Angle-Resolved Photoemission Study of the MX-Chain Compound $[\mathrm{Ni(chxn)_2Br}]\mathrm{Br_2}$: Spin-Charge Separation in Hybridized d-p Chains

Shin-ichi Fujimori, Akihiro Ino, and Testuo Okane

Synchrotron Radiation Research Center, Japan Atomic Energy Research Institute, SPring-8, Mikazuki, Hyogo 679-5148, Japan

Atsushi Fujimori

Synchrotron Radiation Research Center, Japan Atomic Energy Research Institute, SPring-8, Mikazuki, Hyogo 679-5148, Japan
and Department of Complexity Science, University of Tokyo, Bunkyo-ku, Tokyo 113-0033, Japan

Kozo Okada

Department of Physics, Faculty of Science, Okayama University, Tsushima-naka, Okayama 700-8530, Japan

Toshio Manabe and Masahiro Yamashita

Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University, Hachioji, Tokyo 192-0397, Japan

Hideo Kishida and Hiroshi Okamoto

Department of Advanced Materials Science, Graduate School of Frontier Science, University of Tokyo, Bunkyo-ku, Tokyo 113-8656, Japan

We report on the results of angle-resolved photoemission experiments on a quasi-one-dimensional (1D) MX-chain compound $[\mathrm{Ni(chxn)_2Br}]\mathrm{Br_2}$, which shows a gigantic nonlinear optical effect. A "band" having about 500 meV energy dispersion is found in the first half of the Brillouin zone, but disappears at $kb/\pi \sim 1/2$. These spectral features are well reproduced by the d-p chain model with a small charge-transfer energy Δ compared with that of 1D Cu-O compounds. We propose that this smaller Δ is the origin of the absence of clear spin-charge separation in the photoemission spectra and the strong nonlinear optical effect.

    PACS numbers: 79.60.–i, 78.20.Bh

Recently, one-dimensional (1D) strongly correlated (SC) electron systems have attracted much attention. One of the most striking findings in these systems is the so-called spin-charge separation. The spin and charge degrees of freedom are decoupled, and the low energy properties of the material are governed by a spinless excitation called a holon and a chargeless excitation called a spinon. These elemental excitations were theoretically first predicted by Lieb and Wu [1], and were experimentally observed by recent angle-resolved photoemission spectroscopy (ARPES) experiments on $\mathrm{SrCuO_2}$ [2] and $\mathrm{Sr_2CuO_3}$ [3]. In addition to these purely academic interests, it is recently recognized that these 1D-SC electron systems show strong nonlinear optical (NLO) effects. Kishida *et al.* [4] have observed a significantly enhanced third-order nonlinear dielectric susceptibility $\chi^{(3)}$ in $\mathrm{Sr_2CuO_3}$ and the halogen(X)-bridged transition-metal(M) compounds, designated as the MX-chain compounds. The large $\chi^{(3)}$ is indispensable for optoelectronic switching, modulating, and computing devices, and its magnitude dominates their performances. These 1D-SC electron systems may therefore become key materials for future optical technology.

Among those 1D-SC electron systems, the MX-chain compounds with $M = \mathrm{Ni}$, $X = \mathrm{Br}$, $[\mathrm{Ni(chxn)_2Br}]\mathrm{Br_2}$ (chxn = $1R$, $2R$-cyclohexanediamine), have the largest value of $\max|\mathrm{Im}\chi^{(3)}|$, and are good target materials to study the underlying physics of these properties. A previous x-ray photoemission spectroscopy (XPS) study has revealed that this material is a charge-transfer(CT)-type insulator [5]. However, the core-level experiment alone was insufficient to obtain information about its 1D electronic structure since the charge-transfer satellites in the core-level spectra are originated from not only d-p hybridization along the chain, but also that perpendicular to the chain. In this paper, we have performed ARPES experiments on this compound to reveal its electronic structure. The result is compared with that of Cu-O based systems, such as $\mathrm{Sr_2CuO_3}$, and analyzed with calculations based on the d-p chain model.

The basic crystal structure of $[\mathrm{Ni(chxn)_2Br}]\mathrm{Br_2}$ consists of $\mathrm{Ni(chxn)_2}$-Br chains and counter Br ions. The chains are well separated by the counter Br atoms and (chxn) molecules, and interaction between them is considered to be negligibly weak. The N atoms of ligand

(chxn) molecules are very close to Ni atoms, leading to a strong crystal field on the Ni $3d$ states. The resulting electronic configuration of the Ni^{3+} ion is the filled t_{2g} orbitals plus a singly occupied e_g ($3d_{3z^2-r^2}$) orbital, $(t_{2g})^6(e_g)^1$. The strong overlap between the Ni $3d_{3z^2-r^2}$ orbital and the halogen p_z orbital leads to a strong magnetic coupling along the chain, and the magnetic susceptibility χ is described by the Bonner-Fisher formula with $S = 1/2$ and $J \sim 3600$ K ($= 0.31$ eV) [6]. Thus this material can be viewed as a 1D Heisenberg chain system.

Single crystals of $[Ni(chxn)_2Br]Br_2$ were prepared by an electrochemical method. ARPES experiments were performed using a spectrometer equipped with a GAMMADATA-SCIENTA SES2002 electron analyzer and a monochromatized GAMMADATA-SCIENTA vacuum ultraviolet lamp. Clean sample surfaces were obtained by *in situ* cleaving the sample parallel to the *bc* plane. In order to avoid charging effects, the sample was kept at room temperature. The overall energy resolution was set at about 50 meV. Binding energies are referred to the Fermi edge of an evaporated gold film.

During the course of the measurement, gradual changes in the line shape of the photoemission spectra were observed. These were not due to charging effects of the sample surface since the line shape changes were not associated with rigid shifts of the spectra. Therefore, we concluded that the changes were due to the degradation of the sample surface caused by the irradiation, which had also been observed in the previous XPS measurements [5]. We then decided to use He IIα ($h\nu = 40.8$ eV) radiation for the present measurements, whose intensity is about 20 times weaker than that of the often-used He Iα ($h\nu = 21.2$ eV) radiation. In addition, we took all the spectra within 20 minutes. We have carefully checked the time dependence of the spectral line shape, and confirmed that no remarkable changes were observed within this period.

Figure 1 shows the ARPES spectra of $[Ni(chxn)_2Br]Br_2$. The momentum scan was performed along the *b* axis (chain axis). All spectra have been normalized to the integrated intensities between E_F and 1.0 eV. There is a weak but distinctive peak structure around $0.3–0.8$ eV. The peak is located at about 0.8 eV at $kb/\pi = 0$, and moves toward lower binding energy as kb/π increases. It reaches to about 0.3 eV at $kb/\pi = 1/2$, and suddenly disappears with an additional increase in kb. To see these features more clearly, we have derived the "image" of the band dispersion from these spectra by taking second derivatives of smoothed ARPES spectra. This method is very sensitive to peak structures. Figure 2 shows their gray plot as a function of binding energy and momentum, where the dark part corresponds to peak position. We have tested different smoothing procedures in making images carefully, and confirmed that the essential spectral feature does not depend on the procedures. The above-mentioned spectral feature is more clearly understood from this image. The sine-curve-like dispersion is observed in the first half
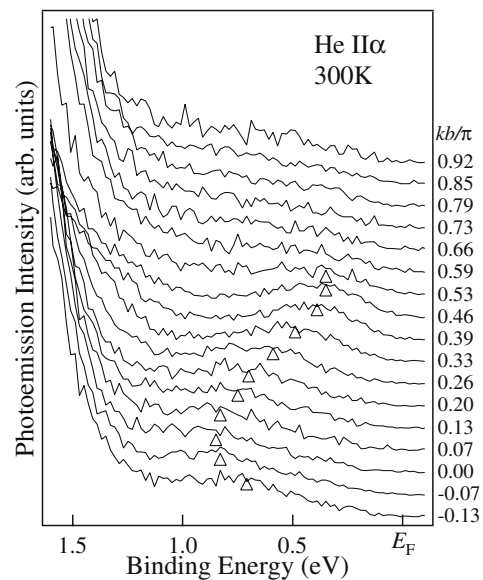

FIG. 1. ARPES spectra of $[Ni(chxn)_2Br]Br_2$ taken with He IIα ($h\nu = 40.814$ eV). An approximate value of k is also shown in each spectrum.

$(0 \le kb/\pi < 1/2)$ of the Brillouin zone, but it suddenly disappears at $kb/\pi \sim 1/2$, and then is not seen in the second half $(1/2 \le kb/\pi < 1)$ of the Brillouin zone. The dotted white line is a guide to the eye. The size of the energy dispersion is estimated to be about 500 meV. In this scan, the spectra were measured only up to $kb/\pi \sim 0.92$, but spectra in the remaining part of the Brillouin zone were also measured in a different scan, and it is confirmed that there is no prominent feature at $kb > 0.92$. This result is qualitatively different from those of Cu-O based 1D-SC compounds like $SrCuO_2$ or Sr_2CuO_3. In the first half of the Brillouin zone, two bands originating from
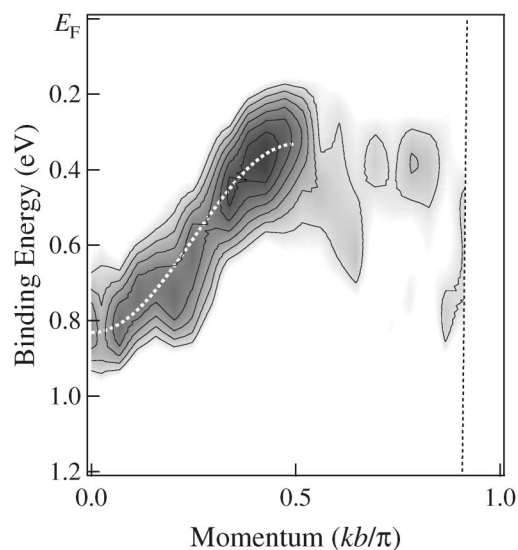

FIG. 2. Grey-scale plot of the negative second derivative of the ARPES spectra. The dotted white line is a guide to the eyes.

the spinon and holon excitations are observed in the Cu-O based 1D-SC compounds, while only one band is observed in $[Ni(chxn)_2Br]Br_2$. Moreover, in the second half of the Brillouin zone, one band, originating from a holon, is observed in the Cu-O based 1D-SC compounds, while no band is observed in $[Ni(chxn)_2Br]Br_2$.

In order to better understand the ARPES spectra of $[Ni(chxn)_2Br]Br_2$, we have calculated the spectral function of these materials within the framework of the d-p chain model. We have employed this model, because the model incorporates large enough degrees of freedom to properly treat the CT-type system. Moreover, the d-p model can include photoemission cross section effects, which cannot be taken into account in the t-J model. In this model, the d and p orbitals are arranged alternatively in a chain, and hybridization between the nearest neighbor d and p sites is considered. The model is expressed by the Hamiltonian

$$H_{dp} = \Delta \sum_{i\sigma} n_{i\sigma}^p + U \sum_i n_{i\uparrow}^d n_{i\downarrow}^d$$
$$- t \sum_{\langle ij \rangle} (d_{i\sigma}^\dagger p_{j\sigma} + d_{i\sigma} p_{j\sigma}^\dagger), \quad (1)$$

where $n_{i\sigma}^d$ and $n_{i\sigma}^p$ are the number operators of the d and p holes with spin σ at site i, and $d_{i\sigma}$ and $p_{i\sigma}$ are the annihilation operators of the d and p holes with spin σ at a site i, respectively. The sum $\langle ij \rangle$ takes all combinations of the nearest neighbor d and p sites. Δ is the charge-transfer energy between d and p sites, U is the Coulomb interaction between d electrons on the site, and t is the transfer integral between the nearest d and p states. We have performed numerical diagonalization of the Hamiltonian matrix for a finite size cluster, and calculated the single particle spectral function. This method is exact, but requires the diagonalization of a huge Hamiltonian matrix. Here we took an eight-molecule d-p chain model with four holes per spin. In these calculations, the p hole levels are empty and the d hole levels are half-filled in the initial state. To check the validity of these parameters, the exchange interaction J between the d sites, which can be compared with the experimental value, was also evaluated in the following ways. We considered a $2\frac{1}{2}$-molecule d-p cluster (p-d-p-d-p), and calculated the total energy for the total spin $S_z = 0$ and $S_z = 1$ with these parameters. The exchange energy is then evaluated by $J = E(S_z = 1) - E(S_z = 0)$.

First we present the calculations for a Cu-O chain to reproduce the previous theoretical and experimental results [2,3]. Figures 3(a) and 3(b) show the results of the calculations for $t = 1$, $\Delta = 2.4$, and $U = 7$ eV. These parameters are similar to those used in the calculation of Ref. [2], but Δ and U have been slightly changed from $\Delta = 3$ eV and $U = 8$ eV in order to reproduce the observed value of J. J is estimated to be 0.15 eV for these parameters, and is very close to the observed $J \sim 0.16$ eV [3]. The obtained spectra are broadened with a Gaussian function to compare with the experimental spectra. These are indeed indistinguishable from those in Ref. [2]. Con-
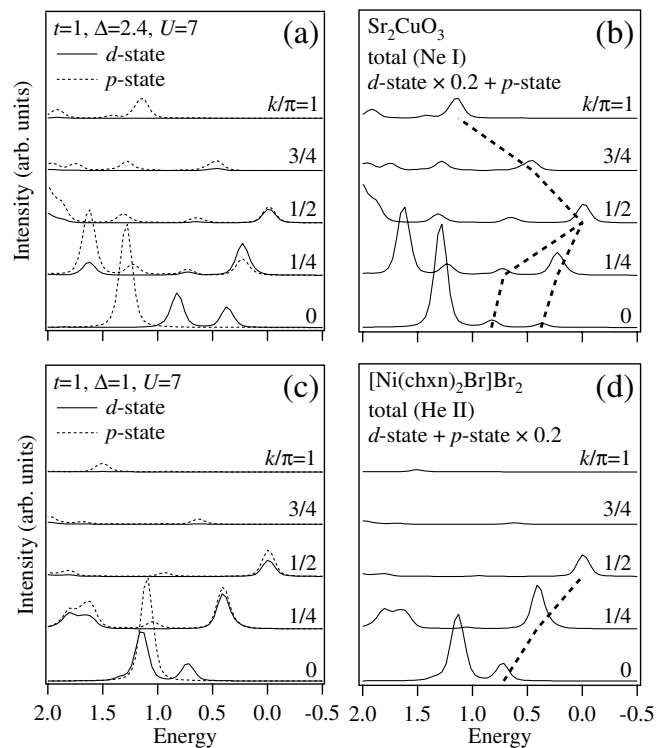

FIG. 3.   Results of finite-size cluster calculation based on the d-p chain model.   (a) Partial spectral function for $t = 1$, $\Delta = 2.4$, and $U = 7$ ($J = 0.15$) corresponding to Sr_2CuO_3. (b) Total spectral function for Ne Iα. (c) Partial spectral function for $t = 1$, $\Delta = 1$, and $U = 7$ ($J = 0.31$) corresponding to $[Ni(chxn)_2Br]Br_2$. (d) Total spectral function for He IIα.

tributions from each of the d and p states are shown separately in Fig. 3(a). To compare them with the experimental spectra of Sr_2CuO_3 of Ref. [3], the photoemission cross section effects are considered as shown in Fig. 3(b) as the total spectra, where the contributions from the d states are 0.2 times smaller since the He Iα or Ne Iα ($h\nu = 16.8$ eV) radiation was used for the measurements. There are two branches for $0 \leq kb/\pi < 1/2$, and only one branch for $1/2 \leq kb/\pi < 1$, agreeing well with the results of Sr_2CuO_3 of Refs. [2,3]. Comparison of the spectra calculated by the d-p chain model with those calculated by the t-J model suggests that two branches in $0 \leq kb/\pi < 1/2$ are interpreted as a holon and a spinon band, and one branch in $1/2 \leq kb/\pi < 1$ is interpreted as a holon band [7].

Next, we simulate the ARPES spectra of $[Ni(chxn)_2$-$Br]Br_2$. We assume that the difference between $[Ni(chxn)_2Br]Br_2$ and Sr_2CuO_3 is only that in Δ, for simplicity. Qualitatively, t and U should be changed for different cation and anion atoms, but their changes are considered to be not so significant compared with that of Δ [8,9]. To simulate the ARPES spectra of $[Ni(chxn)_2$-$Br]Br_2$, we have estimated Δ of this compound in the following steps. First, we consider the difference in Δ due to different cation atoms. In transition-metal oxides, Δ is increased by about 2.0 eV on going from CuO to

NiO [10,11]. The difference in Δ between CuS and NiS is also estimated to be about 2 eV [10], and therefore we consider that the difference in Δ from the difference in the cation atoms is $+2$ eV. Next, the valencies of the cations are different between Sr_2CuO_3 (Cu^{2+}) and $[Ni(chxn)_2Br]Br_2$ (Ni^{3+}). In general, it is considered that Δ of $3d$ transition-metal oxides is lowered about 2.5 eV with increasing cation valency [10], and here we consider that the difference is -2.5 eV. Finally, the difference in Δ due to the difference in the ligand atoms are considered. For the compounds with the same cation, a decrease in ligand electronegativity will raise the ligand p bands with respect to the metal d orbitals, resulting in a decrease in Δ. From the core-level line shape analysis of $CuCl_2$, CuO, and La_2CuO_4, Δ is decreased by about 0.8–0.9 eV in going from CuO and La_2CuO_4 to $CuCl_2$ [12]. There is no core-level line shape analysis for $CuBr_2$, but its core-level spectrum is very similar to that of $CuCl_2$ [8]. Hence we assume that the difference in Δ due to the different ligand atoms (O and Br) is -1 eV. Totally, Δ should be lowered by about 1.5 eV, and therefore we have taken $\Delta = 1$ for $[Ni(chxn)_2Br]Br_2$. The large exchange of $J = 0.3$ eV is obtained for the smaller Δ with the same t and U, which agrees well with the larger experimental $J = 0.31$ eV of $[Ni(chxn)_2Br]Br_2$. Figure 3(c) shows the calculated spectral function for $t = 1$, $\Delta = 1$, and $U = 7$. Figure 3(d) shows the total spectra where the contributions from the p states are 0.2 times smaller since He IIα ($h\nu = 40.8$ eV) radiation was used for the measurements. In contrast to Fig. 3(b), only one branch is observed in $0 \leq kb/\pi \leq 1/2$, and it disappears in $1/2 < kb/\pi \leq 1$. Consequently, the characteristic features of the experimental spectra are well explained by these parameters, which are consistent with exchange energy J. In these calculations, the hybridization between Ni $3d$ and N $2p$ is not considered. The N atoms of (chxn) molecules are very close to Ni atoms, and, in addition to the strong crystal field which splits the Ni $3d$ level, the hybridization between the Ni $3d$ and N $2p$ might influence the electronic structure [13].

Accordingly, we have successfully described the ARPES spectra of $[Ni(chxn)_2Br]Br_2$ and Sr_2CuO_3 by the same d-p chain model Hamiltonian with different charge-transfer energy Δ. Here we relate the present results and the strong NLO effects in these compounds. The NLO effects in 1D SC system have been studied by some theoretical works, and $\chi^{(3)}$ spectra have been calculated [14–16]. However, such theoretical approaches require the large cluster size, and it is difficult to calculate the spectra within the framework of the present model. Therefore, we qualitatively consider the relationship between the present results and the NLO effects. The optical nonlinearity of $[Ni(chxn)_2Br]Br_2$ is much stronger than that of Sr_2CuO_3, and this difference is ascribed to the difference in the dipole moment ($\langle 0|x|1\rangle$) between the ground state ($|0\rangle$) and the one-photon-allowed excited state ($|1\rangle$) and the dipole moment ($\langle 1|x|2\rangle$) between the one-photon-allowed excited state ($|1\rangle$) and the one-photon forbidden excited state ($|2\rangle$) [4]. The $\chi^{(3)}$ is proportional to the square of $\langle 0|x|1\rangle$ and $\langle 1|x|2\rangle$, and therefore the material with larger $\langle 0|x|1\rangle$ or $\langle 1|x|2\rangle$ give larger NLO effect. In our analysis, the smaller charge-transfer energy Δ for the Ni-Br system should make the d and p levels hybridized well. It leads to larger spatial extensions of electron-hole wave functions in the two CT-excited states $|1\rangle$ and $|2\rangle$, and then a larger dipole moment $\langle 1|x|2\rangle$. Consequently, the smaller Δ gives stronger NLO effects, and we predict that $[Ni(chxn)_2I]I_2$, which has a lower Δ, should have stronger NLO effect compared with that of $[Ni(chxn)_2Br]Br_2$.

In conclusion, we have studied the electronic structure of $[Ni(chxn)_2Br]Br_2$ by ARPES. The essential features of the spectra are well explained by the d-p chain model calculations with a small charge-transfer energy Δ compared with that of the Cu-O based 1D-SC compounds. This result is consistent with the stronger NLO effect in $[Ni(chxn)_2Br]Br_2$, compared with Sr_2CuO_3. We propose that Δ is an essential parameter for tuning the NLO effects of CT-type 1D-SC electron system.

[1] E. Lieb and F. Y. Wu, Phys. Rev. Lett. **20**, 1445 (1968).
[2] C. Kim *et al.,* Phys. Rev. Lett. **77**, 4054 (1996); Phys. Rev. B **56**, 15 589 (1997).
[3] H. Fujisawa *et al.,* Phys. Rev. B **59**, 7358 (1999).
[4] H. Kishida *et al.,* Nature (London) **405**, 929 (2000).
[5] H. Okamoto *et al.,* Phys. Rev. B **54**, 8438 (1996).
[6] H. Okamoto *et al.,* Phys. Rev. B **42**, 10 381 (1990).
[7] S. Maekawa and T. Tohyama, J. Phys. Chem. Solids **59**, 1897 (1998).
[8] G. van der Laan *et al.,* Phys. Rev. B **23**, 4369 (1981).
[9] J. Zaanen *et al.,* Can. J. Phys. **65**, 1262 (1987).
[10] A. E. Bocquet *et al.,* Phys. Rev. B **46**, 3771 (1992).
[11] J. Ghijsen *et al.,* Phys. Rev. B **42**, 2268 (1990).
[12] K. Okada and A. Kotani, J. Electron. Spectrosc. Relat. Phenom. **52**, 313 (1990).
[13] The explicit treatment of these effects increases the number of Hamiltonian matrix elements enormously, and its exact diagonalization becomes impossible. One realistic way to consider these effects is taking them into account as a renormalization effect on t, U, and Δ of the present model under the constraint that the estimated J remains unchanged. Such theoretical calculations have been performed, and the results suggest that the essential conception of these analyses remains unchanged even after such parameter readjustments. [Okada (unpublished)].
[14] A. Saxena *et al.,* Synth. Met. **86**, 2231 (1997).
[15] K. Iwano and K. Nasu, J. Phys. Soc. Jpn. **62**, 1778 (1993).
[16] Y. Mizuno *et al.,* Phys. Rev. B **62**, R4769 (2000).