The Organic $\pi$-Electron Metal System Interacting with Mixed-Valence Copper Ions ($R_1$,$R_2$-DCNQI)$_2$Cu
(DCNQI = N,N'-dicyanoquinonediimine; $R_1$, $R_2$ = CH$_3$, CH$_3$O, Cl, Br)

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Abstract. A solid-state chemistry of highly conducting anion-radical salts ($R_1$, $R_2$-DCNQI)$_2$Cu is described based on the systematic crystal structure analyses and the tight-binding band calculations. The essence of this system is the mixed valency of Cu which brings about the mixing of the organic $p_H$ orbitals and metallic $d$ orbitals.

1. Introduction

Since the discovery of (DMe-DCNQI)$_2$Cu (DMe-DCNQI = 2,5-dimethyl-N,N'-dicyanoquinonediimine) by Axmüller et al. in 1986 [1], increasing attention has been devoted to a new class of molecular materials, ($R_1$,$R_2$-DCNQI)$_2$Cu. This paper will give an outline of this exotic molecular system according to our "multi-Fermi surface" model.

2. Preparation and Structure

The copper salts of DCNQI can be prepared by various methods. In our study, the single crystals were obtained electrochemically using [Cu(CH$_3$CN)$_4$]ClO$_4$ as the supporting electrolyte and acetonitrile as solvent. The large crystals were prepared by the diffusion method using the chemical reaction with CuI in acetonitrile. The single crystals were grown under nitrogen, and studied in the air. All these crystals prepared from two different routes gave the same physical properties. All these copper salts are isomorphous [2]. The planar DCNQI molecules are uniformly stacked and form a one-dimensional column. The most important feature of this system is that the Cu cation is coordinated to the nitrogen atoms of the DCNQI molecule in a $D_{2d}$ distorted tetrahedral fashion.

3. Temperature Dependence of Resistivity (at Ambient Pressure)

Temperature dependence of the electrical conductivity at ambient pressure classifies these Cu salts into two groups (Table 1). The group I compounds are metallic down to about 0.5 K. The group II compounds show a sharp metal-insulator (M-I) transition at rather high temperatures. Although all these salts have the same structure, they are quite different in their electrical behavior.
Table 1. Metal-insulator transition temperature \( T_{M-I} \) of \( (R_1, R_2 - DCNQI)_2 Cu \)

<table>
<thead>
<tr>
<th>DCNQI</th>
<th>( R_1 )</th>
<th>( R_2 )</th>
<th>( T_{M-I}/K )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Group I</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DMe-DCNQI</td>
<td>( \text{CH}_3 )</td>
<td>( \text{CH}_3 )</td>
<td>metal</td>
</tr>
<tr>
<td>DMeO-DCNQI</td>
<td>( \text{CH}_3\text{O} )</td>
<td>( \text{CH}_3\text{O} )</td>
<td>metal</td>
</tr>
<tr>
<td>MeI-DCNQI</td>
<td>( \text{CH}_3 )</td>
<td>I</td>
<td>metal [3]</td>
</tr>
<tr>
<td>Group II</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MeBr-DCNQI</td>
<td>( \text{CH}_3 )</td>
<td>Br</td>
<td>152</td>
</tr>
<tr>
<td>DBr-DCNQI</td>
<td>Br</td>
<td>Br</td>
<td>161</td>
</tr>
<tr>
<td>MeCl-DCNQI</td>
<td>( \text{CH}_3 )</td>
<td>Cl</td>
<td>210</td>
</tr>
<tr>
<td>BrCl-DCNQI</td>
<td>Br</td>
<td>Cl</td>
<td>213</td>
</tr>
<tr>
<td>DCl-DCNQI</td>
<td>Cl</td>
<td>Cl</td>
<td>230</td>
</tr>
</tbody>
</table>

4. Nature of the M-I Transition of the Group II

This M-I transition is a cooperative structural phase transition induced by the CDW formation on the DCNQI column and the intensive distortion of the coordination tetrahedron around Cu [2]. At the transition temperature \( T_{M-I} \), the satellite reflections indicating the superstructure wavevector \( (0,0,c/3) \) develop discontinuously. These spots come from the CDW on the DCNQI column and the superstructure wavevector indicates that the formal charge of Cu is +4/3, in other words, the mixed valence state of Cu. The XPS measurements also indicated the mixed valency of Cu, and suggested that the formal charge of Cu in the group I is also +4/3 [4]. This transition is not a simple CDW transition of the one-dimensional system because there is no one-dimensional precursor diffuse scattering, and this transition is accompanied by an abrupt distortion of the coordination tetrahedron of Cu.

The static magnetic susceptibility jumps at \( T_{M-I} \), indicating that the localized magnetic moment appears on the Cu\(^{2+}\) cation when the conduction electrons on the DCNQI column disappear. The g-value of ESR signal and the Curie-Weiss behavior of its intensity below the transition temperature indicate an antiferromagnetic ordering of the spins on Cu\(^{2+}\) [5].

5. Mechanism of the M-I Transition

We have proposed a mechanism of this transition, based on the extended Hückel MO calculation and tight-binding band calculation [2]. The essential point is that the mixed valence state of Cu brings about the mixing of the organic \( p_\pi \) orbitals and d orbitals and stabilizes the metallic state. At first we consider the system with no \( p_\pi-d \) mixing. The DCNQI column forms a one-dimensional metallic band. Since the Cu cation is coordinated in \( D_{2d} \) distorted tetrahedral fashion, the highest d orbital is \( d_{xy} \) (Fig. 1). The energy splitting \( (\Delta E) \) depends on the degree of the distortion and has an important effect on the electronic structure. When there is no \( p_\pi-d \) mixing, the band structure consists of a one-dimensional \( p_\pi \) band and d bands with constant energy level. It should be noted that the one-dimensional \( p_\pi \) band is four-fold degenerate because the unit cell contains four columns and the mixed valency of Cu locates the highest d level near the Fermi level of the organic one-dimensional band. The introduction of the \( p_\pi-d \) mixing removes the degeneracy of the \( p_\pi \) bands and generates a multiple Fermi surface (Fig. 2a). The DCNQI bands give three pairs of waving planes. The closed Fermi surface represented by a dotted line in Fig. 2 arises mainly from
the narrow d bands. The electrons in the narrow d bands will tend to localize. The characteristic feature is that there is no single modulation wave vector which can nest all the Fermi surface. In the simple electronic structure examination of the dmit (dmit = 4,5-dimercapto-1,3-dithirole-2-thione) compounds, we have noticed that all the superconducting salts have such a multiple Fermi surface [6]. We propose that such a multiple Fermi surface will be related to the stable metallic state and the distortion of the coordination tetrahedron makes the Fermi surface simpler and brings about the one-dimensional instability. The distortion will stabilize the lower d orbitals and the total energy of Cu cation will be lowered, like the case of the Jahn-Teller distortion. When the lower d level is located far below the Fermi level, the planes I and II are merged into one and there appears a single nesting vector (Fig. 2b). This feature well explains the CDW formation coupled with the intensive distortion of the coordination tetrahedron at T_{M-I}.

6. Nature of the Group I

In the light of our model, the group I is considered to be a system with smaller \( \Delta E \) value. The multiple Fermi surface in the group I remains down to lower temperature. The transition temperature \( T_{M-I} \) and the energy splitting \( \Delta E \) calculated from the crystal structure data show an excellent correlation [2]. Application of pressure will cause the distortion of the coordination tetrahedron and the group I will turn to the group II at higher pressure. This is a possible mechanism of the pressure-induced M-I transition of the group I compounds. On the way from the group I to the group II, the system shows a very interesting behavior. Tomic et al. first reported a reentrant behavior in the temperature dependence of the resistivity of (DMe-DCNQI)\(_2\)Cu under pressure [7]. We have found the same behavior in another group I compound, (DMeO-DCNQI)\(_2\)Cu (Fig. 3) [8]. Such a reentrant behavior is also observed when the group I compound is alloyed with small amounts of the group II compound. For example, in the alloy \[(\text{DMe-DCNQI})_1-x(\text{MeBr-DCNQI})_x\]\(_2\)Cu (\( x < 0.1 \)), reentrant behavior is observed (Fig. 4) [9]. Temperature-dependence of the resistivity suggests an interaction of the conduction electrons and the magnetic ions (Cu\(^{2+}\)). In the case of (DMeO-DCNQI)\(_2\)Cu under pressure, between \( T_{\text{min}} \) and \( T_{\text{max}} \), the resistivity \( \rho \) linearly depends on \( \log T \), indicating the
scattering of the conduction electrons by the magnetic ions (Fig. 3). The lower-temperature resistivity shows a power law \( \rho = \rho_0 + AT^n \) (\( n = 2.4 \)) similar to that of the dense-Kondo material. Of course, the situation is not so simple because the electron-lattice coupling, which is important in the M-I transition of the group II, will also play an important role. But it should be noted that the M-I transition of the group II is coupled with the appearance of the magnetic moment. Therefore, it is quite natural that the "partial insulating" state in the reentrant region is accompanied by the "partial appearance" of the magnetic moment. In order to understand the reentrant behavior, there remain the following questions; (1) Is the CDW formed or not? (2) Are the electrons heavy or not? (3) Does the oxidation state of Cu change or not? Anyway, we feel that the existence of the Cu\(^{2+}\) cation will play a central role in the transport properties at the reentrant region.

7. Conclusion

The Cu-DCNQI salts contain fertile solid state chemistry and physics. They come from the mixing of the organic \( p_\pi \) orbitals and the metallic \( d \) orbitals. In this sense, this system is a new material situated between the organic system and the coordination system. Further study will open the way for new molecular materials.

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References