins have been found to be aligned within the *ab*-plane by the observation of anisotropic χ and spin-flop type magnetization curve for the fields perpendicular to the *c*-axis[7] (Figure 1). The spin-flop field seems to distribute over 2- 8 kOe. Recent observation of antiferromagnetic resonance (AFMR) in (DMe-DCNQI-d_7)$_2$Cu (d_7 salt), which is known to be very similar to the d_8 salt, shows that the resonance field varies over the same range with the field direction within the *ab*-plane.[9] Therefore, the

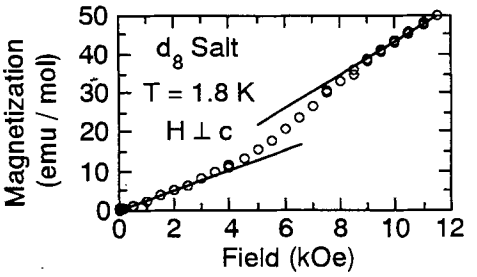


FIGURE 1 Spin-flop type magnetization curve of the d_8 salt.

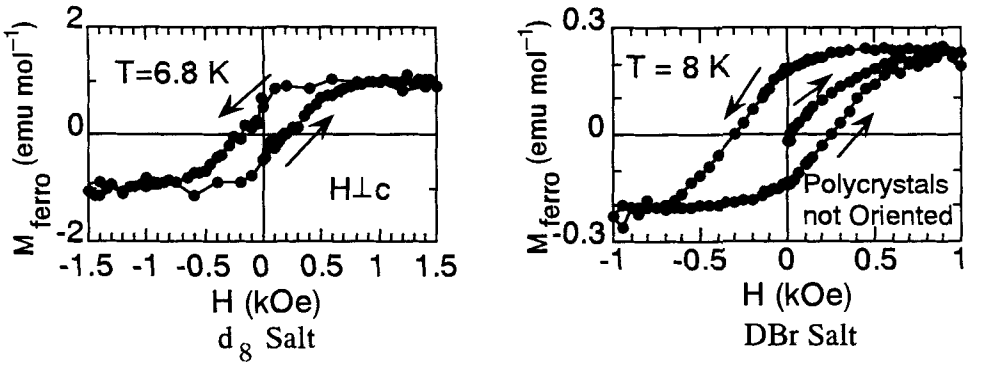


FIGURE 2 Hysteretic behavior of the ferromagnetic component of the oriented single crystals of the d8 salt (left) and a polycrystalline sample of the DBr salt (right), obtained by subtracting the linear contributions from the observed magnetization.

distribution of the spin-flop field is interpreted as a result of random orientation of the crystals within the *ab*-plane in the measurement.

Nonlinear field dependence of magnetization,[7] hysteretic magnetization curve[7] (Figure 2) and thermoremanent magnetization[8] appear perpendicular to the *c*-axis around the Néel temperature. This behavior has been ascribed to weak ferromagnetism due to canting of the spins. Similar behavior has been observed also for $(DBr\text{-}DCNQI)_2Cu$ (DBr salt) below *ca.* 16 K.[8] The ferromagnetic component of the d_8 salt disappears at *ca.* 2 K,[7] whereas that of the DBr salt tends to saturate below *ca.* 8 K.[8] The AFMR results for the d_7 salt[9] suggest that the orientation of the spins is governed by the coordination geometry around the Cu ions. This can explain the origin of the canting, because there are two inequivalent Cu^{2+} sites in the insulating state.[1] If this is the case, the weak ferromagnetism in the insulating $(DCNQI)_2Cu$ is unique in the sense that the alignment of the S=1/2 spins is controlled by the chemical structure around the magnetic ions.

Reentrant Transitions in $(DMe\text{-}DCNQI\text{-}\alpha,\alpha'\text{-}d_2)_2Cu$ (d_2 Salt)[10]

The purpose of the magnetic study of the d_2 salt, a reentrant system, is to elucidate whether there is any anomaly, such as enhancement of χ, in the M_L phase near the localized insulating phase. As shown in Figure 3, we have found that the M_L phase exhibits χ as small as that of the M_H phase, which indicates that both the metallic phases are identical to each other. Concurrently, the insulating state of the reentrant system has been found to exhibit the same Curie-Weiss-like χ as those of the d_8 salt. It was recognized that annealing of the sample is efficient to suppress the overcooling effect. Thus, neither incomplete nor intermediate state have been found, even in the vicinity of

the boundary between the metallic and insulating states. From the magnetic viewpoint, the M-I transition of the system is characterized by the abrupt change of Cu 3d electrons from the entirely itinerant state to the localized state. This is considered to be caused by the coupled formation of the local spins on 1/3 of Cu ions and the charge density wave with 3c period along the DCNQI columns.

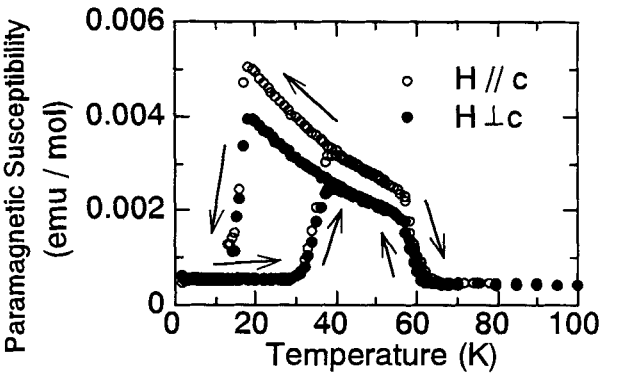


FIGURE 3 Temperature dependence of the paramagnetic susceptibility of the reentrant system (DMe-DCNQI-α,α'-d_2)$_2$Cu.

Enhanced Susceptibility in (DI-DCNQI)$_2$Cu and Related Systems[11]

Figure 4 shows the temperature dependence of χ of single crystals of the (DI-DCNQI)$_2$Cu (DI salt), where DI-DCNQI is 2,5-diiodo-DCNQI. A maximum appears around 110 K, and χ is 2-3 times as large as those of the conventional metallic (DCNQI)$_2$Cu. The DI salt exhibits no M-I transition up to *ca.* 15 kbar,[12] which indicates the appreciable stability of the metallic state in this salt. A preliminary measurement of the infrared vibrational spectra of the DI salt shows that the valence of Cu ions is close to $Cu^{1.3+}$ even in this salt. By taking account of the small anisotropy and T^2 dependence of the low temperature resistivity,[11,12] the anomalous magnetism is ascribed to the exchange enhanced paramagnetism of the itinerant electrons. The temperature dependence should reflect the spin fluctuations in a narrow d band. This is a common feature with those of the intermediate valence Ce compounds (*e.g.*, $CeSn_3$) and the nearly ferromagnetic metals (*e.g.*, Pd and YCo_2). The DI salt is a unique molecular conductor, in which the narrow band character of the d electrons manifests itself as such a novel magnetism.

In order to extract the information on the pπ-d interactions determining the spin fluctuations in the system, we have analyzed the temperature dependence of χ in the light of the phenomenology applied to $CeSn_3$.[13] By introducing the characteristic temperature of spin fluctuation, T^*, the susceptibilities at high and low temperatures are described by the equations,

$$\chi(T) = C/(T + T^*), \qquad T > T^* \tag{1}$$

and,

$$\chi(T) = \chi_0[1 + a(T/T^*)^2 + b(T/T^*)^4 + \ldots], \qquad T < T^* \tag{2}$$

respectively. And in the framework of this phenomenology, χ should approach $C/2T^*$ as $T = 0$ is approached. The maximum of χ should appear around $T_{max} \sim T^*/2$. All these conditions are consistently satisfied, when we take $C = 0.4$ emu K/mol, $T^* \sim 200$ K, $\chi_0 = 0.9\times10^{-3}$ emu/mol, $a = 2.7$ and $b = -9.8$. Note that C is too large to be justified by the picture of the local spins on 1/3 of Cu ions. Thus, the temperature dependence of χ of the DI salt is characterized by $T^* \sim 200$ K, which corresponds to the energy scale of the peak structure of the density of states measured from the Fermi level, *i.e.*, a measure of the pπ-d interactions determining the structure of the narrow 3d band. The coefficient of the $(T/T^*)^2$ term in Equation (2), a, stands for the temperature induced spin fluctuations and corresponds to the positive curvature of the density of states at the Fermi level.

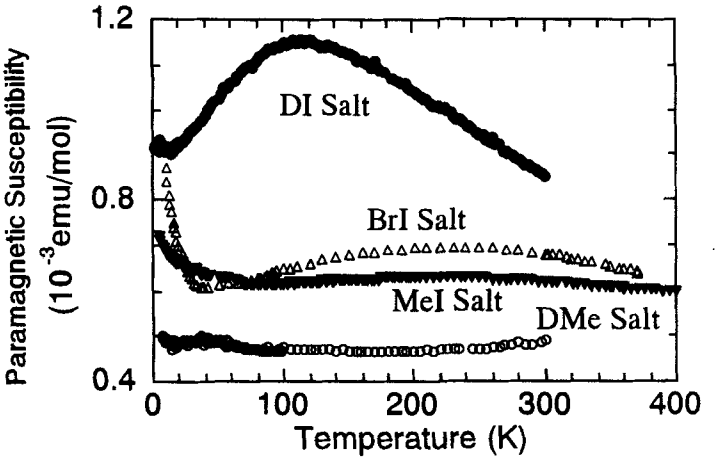


FIGURE 4 Temperature dependence of the paramagnetic susceptibilities of the DI, MeI, BrI and DMe salt.

In order to see the effect of chemical modification, we have measured χ of (MeI-DCNQI)$_2$Cu and (BrI-DCNQI)$_2$Cu (MeI salt and BrI salt), where one of the iodine atoms in DI-DCNQI is replaced with a methyl group and a bromine atom, respectively. Both these salts are metallic down to low temperature at ambient pressure and exhibit χ values intermediate between those of the DMe and DI salts, with a broad maximum of χ around 200 K (Figure 4). Below about 80 K, the Curie-like χ of defects caused presumably by the orientational disorder obscures the intrinsic behavior. However, the concave temperature dependence around the maximum, as that in the DI salt, makes a remarkable contrast to the convex one of the DMe salt. It is likely to consider the same phenomenology is operative in these salts; These features can be qualitatively understood by assuming that T^* in the MeI and BrI salts are about twice as large as that of the DI salt. The origin of the subtle difference between the MeI and BrI salts remains an open question.

Our results indicate that it is possible to control the pπ-d interactions as measured by T^* by chemical modification of $(DCNQI)_2Cu$ systems. We expect the appearance of Kondo-like behavior or magnetic order of the itinerant electrons by lowering T^*.

CONCLUDING REMARKS

Various types of magnetism resulting from the pπ-d interactions have been observed in $(DCNQI)_2Cu$ systems: the antiferromagnetism and weak ferromagnetism of the local spins, the abrupt change from the localization of the d spins to the entire hybridization of the pπ and d electrons, and the exchange enhanced paramagnetism of itinerant electrons in a narrow d band. From these, further insight into the physical roles of pπ-d interactions would be obtained. It is also desired to improve the way of chemical control of the pπ-d interactions.

ACKNOWLEDGMENT

We are indebted to Professor Kazuo Ueda, Professor Tsuneaki Goto and Dr. Masashi Hasegawa for helpful comments. This work is partly supported by Grants-in-Aid for Scientific Research, No. 05640648 and Priority Area "Molecular Magnetism" (Area No. 228/04242103), from the Ministry of Education, Science and Culture. Support from the New Energy and Industrial Technology Development Organization (NEDO) is also acknowledged.

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