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Unified view on conductivity and specific heat in DCNQI–Cu systems

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Abstract. We point out the possibility that the coupling between d hole and Jahn–Teller distortion plays an important role for the large T-linear specific heat (γ) of DCNQI–Cu; the Coulomb repulsion between d holes (U) is not important for the enhancement of γ. On the contrary, U is the origin of the large T^2 term of the electrical resistivity (A). Yet, γ and A have a correlation ($A \propto \gamma^2$). We present a picture in which all these facts can be explained without any contradiction. On the basis of the picture we can understand naturally the essential properties of DCNQI–Cu in the metallic phase, including the anomalous behaviour near the metal–insulator transition, although there remain many details to be confirmed with the developing experiments.

1. Introduction

Some of the DCNQI–Cu systems show a metal–insulator–metal transition with increasing temperature [1]; the remarkable point is that a metallic state appears again above the insulating state. In our previous paper, we showed that the re-entrant transition in DCNQI–Cu systems can be understood by the Clausius–Clapeyron equation [2]. The free energy of the higher metallic state is lower than the insulating state, because the entropy of the metallic state is higher than that of the insulating state. The high entropy originates from the large T-linear specific heat. The T-linear terms of entropy in the higher metallic state overcome the entropy due to localized spins in the insulating state. Owing to the large T-linear term, the entropy in the metallic state decreases rapidly with decreasing temperature.

Thus, in the lower metallic state the T-linear term of entropy is smaller than that in the insulating state. If the antiferromagnetic ordering is realized, this state has lower entropy than the lower metallic state and remains as the ground state. The entropy change in the phase diagram can be confirmed by the sign of dP/dT along the phase boundary. Another example in which the T-linear term of the specific heat plays an essential role in phase transition is the antiferromagnetic and ferromagnetic transition of $Ce(Fe_{1-x}Co_x)_2$ with increasing temperature [3]. In this case the T-linear term of the specific heat in the ferromagnetic state is larger than that in the antiferromagnetic state. Therefore, the ferromagnetic state appears at high temperatures.

Thus, it is expected that the metal–insulator (M–I) transition is not due to the conduction electrons but mainly due to the d holes. Actually, in [1], the sharp M–I transition is considered to be triggered mainly by the charge ordering at the Cu sites, which is followed by the gradual development of the CDW on DCNQI stacks [1]. This point will be discussed in detail later.

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The origin of heavy d hole mass is an important problem and has been discussed by several authors [4]–[7]. In this paper we discuss the origin of the large coefficient of the T-linear specific heat. There are two possible mechanisms. One is the electron correlation effect between d holes. In our system, however, the number of d holes, n_h, is $\frac{1}{3}$ of Cu sites, namely $\frac{1}{6}$ filling. The occupation number is small and far from the Mott transition which occurs at half filling $n_h = 1$. Although the large enhancement cannot be expected, the electron correlation might enhance the electron mass depending on the bare electron mass [8, 9]. We discuss this point in detail by using scaling theory and show that the mass enhancement due to correlation is negligible.

Another mechanism is due to the Jahn–Teller effect of the Cu^{2+} ion. As the motion of d holes becomes slower, the Jahn–Teller distortion surrounding the d holes follows more completely the d hole motion. The composite particles composed of d holes and the lattice distortion become heavy. At least near the boundary of the metal–insulator (M–I) transition, this mechanism makes the hole mass heavy, since the kinetic energy is nearly equal to that of the lattice distortion at low temperatures [2]. In the following we discuss mainly this mechanism and try to explain by this mechanism the behaviour of the physical quantities, such as the specific heat and the electrical resistivity near the M–I transition.

Now we describe the details of the system surrounding the d holes. In the ideal T_d crystal field, the high-lying d orbitals are d_{xy}, d_{yz} and d_{zx} (T_{2g}) orbitals. The D_{2d} distortion of the coordination tetrahedron lifts the degeneracy among T_{2g} orbitals, leaving the higher d_{xy} level and the lower doubly degenerate d_{yz} (d_{zx}) level [1]. The D_{2d} distortion is the Jahn–Teller effect. Our Hamiltonian is written in the hole picture as

$$\mathcal{H} = \mathcal{H}_d + \mathcal{H}_p + \mathcal{H}_\ell + \mathcal{H}_{pd} + \mathcal{H}' \tag{1.1}$$

$$\mathcal{H}_d = \sum_{n,\sigma} E_d d^+_{n\sigma} d_{n\sigma} + \sum_n U n_{n\uparrow} n_{n\downarrow} \tag{1.2}$$

$$\mathcal{H}_{pd} = \sum_{\ell,k,\sigma,n} \frac{1}{\sqrt{N}} (V_{pd} c^+_{\ell k\sigma} d_{n\sigma} e^{ik\cdot n} + V_{dp} d^+_{n\sigma} c_{\ell k\sigma} e^{-ik\cdot n}). \tag{1.3}$$

Here, U is the Coulomb repulsion between d holes on the same atomic site. E_d is the energy of a d hole; V_{pd} is the matrix element of hybridization between a d hole and a pπ hole. Hamiltonian $\mathcal{H}_\ell$ is that of phonons surrounding Cu ions.

$$\mathcal{H}_\ell = \sum_\lambda \omega_\lambda b^+_\lambda b_\lambda \qquad (\lambda = q, \alpha) \tag{1.4}$$

where λ denotes the wave-vector q and polarization α.

The interaction Hamiltonian $\mathcal{H}'$, which gives rise to the Jahn–Teller distortion, is given by

$$\mathcal{H}' = \frac{1}{\sqrt{N}} \sum_{\substack{n,\sigma \\ \lambda}} \omega_\lambda X^n_\lambda d^+_{n\sigma} d_{n\sigma} (b_\lambda + b^+_{-\lambda}) \tag{1.5}$$

where $\omega_\lambda X_\lambda$ is the coupling constant between a d hole and phonons. There exist two pπ bands along the c axis in the unit cell. The Hamiltonian of pπ holes in the two bands is given by

$$\mathcal{H}_p = \sum_{\ell=1,2} \sum_{k,\sigma} \varepsilon_k c^+_{\ell k\sigma} c_{\ell k\sigma}. \tag{1.6}$$

If we neglect the Coulomb interaction on DCNQI molecules, we have a non-bonding pπ band along the c axis which is free from electron scattering at Cu sites and possesses long life-time. In this case we cannot understand the reason why the coefficient of T^2 term of the resistivity along the c axis is proportional to γ^2 [1]. Therefore, it is necessary to include the Coulomb interaction between pπ holes. This point is important and will be discussed later. In this paper we neglect the coupling between pπ holes and phonons, which is necessary to describe the insulating state, but is unimportant to describe the metallic state.

This paper discusses the following points. In section 2, it is shown that the mass enhancement due to the electron correlation is negligible. In section 3, the Jahn–Teller effect is discussed in detail, related to the mass enhancement near the M–I transition. The resistivity and its anisotropy are discussed in section 4, which makes clear the picture of our system.

2. Absence of mass enhancement due to the electron correlation

In this section we discuss the possibility of mass enhancement due to the electron correlation in the DCNQI–Cu system. Here, it should be noted that the number of d holes per Cu site is $\frac{1}{3}$. We employ two procedures to discuss the mass enhancement. One is the scaling theory of Haldane [10]. The $\frac{1}{6}$ filling without electron correlation U is described in a picture of a single impurity as

$$\frac{1}{6} = \frac{1}{\pi}\left(\frac{\pi}{2} + \tan^{-1}\frac{\mu - E_d}{\Delta}\right) \tag{2.1}$$

where Δ and μ are the width of the d level and the chemical potential, respectively. This equation gives

$$E_d - \mu = \Delta \tan(\pi/3) = \sqrt{3}\Delta. \tag{2.2}$$

In this paper we put $\mu = 0$. Now, we consider the strong correlation between d holes on the basis of Haldane's scaling law. When $U = \infty$, the energy gain due to the mixing with conduction electrons is important. The energy gain of the state unoccupied with a d hole is given by

$$E_0 = -\sum_{\substack{k\sigma \\ \varepsilon_k < \mu}} \frac{|V_k|^2}{E_1 - E_0 - \varepsilon_k} = -\frac{2\Delta}{\pi}\log\frac{D}{\Delta} \tag{2.3}$$

where D is the band width of the conduction bands. Here, conduction electrons with both spins can be mixed. On the other hand, that of the state occupied with a d hole is given by

$$E_1 = E_d - \sum_{\substack{k \\ \varepsilon_k > \mu}} \frac{|V_k|^2}{\varepsilon_k + E_0 - E_1} \simeq E_d - \frac{\Delta}{\pi}\log\frac{D}{\Delta}. \tag{2.4}$$

Here, only the conduction electrons with the same spin as the d hole can be mixed with the d hole. From (2.3 and 2.4), we obtain

$$E_d^* = E_1 - E_0 = E_d + \frac{\Delta}{\pi}\log\frac{D}{\Delta}. \tag{2.5}$$

Here, when U is smaller than D, D is replaced by U. The scaled d level E_d^* is higher than E_d ($U = 0$) by $(\Delta/\pi)\log(D/\Delta)$; the d level shifts to a higher level from $E_d = \sqrt{3}\Delta > \mu$ and the system stays always in the regime possessing a small number of d holes.

According to Haldane, the criterion for the mixed valence regime is not $|E_d| \leqslant \Delta$ but $|E_d^*| \leqslant \Delta$. In the mixed valence regime, with decreasing D and/or U, E_d in (2.5) tends to E_d^* at the limit $D = U = \Delta$. Therefore, at this scaling limit we can consider our system as a non-interacting system with the renormalized d hole level E_d^*. Thus, by replacing E_d in (2.1) with E_d^*, we obtain $E_d^* = \sqrt{3}\Delta$, which means that our system belongs to the boundary between the mixed valence ($|E_d^*| \leqslant \Delta$) and low-density ($E_d^* \gg \Delta$) regimes. In the DCNQI–Cu system, D/Δ is not so large and takes a value around five. Even for $U = \infty$, the bare d hole level E_d is still situated above the Fermi level. Thus, we can scale down U to a small value Δ, shifting E_d to $E_d^* = \sqrt{3}\Delta = E_d + (\Delta/\pi)\log(U/\Delta)$, ($U \leqslant D_0$). The density of states for d holes in the scaled system is given by $\rho_d(0) = 1/(4\pi\Delta)$. Therefore, in this case d hole mass cannot be enhanced. This result can be understood also by replacing E_d in (2.1) with $E_d + \Sigma(\mu)$, where $\Sigma(\mu)$ is the self-energy part due to correlation U. From this equation representing the Friedel sum rule, we obtain $E_d + \Sigma(\mu) - \mu = \sqrt{3}\Delta$, which means the effective level for the d hole is too high above the Fermi energy to be affected by electron correlation.

This result can be derived also by using Ohkawa's single-site equation [11]. According to Ohkawa, if $U \gg E_d > \Delta$, the binding energy E_B is given by

$$E_B \simeq E_d + (n_\ell - 1)\frac{\Delta}{\pi}\log(D/\Delta) \tag{2.6}$$

which is the difference of energy between the singlet ground state and a mutiplet state. Here, n_ℓ is the degeneracy of d orbitals and $n_\ell = 3$ when d orbitals d_{xy}, d_{yz} and d_{zx} are nearly degenerate. The binding energy E_B can be written also by the number of d holes n_d as

$$E_B = n_\ell\frac{\Delta}{\pi}\left(\frac{1}{n_d} - 1\right). \tag{2.7}$$

Putting $n_d = \frac{1}{3}$, we obtain $E_B = 2n_\ell\Delta/\pi$. The binding energy is of the order of Δ, which is the band width of bare d hole bands. Thus, we conclude that the specific heat given by the T-linear term is not enhanced by the electron correlation, since the filling ($\frac{1}{6}$) is too small to make a correlated electron system even if U is large. In this section, we have adopted a picture of a single site and used the scaling theory. As far as the effect of electron correlation is concerned, our discussion is reliable and much better in low-density cases. Recently, the de Haas–van Alphen effect was observed in the metallic state of (DMe-DCNQI)$_2$Cu material [12]. From this experiment, the enhancement factors of electron mass are estimated to be from three to 10. These electron masses are equal to the band masses calculated by Kato. *The T-linear term of the specific heat with $\gamma = 20$ mJ mol^{-1} K^{-2} as observed is in good* agreement with the density of states given by the band calculation. Thus, the above results show the absence of the mass enhancement due to the electron correlation. The large γ value originates from the bare band mass of three-dimensional flat d bands.

3. Jahn–Teller effect

Now, we consider in detail the Jahn–Teller effect around Cu^{2+} ions. For simplicity we consider only the d_{xy} orbital wave function. It is shown that the main structure of the

Fermi surface can be obtained without taking d_{yz} and d_{zx} orbitals into account by Uji *et al* [12]. The d holes undergo three-dimensional motion through the hybridization with DCNQI molecules. When a d hole occupies a d_{xy} orbital at a Cu site with a tetragonal symmetry, the lattice surrounding the d hole distorts to lower energy by the Jahn–Teller effect. The coupling between the Jahn–Teller distortion and d holes is given by (1.5). In this paper the Jahn–Teller effect means the deviation of DCNQI molecules from the average angle of the N–Cu–N bond in tetragonal symmetry. Now we discuss the effect of the lattice distortion on the hybridization V_{pd} between d holes and pπ bands. The matrix element of hybridization is given by

$$V_{dp} = \langle \psi_d(r)|V(r)|\psi_p(r-a)\rangle \tag{3.1}$$

where $\psi_d(r)$ and $\psi_p(r-a)$ are the wave functions of d electrons and p electrons separated by a, respectively. $V(r)$ is the one-body potential for electrons. Near the M–I transition, the lattice distortion due to the Jahn–Teller effect is important. When the d hole transfers from Cu site n to a pπ orbital at a neighbouring DCNQI molecule, the Jahn–Teller distortion around the d hole disappears. When a pπ hole transfers to a d_{xy} orbital at the neighbouring Cu site m, a lattice distortion is created by the Jahn–Teller effect. In this process, the effective matrix element of hybridization $\widetilde{V}_{dp}$ is reduced by the overlap integral of the lattice distortion,

$$\widetilde{V}_{dpn} = V_{dp}\langle \Psi_d(R_n)|\Psi_d^0(R_n)\rangle \tag{3.2}$$

where Ψ_d and Ψ_d^0 represent the wave functions of the lattice with and without lattice distortion around d hole, respectively.

Now we perform the canonical transformation to eliminate the d hole–phonon coupling term (1.5). For an operator $\hat{q}$, the transformed operator $\widehat{Q}$ is given by [13, 14]

$$\widehat{Q} = U^+\hat{q}U \tag{3.3}$$

$$U = \exp\left[\frac{1}{\sqrt{N}}\sum_{\substack{n,\lambda\\ \sigma}} X_\lambda^n d_{n\sigma}^+ d_{n\sigma}(b_\lambda^+ - b_{-\lambda})\right]. \tag{3.4}$$

By this transformation, our Hamiltonian is rewritten as

$$\mathcal{H} = \sum_{n,\sigma} E_n A_{n\sigma}^+ A_{n\sigma} + \frac{1}{\sqrt{N}}\sum_{\ell,k,\sigma,n}(V_{dp}A_{n\sigma}^+ c_{\ell k\sigma}\,e^{-ik\cdot n}\theta_n^+ + V_{pd}c_{\ell k\sigma}^+ A_{n\sigma}\,e^{ik\cdot n}\theta_n)$$
$$+ \sum_{\ell=1,2}\sum_{k,\sigma}\varepsilon_{kz}c_{\ell k\sigma}^+ c_{\ell k\sigma} + \sum_\lambda \omega_\lambda B_\lambda^+ B_\lambda + \sum_n U A_{n\uparrow}^+ A_{n\uparrow}A_{n\downarrow}^+ A_{n\downarrow}. \tag{3.5}$$

Here, operator $A_{n\sigma}$ represents the d hole accompanying the lattice distortion due to the Jahn–Teller effect. The energy of the d hole, E_n is lowered by the further Jahn–Teller distortion and is written as

$$E_n = E_d - \frac{1}{N}\sum_\lambda \omega_\lambda |X_\lambda^n|^2. \tag{3.6}$$

In this form, the composite particle composed of d hole and Jahn–Teller distortion transfers from site to site by the reduced transfer matrix element $t_{nm}\langle\theta_n^+\theta_m\rangle$. Here, operator θ_n is given by

$$\theta_n = \exp\left[-\frac{1}{\sqrt{N}}\sum_\lambda X_\lambda^n(B_\lambda^+ - B_{-\lambda})\right] \tag{3.7}$$

where

$$B_\lambda = U^+ b_\lambda U. \tag{3.8}$$

This result can be explained as follows. The overlap integral between $\Psi_d(R_n)$ accompanying lattice distortion and $\Psi_d^0(R_n)$ without lattice distortion is written as

$$\langle \Psi_d(R_n) | \Psi_d^0(R_n) \rangle = \langle \theta_n \rangle. \tag{3.9}$$

The d holes transfer from Cu site n to Cu site m through the hybridization with DCNQI molecules. The effective transfer integral is given by the effective hybridization in (3.2) as

$$\tilde{t}_{nm} = \tilde{V}_{dpn} \frac{1}{E_d - \mu} \tilde{V}_{pdm} = V_{dp} \frac{1}{E_d - \mu} V_{pd} \langle \theta_n \theta_m \rangle = t_{nm} \langle \theta_n \theta_m \rangle \tag{3.10}$$

where the site correlation of lattice distortions is included and

$$t = V_{dp} \frac{1}{E_d - \mu} V_{pd}. \tag{3.11}$$

The thermal average $\langle \theta_n^* \theta_m \rangle$ is given by

$$\langle \theta_n^+ \theta_m \rangle = \exp[-S(T)] \tag{3.12}$$

$$S(T) = \frac{1}{N} \sum_\lambda |X_\lambda^n X_\lambda^{*m}| (2n_\lambda + 1) \tag{3.13}$$

where n_λ is the number of phonons. At low temperatures the average value of $\theta_n^+ \theta_m$ means the overlap integral between the two lattice distortions situated at site n and m respectively.

Now we assume that the whole enhancement of d hole mass originates from the overlap integral between Jahn–Teller distortions. In this case, the enhancement factor of the T-linear specific heat, $\tilde{\gamma}$, is given by

$$\tilde{\gamma} = \gamma / \gamma_0 = \exp[S(T = 0)] \tag{3.14}$$

where γ and γ_0 are the coefficients of the T-linear specific heat in the real and bare electron systems, respectively. By this assumption, the coupling S between d hole and Jahn–Teller distortion can be estimated as

$$S(T = 0) = S_0 = \log \tilde{\gamma}. \tag{3.15}$$

We show in figure 1 the experimental values of γ obtained for $[(\text{DMe-DCNQI-h8})_{1-x}(\text{DMe-DCNQI-d8})_x]_2\text{Cu}$ by Kato [15], and in addition to this, give the value of S_0 obtained by (3.15) under the assumption that γ_0 is equal to 1 mJ mol^{-1} K^{-2}. For the case of positive muons in the copper metal, $S = 5$ gives a good fit for the hopping rate of muons [16]. However, in our case only the difference of S, $\Delta S = S(x) - S(x = 0)$, has meaning, since we do not know the bare d hole mass. Fortunately, [12] gives $\gamma_0 = 20$ for the case $x = 0$ as the bare hole mass. Therefore, we can obtain ΔS as the mass enhancement due to the Jahn–Teller effect. From this result, we can see that the d hole-phonon coupling becomes strong on approaching the metal–insulator transition point. The obtained value of ΔS is rather small corresponding to the increase of a few degrees in N–Cu–N bond angle. Now we consider the role of the Jahn–Teller effect in our system. By the effect, the bond angle

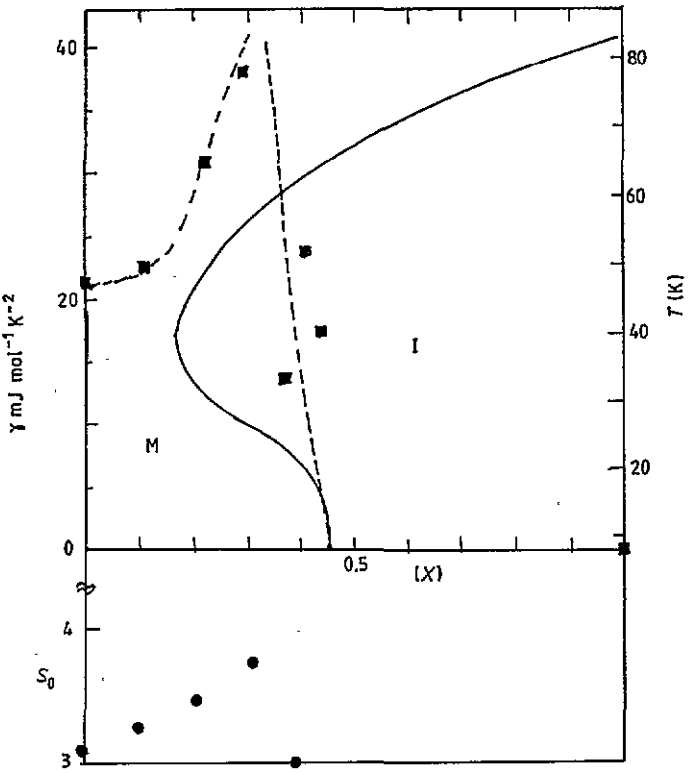

Figure 1. Phase diagram of $[(\text{DMe-DCNQI-h8})_{1-x}(\text{DMe-DCNQI-d8})_x]_2\text{Cu}$. The coefficient of the T-linear term of the specific heat γ and S_0 are shown. γ can take the value 80 mJ K^{-2} mol^{-1} at the phase boundary. (This figure is borrowed from [15] to help understanding.)

of N–Cu–N increases and lattice spacing in the ab plane increases, while it decreases along the c axis. From these facts, the hybridization V_{dp} between d holes and pπ holes is reduced owing to the longer distance between them. This effect plays the same role as the overlap integral between lattice distortions and enhances the d hole mass. We include this effect in the change of ΔS. On the other hand, the band width of pπ holes increases owing to the shorter distance between DCNQI molecules. These effects are expected to enhance the anisotropy of the resistivity.

Here, it is noted that the overlap integral is always finite. Therefore, the mass enhancement due to the Jahn–Teller effect cannot lead to the metal–insulator transition without any help of other effects such as a cooperative Jahn–Teller effect.

4. Resistivity

In figure 2 we show the resistivity observed in the deuterated system of (DMe–DCNQI α, α': $3 - d^3)_2\text{Cu}$ [15]. This figure shows the T^2 dependence of the electrical resistivity in the upper metallic regions separated by an insulating phase, while the T^2 dependence is not clear in the lower metallic region. Since we believe that the metallic states in both regions are the same, we assume the following relations common to both metallic regions,

$$R = R_0 + AT^2 \tag{4.1}$$

$$A \propto \gamma^2 \tag{4.2}$$

where γ is almost independent of temperature. The anisotropy of the resistivity will be discussed later and we confine ourselves to that perpendicular to the c axis. Thus, we assume S is also temperature independent, $S(T) \simeq S(T=0) = S_0$. In this case we can explain the heavy-fermion behaviours in the DCNQI–Cu system as follows. The band width of d holes is reduced as

$$\tilde{t} = t_0 \, e^{-S_0}. \tag{4.3}$$

The coefficient of the T-linear specific heat is enhanced by

$$\gamma = \gamma_0 \, e^{S_0}. \tag{4.4}$$

The band energy of quasiparticles is reduced by the same factor as $\tilde{t}$ in (4.3), and the velocity of the d hole is reduced as

$$\tilde{v} = 2a\tilde{t} = v_0 \, e^{-S_0}. \tag{4.5}$$

Here $v_0 = 2at$ is the velocity of the bare d hole band, $2a$ being the distance between two neighboring Cu sites. As is seen, the renormalization factor of quasiparticles z_k in our case is given by e^{-S_0}.

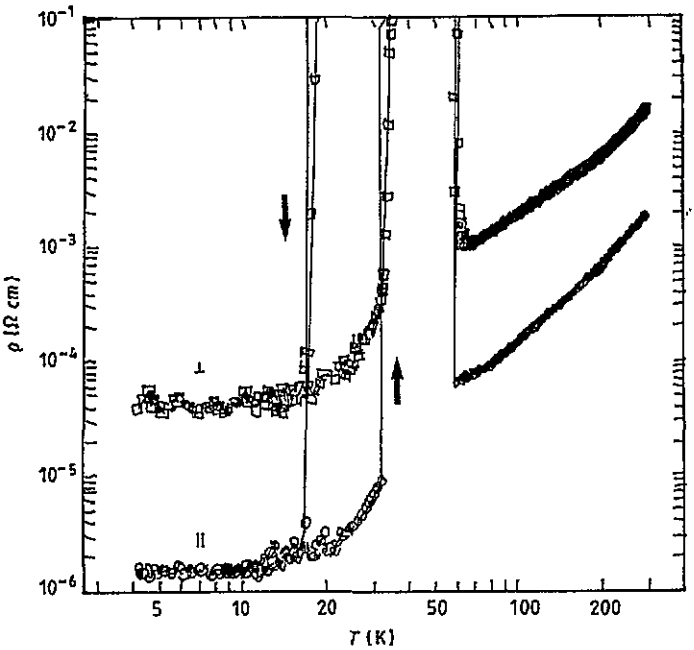

Figure 2. Resistivity in [DMe-DCNQI α, α', 3 – d3]$_2$Cu. (This figure is borrowed from [15] to help understanding.)

Now we consider the electrical conduction due to the d holes accompanying the Jahn–Teller distortion. The conductivity is given by [17]

$$\sigma_{\mu\mu} = e^2 \sum_{k,\sigma} \tilde{v}_{k\mu} \left(-\frac{\partial f(\varepsilon_k)}{\partial \varepsilon_k} \right) \frac{C}{2\Gamma_k^*} \tilde{v}_{k\mu} \tag{4.6}$$

where C and Γ_k^* are the numerical constant determined by the Umklapp scattering and the damping rate of the quasi-d hole. In this case the composite particles interact via the Coulomb repulsion between d holes. As is well known, all the renormalization factors cancel each other out in (4.6). That is, $\tilde{v}$ and Γ_k^* have the factor z_k and the summation over k gives the density of state enhanced by $1/z_k$ at the Fermi energy. Thus we obtain the conductivity perpendicular to the c axis

$$\sigma = e^2 \rho_d(0) v_0^2 \tau_k / \hbar \tag{4.7}$$

where $\rho_d(0)$ is the state density of d holes at the Fermi energy. The mean free time is given by

$$\begin{aligned} 1/\tau_k = \frac{2\pi}{\hbar} \frac{2}{3} (\pi k_B T)^2 \sum_{k',q} U^2 \delta(\mu - \tilde{\varepsilon}_{k-q}) \delta(\mu - \tilde{\varepsilon}_{k'}) \\ \times \delta(\mu - \tilde{\varepsilon}_{k'+q}) = \frac{4\pi}{3\hbar} (\pi k_B T)^2 U^2 \{\rho_d(0)\}^3 \frac{1}{z_k^2} \\ = \frac{4\pi}{3\hbar} (\pi k_B T)^2 U^2 \rho_d^3(0) \, e^{2S_0}. \end{aligned} \tag{4.8}$$

Here, we have the inverse square of the renormalization factor corresponding to two momentum summation over the renormalized band. Thus, we obtain the coefficient of the T^2 term of the resistivity in (4.1) as

$$A = \left\{ \frac{4\pi^3}{3\hbar} U^2 \rho_d^2(0) \Big/ (e v_0)^2 \right\} e^{2S_0} \propto \gamma^2. \tag{4.9}$$

It should be noted that the relation $A \propto \gamma^2$ holds independently of the mechanism of renormalization [18]. This relation holds also in the case where the electrical conduction is given mainly by the conduction electrons, such as pπ electrons along the linear chains, as shown below.

Now we discuss also the resistivity along the c axis. The T^2 dependence is not clear at low temperatures in figure 2. Usually, the resistivity is measured along the c axis, since the c axis is easy axis for the electrical conduction. The relation $A \propto \gamma^2$ is observed in several DCNQI–Cu systems [1]. Here, we assume this relation holds always, although it needs to be confirmed. By the experiment of the de Haas–van Alphen effect it is confirmed that d holes undergo three-dimensional band motion and pπ bands along the c axis hybridize with d bands. In this case the scattering of conduction electrons arises from the following three mechanisms. One of mechanisms is a mutual interaction among pπ holes. If this scattering process is dominant, we cannot understand why coefficient A parallel to the c axis also is proportional to γ^2, which is determined mainly by d holes. Therefore, other mechanisms of scattering should dominate over the pπ scattering. The second one is the scattering of pπ holes on the d holes via the interaction between d holes and pπ holes. In this case the scattering probability is given by (4.8) with one of $\rho_d(0)$ replaced by $\rho_c(0)$

[19]. However, the Coulomb interaction between d and pπ holes seems to be weak because of the long distance between them. It is most probable that the lifetime of conduction electrons is determined by that of d holes through the mixing terms between d holes and pπ holes and via the Coulomb interaction between pπ holes. Here, we stress a role of the Coulomb repulsion between pπ holes. When we consider only the d_{xy} orbital, we obtain one non-bonding orbital. However, if we take the Coulomb interaction between pπ holes into account, the non-bonding band possesses the lifetime due to that of d holes through the Coulomb interaction between pπ holes, one of which is mixed with d orbitals. The Coulomb interaction between pπ holes cannot be neglected, since it works in the same DCNQI molecules. Thus, we stress that the so called non-bonding orbitals are also affected by the Coulomb interaction at Cu sites. The third picture is the most plausible and consistent with the three-dimensional d hole band picture. The d bands give the main contribution of the T-linear specific heat [12].

The conductivity along the c axis $\sigma_\parallel$ is larger than that perpendicular to the c axis, $\sigma_\perp$. In the low-temperature side $\rho_\perp/\rho_\parallel \simeq 30$, while at high temperature $\rho_\perp/\rho_\parallel \simeq 20$. The decrease of anisotropy of resistivity can be explained as the phonon contribution to the scattering at high temperatures. The conductivity along the c axis is given by the conduction of pπ holes

$$\sigma_\parallel = e^2 \sum_{k,\sigma} \left\{ v_{kp}^{A} \left(-\frac{\partial f(\varepsilon_k)}{\partial \varepsilon_k} \right) \frac{C_\parallel^{A}}{2\Gamma_{kp}^{A*}} v_{kp}^{A} + v_{kp}^{B} \left(-\frac{\partial f(\varepsilon_k)}{\partial \varepsilon_k} \right) \frac{C_\parallel^{B}}{2\Gamma_{kp}^{B*}} v_{kp}^{B} \right\} \tag{4.10}$$

where A and B represent bonding and non-bonding orbitals, respectively. The main contribution is determined by the non-bonding part, since the velocity and mean free time of the pπ hole in non-bonding band are large compared with those in the bonding band. The conductivity perpendicular to the c axis is given by d holes

$$\sigma_\perp = e^2 \sum_{k,\sigma} v_{k\perp} \left(-\frac{\partial f(\varepsilon_k)}{\partial \varepsilon_k} \right) \frac{C_\perp}{2\Gamma_{kd}^{*}} v_{k\perp}. \tag{4.11}$$

The resistivity seems to show the T^2 dependence due to the electron–electron scattering in both directions of $c_\parallel$ and $c_\perp$. In our system d holes make three-dimensional heavy bands with d hole scattering between them. The pπ bands along the c axis possesses the damping effect through the hybridization with d holes. As given in (4.7), $\sigma_\perp$ is given with use of the damping rate of d hole, Γ_d by

$$\sigma_\perp = e^2 \rho_d(0) v_d^2 / \Gamma_d \tag{4.12}$$

where Γ_d is given by $\hbar/\tau_k$ in (4.8).

On the other hand, $\sigma_\parallel$ is given by the non-bonding part as

$$\sigma_\parallel = e^2 \rho_p(0) v_p^2 / \Gamma_p \tag{4.13}$$

where $\rho_p(0)$, v_p and Γ_p are the density of states, velocity and damping rate of pπ holes in the non-bonding band, respectively. The damping rate of pπ holes is given by

$$\Gamma_p = \alpha \left(\frac{|V_k|}{\mu - E_d} \right)^2 \Gamma_d. \tag{4.14}$$

The coefficient $\alpha|V_k|^2/(\mu - E_d)^2$ is of the order of unity. The ratio $\sigma_\parallel/\sigma_\perp$ is given by

$$\frac{\sigma_\parallel}{\sigma_\perp} = \frac{\rho_p(0)v_p^2\tau_p}{\rho_d(0)v_d^2\tau_d} = \frac{m_d}{m_p}\frac{\tau_p}{\tau_d} \tag{4.15}$$

where we have included only the contribution of non-bonding pπ bands and we have assumed simply

$$\frac{\rho_d}{\rho_p} = \frac{v_p}{v_d} = \frac{m_d}{m_p}. \tag{4.16}$$

If we assume $\sigma_\parallel/\sigma_\perp = 20$, we obtain from (4.13–4.15)

$$\frac{m_d}{m_p} = \frac{\rho_d}{\rho_p} = 20\alpha\frac{|V_k|^2}{(\mu - E_d)^2}. \tag{4.17}$$

Thus, ρ_d/ρ_p is a value around 10. From this result, we can conclude, the T-linear specific heat can be ascribed mainly to d holes.

$$\frac{\gamma_d}{\gamma_p} = \frac{\rho_d(0)}{2\rho_p(0)} \simeq 5 \tag{4.18}$$

where we have put $2\rho_p(0) = \rho_p^A + \rho_p^B$. Thus, we obtain a unified view on the conductivity in the DCNQI–Cu system, although it needs to be confirmed by the experiments.

5. Conclusion and discussion

We have proposed a unified view on DCNQI–Cu systems from our theoretical viewpoint, which need to be compared with recent experimental results. We have argued that the electron mass enhancement is due to the Jahn–Teller effect and not due to the electron correlation. The mass enhancement in the DCNQI–Cu system is remarkable near the metal–insulator transition points. Since the insulating state is always in the distorted state due to the Jahn–Teller effect, it is natural to ascribe the mass enhancement to the Jahn–Teller distortion. Leaving the phase boundary, the value of γ decreases to take a value corresponding to the band calculation.

In this paper, we have shown the electron correlation cannot give rise to the mass enhancement for the system with $\frac{1}{6}$ filling. On the other hand, in the insulating state, only one d hole occupies one of the three fold Cu sites. This magnetic insulating state means the existence of a strong on site correlation between two d holes. However, we cannot expect the mass enhancement due to the electron correlation because of the low density of d holes.

We have shown that while the d hole mass is not enhanced owing to the electron correlation, the resistivity is mainly due to the electron correlation, which dominates the electron–phonon scattering. We can explain both facts without any contradiction. As we have shown, γ is not enhanced owing to small d hole occupation even for a large value of U but it is large due to the flat d hole band. The coefficient A of the T^2 term of the resistivity is proportional to γ^2 and is large enough to dominate the resistivity due to the electron–phonon scattering. At this point we need a large value of γ, the origin of which need not necessarily be electron correlation. In our case large γ originates from the large bare mass and accompanying lattice distortion.

At high temperatures, $\rho_{\parallel}$ increases more rapidly than $\rho_{\perp}$ (figure 2). This is because the electron–phonon scattering begins to affect $\rho_{\parallel}$, while the electron–electron scattering is still dominant for $\rho_{\perp}$.

The picture adopted here is considered to be appropriate at least near the M–I transition. If d holes move more quickly than the lattice distortion, it cannot follow the motion of d holes. Therefore, the lattice distortion with frequency $\omega \geqslant \tilde{t}$ can follow but that with $\omega < \tilde{t}$ cannot. As a result, the mass of d holes increases rapidly near the M–I phase boundary, where the kinetic energy $\tilde{t}$ is close to the energy of lattice distortion at low temperatures [2]. In this case the paramagnetic susceptibility in the metallic state is given by the enhanced Pauli paramagnetism. Here, it is noted that the overlap integral between lattice distortions is always finite in contrast to the electron clouds. Therefore, the mass enhancement due to the Jahn–Teller effect cannot lead to the metal–insulator transition without any help of other effects. At this point, we need thermodynamical considerations and employ the Clausius–Clapeyron equation for the first-order transition. The equation shows clearly the role played by the entropy at finite temperature. At $T = 0$, we must compare the energy of the metallic state with that of the antiferromagnetic state. This is a future problem.

Recently, the magnetic susceptibility in (DMe-DCNQI–α, $\alpha' - d_2)_2$Cu has been measured carefully [20]. The experiment has shown that the Pauli susceptibility in the lower metallic state is the same as that of the higher metallic state. This result is natural because both the metallic states are same. However, in contrast to the specific heat, the susceptibility does not show any remarkable change on approaching the insulating state and seems not to be enhanced near the phase boundary. As we noted above, the transition is of the first order and the appearance of the fluctuation of lattice distortion is not necessary. At this point, it should be noted that the enhancement of the specific heat and the susceptibility observed before might be related to a metastable state approaching closely the insulating state. The metastable state is nearer than the stable metallic state to the insulating state.

As an example, we consider the experimental results on $(DMe_{1-x}MeBr_x\text{-DCNQI})_2Cu$ shown in [1]. The resistivity in figure 13 in [1] shows clearly a discontinuity between the two metallic states, below and above the insulating state. This result shows that the enhanced T^2 term of the resistivity is related to a metastable state inherent to the lower side. If the origin of heavy electrons is the mechanism proposed in this paper, the resistivity must be universal in both metallic regions.

The paper [1] shows the distribution of x, and the spatial randomness might be the origin of heavy electrons. If the randomness of the lattice distortion is a static and spatial one, the enhancement of the T^2 term of the resistivity cannot be understood. The static randomness appears as the residual resistivity. The metallic state below the insulating state shows an enhanced specific heat, susceptibility and T^2 term of the resistivity. These might be due to the dynamical effect of the Jahn–Teller distortion proposed here. In order to observe the effect we need a system with small $\tilde{t}$, which means small conductivity along the direction perpendicular to the c axis. In what situation the mass enhancement proposed here appears is a future problem to be compared in detail with experiments.

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