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Electron Spin Dynamics in $(DMe\text{-}DCNQI)_2M$ ($M = Li_{1-x}Cu_x$ ($x < 0.14$), Ag)

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The quarter-filled π band systems, $(DMe\text{-}DCNQI)_2M(M = Li_{1-x}Cu_x$ ($x \leq$ 0.14), Ag) were systematically studied with electron paramagnetic resonance (EPR). The intercolumn spin hopping rate $D_\perp$ in $Li_{1-x}Cu_x$-salt was obtained from the EPR linewidth. The temperature dependence of $D_\perp$ can be understood with the hole soliton model which also explains the DC conductivity. The $\pi - d$ mixing of the Cu-salt enhances both $D_\perp$ and $\sigma_\perp$ by 10^3 times more than the Li-salt, which is consistent with the fact that the only Cu-salt has three-dimensional Fermi surface, but that Ag-salt is one-dimensional in spite of the mixing enhancement of $D_\perp$ by 10 times more than the Li-salt.

$(DMe\text{-}DCNQI)_2M(M = Li_{1-x}Cu_x(x \leq 0.14)$, Ag) are known to be strongly electron–electron correlated one-dimensional system which forms the $4k_F$-CDW insulating state but show the relatively high DC conductivity of $\sigma = 10 \sim 200$ S/cm.[1–3] Up to now, we have suggested that the DC conductivity in Li- and Ag-salt is limited by the slower hopping motion of the electrons along intercolumn directions.[4,5] That is understood by the thermal excitation of the hole and the spin soliton pairs in the $4k_F$-CDW gap, which enables the intercolumn electron hopping irrespective of the loss of the on-site Coulomb energy U. Since the intercolumn hopping of electrons via metal ion might be accompanied with the electron spin relaxation by the spin-orbit coupling at the metal site, the EPR linewidth $\Delta H_{1/2}$ is proportional to $D_\perp$.[5] In the case of $Li_{1-x}Cu_x$-salt, the doping of Cu ion into the Li-salt causes $\pi - d$ hybridization between the columns, and, as a result, the electrical conductivity at RT increases from 15 S/cm at $x = 0$ to 200 S/cm at $x = 0.14$. The EPR linewidth could also be enhanced with the doping effect.

The EPR study was done with X-, Q- and W-band operated around 9, 35, and 94 GHz, respectively. The temperature dependence between 5 and 300 K with the angular dependence for c-axis versus magnetic field was examined.

The X-band EPR spectra at RT in $Li_{1-x}Cu_x$-salts is shown in Fig. 1, which indicates the broadening of $\Delta H_{1/2}$ with increasing the concentration of Cu ion. Figure 2 shows the temperature dependence of the angular averaged $\Delta H_{1/2}$ which is proportional to $D_\perp$. The angular dependence of the observed linewidth showed $\cos 2\theta$ periodicity with the amplitude of ~2G, which is less than 5% of the absolute linewidth at RT for Q- and W-band EPR. For a precise analysis, the angular dependence must be taken into account, but now we consider the oder of $D_{\perp,\mathrm{Li}_{0.94}\mathrm{Cu}_{0.06}}$. When the electron hops to the neighboring columns via metal ion with the probability $P_\perp$, the spin-orbit interaction of the metal ion governs the spin flip-flop transition rate, resulted in the linewidth broadening as shown in Fig. 1. Since $\Delta H_{1/2}$ is strongly affected by the 6% of Cu ion with a larger spin-orbit coupling constant than that of the Li ion, $\Delta H_{1/2}$ could be represented as

$$\Delta H_{1/2,\mathrm{Li}_{1-x}\mathrm{Cu}_x} \propto n_{\mathrm{hs}}\{(1-N_{\mathrm{Cu}})P_{\perp,\mathrm{Li}}\lambda_{\mathrm{Li}}^2 + N_{\mathrm{Cu}}P_{\perp,\mathrm{Cu}}\lambda_{\mathrm{Cu}}^2\} \sim n_{\mathrm{hs}}N_{\mathrm{Cu}}P_{\perp,\mathrm{Cu}}\lambda_{\mathrm{Cu}}^2, \tag{1}$$

where n_{hs} is the number of the hole solitons, $N_{\mathrm{Cu}} = 0.06$ is the Cu concentration, λ is the spin-orbit coupling constant. The observed linewidth

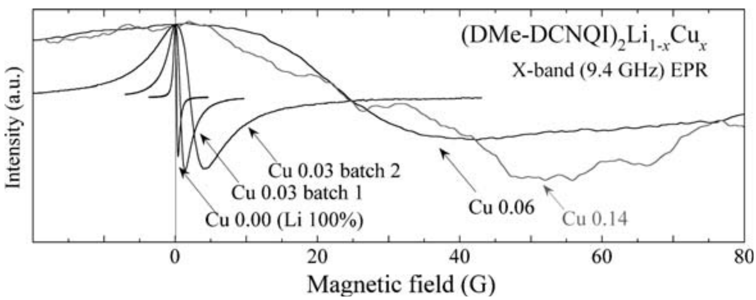

Fig. 1. Derivative EPR spectra taken at X-band in single crystals of (DMe-DCNQI)$_2$Li$_{1-x}$Cu$_x$ ($x \leq 0.14$). The abscissa is measured from the positive peak of the spectrum.

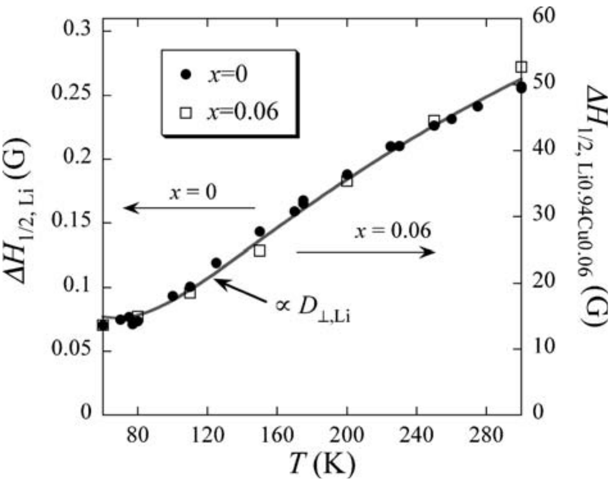

Fig. 2. The temperature dependence of EPR linewidth in Li$_{0.94}$Cu$_{0.06}$-salt (Right axis, open square) is proportional to the linewidth in Li-salt (Left axis, closed circle). The solid curve is proportional to $D_{\perp,\mathrm{Li}}$.

in Li$_{0.94}$Cu$_{0.06}$-salt is 200 times larger than the linewidth in the Li-salt that could be accounted for with the larger λ_{Cu} and $P_\perp$ due to the strong $\pi - d$ hybridization. $D_\perp$ in Li$_{0.94}$Cu$_{0.06}$-salt at RT can be roughly estimated. If we use $\lambda_{\mathrm{Ag}} \sim 2.6\lambda_{\mathrm{Cu}}$, $\Delta H_{1/2,\mathrm{Ag}} = 14$ (G), $\Delta H_{1/2,\mathrm{Li}_{0.94}\mathrm{Cu}_{0.06}} \sim 50$ (G), and $D_{\perp,\mathrm{Ag}} = 5 \times 10^{10}$ (rad/s),[5] we obtain

$$D_{\perp,\mathrm{Li}_{0.94}\mathrm{Cu}_{0.06}} = \frac{\lambda^2_{\mathrm{Ag}}}{\lambda^2_{\mathrm{Cu}}} \frac{\Delta H_{\perp,\mathrm{Li}_{0.94}\mathrm{Cu}_{0.06}}}{\Delta H_{\mathrm{Ag}}} D_{\perp,\mathrm{Ag}} \sim 20 D_{\perp,\mathrm{Ag}} = 10^{12} (\mathrm{rad/s}). \quad (2)$$

The reliability would be limited to the orders of magnitude because of the rough estimation. The intercolumn electrical conductivity is expressed as $\sigma_\perp \propto n_{\mathrm{hs}} P_\perp = D_\perp$. Note that the obtained ratio of the intercolumn hopping rates, 4.5×10^9 rad/s:5.3×10^{10} rad/s:10^{12} rad/s in $D_\perp$ does not correspond to that of the dc conductivities, 15 S/cm:100 S/cm:400 S/cm for the Li-, Ag-, and Li$_{0.94}$Cu$_{0.06}$-salts, respectively. This fact suggests that the electrical conductivity at RT is no longer limited by $D_\perp$ in Li$_{0.94}$Cu$_{0.06}$-salt with the highest dc conductivity. We propose the hole soliton model for the electrical resistivity along c-axis as a sum of the intra- and intercolumn resistances as, $\rho(T) = a(n_{\mathrm{hs}} D_\|)^{-1} + b(n_{\mathrm{hs}} P_\perp)^{-1}$, where the first and second terms are the intra- and the intercolumn resistivities, respectively. Since one-dimensional chain is composed of domains with about 100 units[6], ρ should contain $D_\perp$. The first term, $\rho_\|$ is obtained as $\sim$

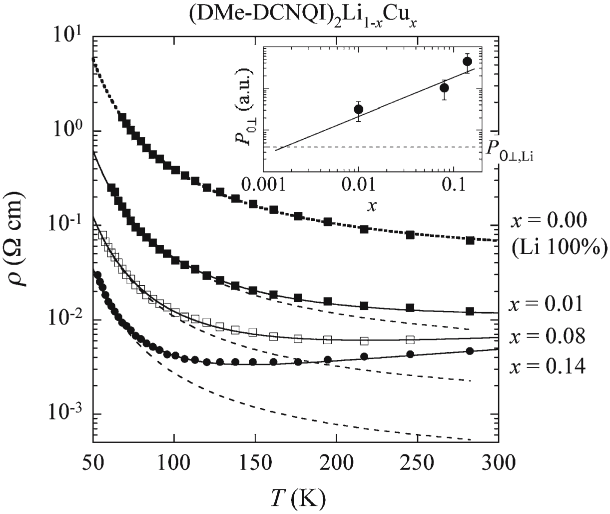

Fig. 3. The temperature dependence of the electrical resistivity reproduced by the hole soliton model in several Cu concentrations. Closed squares are taken from the reported resistivity in Ref. 1. The solid curves show the hole soliton model, $\rho = \rho_{\parallel} + \rho_{\perp}$. Dashed curves represent $\rho_{\perp} = \{\sigma_{0\perp} \exp(-260/T)\}^{-1}$. Inset shows $P_{0\perp}$.

$2.2 \times 10^{-8} \exp(260/T) \cdot T^2 (\Omega\,\mathrm{cm})$ from the fitting to the dc conductivity in Fig. 3. With the hole soliton model for the dc conductivity, the Cu concentration dependence of the electrical resistivity in Fig. 3 could be reproduced simply with the difference of $P_{\perp}$'s in the second term. The detailed discussion will be published elsewhere.

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