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Carrier Doping Effect into Quasi-One-Dimensional Bromo-Bridged Ni(III) Complexes with Strong Electron-Correlation by Cu(II) Ions, $[Ni_{1-x}Cu_x(chxn)_2Br]Br_{2-x}$

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This communication will describe the electron doping effect into Ni^{III} complexes by Cu^{II} ions, $[Ni_{1-x}Cu_x(chxn)_2Br]Br_{2-x}$ ($x = 0.038$ and 0.101) by using an electrochemical oxidation method. A drastic increase of electrical conductivity as well as a new absorption band around 0.5 eV in single crystal reflectance spectra was observed by doping Cu^{II} ions, indicating the electron doping was successfully made. An ESR result shows unpaired electrons locate in the $d_{x^2-y^2}$ orbitals of Cu^{II} and have almost no interaction with those of other ions.

Recently, quasi-one-dimensional halogen-bridged mixed-valence compounds (MX chains) have been attracting much attention because they show very interesting physical properties such as intense and dichroic intervalence charge-transfer (CT) bands, overtone progression of resonance Raman spectra, luminescence spectra with large Stokes shifts, large third-order nonlinear optical properties, midgap absorptions attributable to solitons and polarons, one-dimensional model compounds of high T_c copper oxide superconductors, etc.[1−9] Theoretically, these MX chains are considered as Peierls−Hubbard systems where the electron−phonon interaction (*S*), the electron transfer (*T*), and the intra- and intersite Coulomb repulsion energies (*U* and *V*, respectively) compete or cooperate with each other.[10,11]

Pt and Pd compounds have charge density wave states (CDW) or $M^{II}-M^{IV}$ mixed-valence states due to the electron−phonon interaction (*S*), where bridging halogens are displaced from the midpoints between neighboring metal ions. Accordingly, a half-filled metallic band is split into occupied valence and unoccupied conduction bands with a finite Peierls energy gap. Therefore, these compounds belong to the class II type of the Robin−Day classification for mixed-valence complexes.[1]

On the other hand, Ni compounds have spin density wave states (SDW) or Ni^{III} Mott−Hubbard states due to the strong electron correlation (*U*), where bridging halogens are located at the midpoints between neighboring Ni ions. Therefore, these Ni complexes belong to the class III type of the Robin−Day classification for mixed-valence complexes.[1] The very strong antiferromagnetic interactions among spins located on the $Ni^{III}d_{z^2}$ orbitals through bridging halogen ions are observed in these Ni complexes.[13,14] The intense and dichroic

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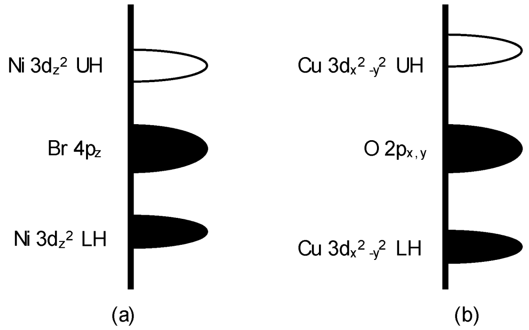

Figure 1. Schematic band structure of $[Ni(chxn)_2Br]Br_2$ and copper-oxide compounds.

CT bands attributable to a transition from bridging halogens to upper Hubbard bands are observed around 1−2 eV along the chain axes. More recently, a gigantic third-order nonlinear optical susceptibility (~10^{-4} esu) has been observed in $[Ni^{III}(chxn)_2Br]Br_2$ (chxn = 1*R*,2*R*-diaminocyclohexane) due to the strong electron correlation and lower CT band.[15] Correctly speaking, the Ni^{III} complexes are not Mott insulators but charge-transfer insulators where energy levels of bridging halogens are located between upper and lower Hubbard bands composed of $Ni^{III}dz^2$ orbitals (Figure 1a). Therefore, electronic structures of the Ni^{III} complexes are very similar to starting materials of high T_c copper-oxide superconductors (Figure 1b) except for their dimensionalities. Then, the hole doping and electron doping into the Ni^{III} complexes are very interesting. According to such a strategy, in the preceding paper we have reported the hole doping (Co^{III}) into the Ni^{III} complexes with strong electron-correlation $[Ni_{1-x}Co_x(chxn)_2Br]Br_2$, where the electrical conductivities increased with increasing amount of doped Co^{III} and a new CT band appeared around 0.5 eV. Therefore, we have succeeded in hole doping into $[Ni(chxn)_2Br]Br_2$ with strong electron-correlation.[16] In this paper, we will describe the electron doping (Cu^{II}) into the $[Ni(chxn)_2Br]Br_2$ with strong electron-correlation.

We have synthesized single crystals of the complexes $[Ni_{1-x}Cu_x(chxn)_2Br]Br_{2-x}$ by an electrochemical oxidation method of mixed methanol solutions of $Ni(chxn)_2Br_2$ and $Cu(chxn)_2Br_2$. $Ni(chxn)_2Br_2$ and $Cu(chxn)_2Br_2$ have been synthesized according to the literature.[12,16] Elemental analyses of Ni and Cu ions were carried out by an ICP method. The oxidation state of the Cu ion is not +3 but +2 as evidenced by ESR spectra, which are discussed in Figure 5 in detail. Therefore, the elemental analyses revealed that defects of the Br counteranions exist so as to keep the charge balance.

X-ray powder patterns of $[Ni(chxn)_2Br]Br_2$ and $[Ni_{1-x}Cu_x(chxn)_2Br]Br_{2-x}$ are similar to each other (Figure 2). Therefore, crystal structures of the $[Ni_{1-x}Cu(chxn)_2Br]Br_{2-x}$ are similar to that of $[Ni(chxn)_2Br]Br_2$, where the planar $[M(chxn)_2]$ are bridged by Br^- ions, forming linear chain structures. Thus, the Cu^{II} ions are successfully incorporated into the one-dimensional Ni^{III} chain system.

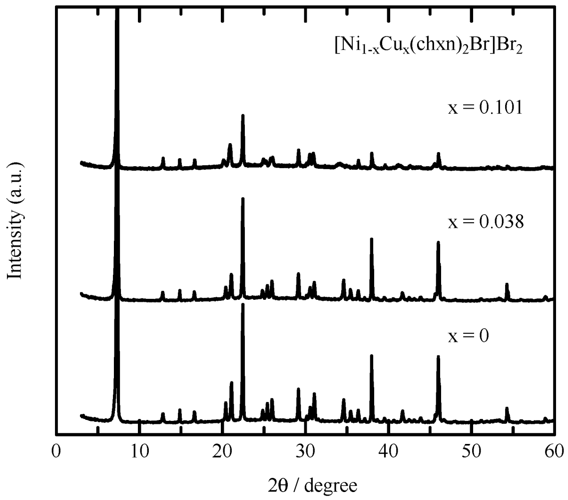

Figure 2. X-ray powder patterns of $[Ni_{1-x}Cu_x(chxn)_2Br]Br_{2-x}$ ($x = 0$, 0.038, and 0.101).

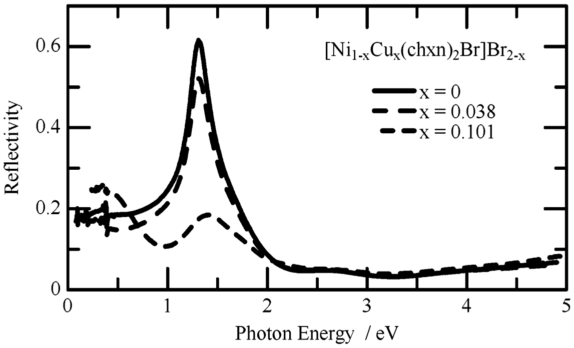

Figure 3. Single crystal reflectance spectra along the chain axis of $[Ni_{1-x}Cux(chxn)_2Br]Br_{2-x}$ ($x = 0$, 0.038, and 0.101).

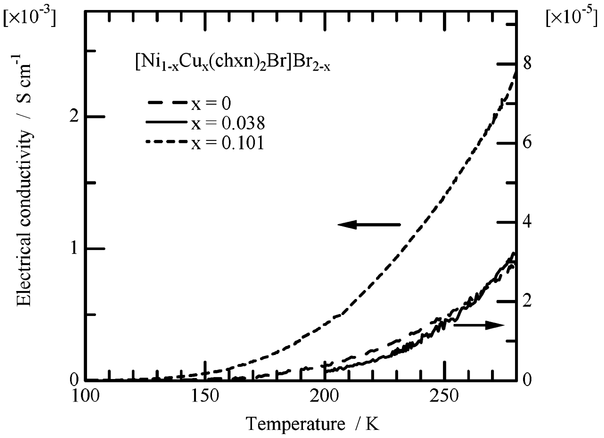

Figure 4. Single crystal electrical conductivities of $[Ni_{1-x}Cu_x(chxn)_2Br]Br_{2-x}$ ($x = 0$, 0.038, and 0.101). The data of $x = 0.101$ and $x = 0$, 0.038 are shown with left and right vertical axes, respectively.

Single crystal reflectance spectra of $[Ni_{1-x}Cu_x(chxn)_2Br]Br_{2-x}$ show intense two peaks around 0.5 and 1.3 eV, where the former peaks newly appear by doping of Cu^{II} ions and the latter peaks are commonly observed in these compounds which are attributable to a transition from the bridging Br^- ion to upper Hubbard of the $Ni^{III}d_{z^2}$ orbital (Figure 3). Therefore, new electronic structures have been

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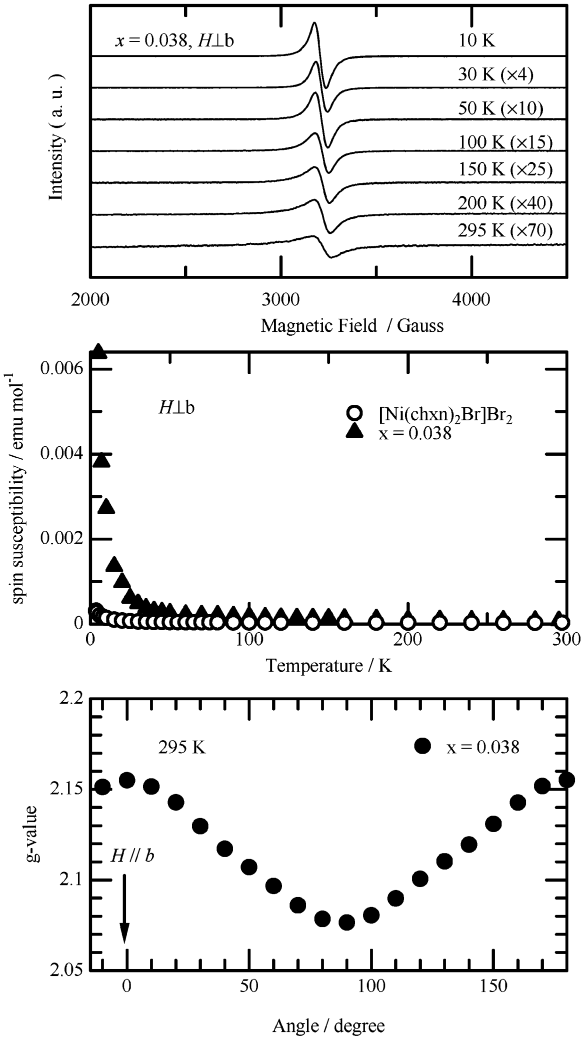

Figure 5. Temperature dependence of ESR spectra (top), spin susceptibility (middle), and angular dependence of *g*-values in single crystal ESR spectra (bottom).

created in $[Ni_{1-x}Cu_x(chxn)_2Br]Br_{2-x}$. As the intensities of the CT bands around 0.5 eV increase, the CT bands around 1.3 eV are weakened with an increase in Cu^{II} doping.

Single crystal electrical conductivity measurements have been carried out for $[Ni_{1-x}Cu_x(chxn)_2Br]Br_{2-x}$ ($x = 0.038$ and 0.101) along with parent complex $[Ni^{III}(chxn)_2Br]Br_2$ by a four-probe method (Figure 4). All compounds show semiconducting behaviors with energy gaps of $E_g = 0.10-0.15$ eV. The energy gaps are much less than the gaps found by the reflectance spectra. However, the electrical conductivities at room temperature of these compounds increase with an increase of the amounts of doped Cu^{II} ions. An electrical conductivity of $x = 0.101$ at room temperature is by 100 times larger than that of the parent complex $[Ni(chxn)_2Br]Br_2$.

This may indicate the amount of charge carriers or mobilities increasing with an increase in the amounts of doping of Cu^{II} ions.

ESR spectra have been measured for the single crystals of $[Ni_{1-x}Cu_x(chxn)_2Br]Br_{2-x}$ down to liquid helium temperature. Temperature dependent ESR patterns reveal that unpaired electrons exist on the $d_{x^2-y^2}$ orbital of Cu^{II} ions (Figure 5). Spin susceptibility shows Curie-like behavior, indicating that the magnetic interactions between Cu^{II} and Cu^{II} and between Cu^{II} and Ni^{III} ions are very weak. The strong antiferromagnetic interactions among unpaired electrons located on the d_{z^2} orbital of Ni^{III} ions are hidden by the Curie-like behavior on Cu^{II} ions. The Curie spin concentration is almost consistent with the elemental analyses of the Cu^{II} ion, $[Ni_{1-x}Cu_x(chxn)_2Br]Br_{2-x}$.

An angular dependence of the *g*-value shows a symmetrical shape, indicating that the Cu^{II} ions are incorporated in the one-dimensional Ni^{III} chain system. Such a result is consistent with those of the elemental analyses, X-ray powder patterns, and single-crystal reflectance spectra.

Solid state ^{13}C NMR spectral measurements were carried out for $[Ni_{1-x}Cu_x(chxn)_2Br]Br_{2-x}$ ($x = 0$, 0.038, and 0.101) at room temperature in order to investigate their electronic structures. The α, β, and γ carbons of the cyclohexanediamine ligand of $x = 0.038$ and 0.101 are broader than those of $[Ni(chxn)_2Br]Br_2$ due to the larger Curie-spin concentration of the Cu^{II} ions.

As conclusions, we have succeeded in both hole (Co^{III}) and electron (Cu^{II}) dopings into the Ni^{III} complexes with the strong electron-correlation. Therefore, the new electronic structures have been created by doping into $[Ni(chxn)_2Br]Br_2$. The new CT bands at the lower energy regions have appeared. Therefore, the larger third-order optical nonlinear susceptibility is anticipated in $[Ni_{1-x}Cu_x(chxn)_2Br]Br_{2-x}$.[15] The investigation is now in progress.

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