

# Anomalous spectral weight in photoemission spectra of the hole-doped Haldane chain $Y_{2-x}Sr_xBaNiO_5$

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In this paper, we present photoemission experiments on the hole-doped Haldane chain compound  $Y_{2-x}Sr_xBaNiO_5$ . By using the photon-energy dependence of the photoemission cross section, we identified the symmetry of the first ionization states ( $d$  type). Hole doping in this system leads to a significant increase in the spectral weight at the top of the valence band without any change in the vicinity of the Fermi energy. This behavior, not observed in other charge-transfer oxides at low doping level, could result from the inhomogeneous character of the doped system and from a Ni  $3d$ -O  $2p$  hybridization enhancement due to the shortening of the relevant Ni-O distance in the localized hole-doped regions.

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## I. INTRODUCTION

Oxides of  $3d$  transition metals have attracted considerable attention in the last two decades because they exhibit very varied and fascinating properties (metal-insulator transition, high  $T_c$  superconductivity, intriguing magnetic properties). These behaviors partly result from an interplay of low dimensionality and electronic correlations. Many transition-metal oxides exhibit a two-dimensional electronic structure. Due to its peculiar crystal structure,  $Y_2BaNiO_5$  is essentially a one-dimensional (1D) divalent nickel oxide. It crystallizes in a body-centered orthorhombic structure within the  $Immm$  space group.<sup>1</sup> The structure is characterized by linear chains of  $NiO_6$  octahedra sharing corners along the  $z$  direction. The octahedra are compressed along the chains resulting in two short Ni-O distances (0.188 nm) and four longer Ni-O distances (0.219 nm).<sup>1</sup> This unusual contraction and vanishing interactions between neighboring chains lead to a quasi-one-dimensional electronic structure.<sup>2</sup> The hybridization between Ni- $3d$  and O- $2p$  states is strong along the chain direction. Yet,  $Y_2BaNiO_5$  has an insulating ground state due to exchange and correlation effects. The superexchange antiferromagnetic coupling between neighboring  $S=1$  spins carried by  $Ni^{2+}$  ions in  $Y_2BaNiO_5$  yields a quantum spin liquid ground state.<sup>3</sup> Large quantum spin fluctuations associated with the 1D character of the Ni-O-Ni network prevent the formation of an ordered magnetic state. The spin liquid can be described as a macroscopically coherent quantum state<sup>4</sup> with a Haldane gap in the spin excitation spectrum.<sup>3,5</sup> Each  $S=1$  spin can be considered as the triplet state formed from the two ferromagnetically coupled  $S=1/2$  holes of  $Ni^{2+}$ . Two  $S=1/2$  holes of neighboring sites form a singlet state. The ground state is then described in the well-known valence bond solid picture. Excitations are triplet states obtained by breaking valence bonds. Hole doping in this spin liquid state

results in interesting behaviors. Low-energy spin excitations are characterized by incommensurate spin-density modulation around impurities, and the dynamical spin structure factor reveals spectral weight in the Haldane gap.<sup>5-7</sup>

From an electronic point of view,  $Y_2BaNiO_5$ , like most of the Ni and Cu oxides, belongs to the charge-transfer regime in the Zaanen-Sawatzky-Allen (ZSA) diagram.<sup>8</sup> Then if the low-energy properties usually associated with spin excitations could be very different, the charge excitations and, in particular, the effect of doping should look very similar in these families. The photoemission spectrum of homogeneously hole-doped systems only exhibits small spectral weight modifications with doping, whereas large spectral weight transfer is observed in the inverse photoemission spectrum. In charge-transfer oxides, a  $p$  symmetry is expected for the first ionization states. Thus, the substitution of Sr or Ca divalent ions for trivalent Y in  $Y_{2-x}Sr_xBaNiO_5$  should yield holes in the ligand  $p$  band. Nevertheless, hybridization between Ni  $3d$  states and O  $2p$  states can modify this picture by shifting highly hybridized  $d^8L$  states toward the top of the O  $2p$  band ( $L$  represents a hole on the ligand). As a consequence, the first ionization states probed by photoemission should have a  $3d$  character. This spectroscopy, by measuring the electron-removal spectrum, can give information about the symmetry of the first ionization states and about the modification of electronic properties in hole-doped compounds. The electronic structure of hole-doped  $Y_2BaNiO_5$  has been investigated with several methods including x-ray absorption spectroscopy (XAS),<sup>5</sup> optical conductivity,<sup>9</sup> photoemission, and inverse photoemission.<sup>10</sup> These experiments show that doped holes have either O( $2p_z$ ) or mixed Ni( $3d_{3z^2-r^2}$ )-O( $2p_z$ ) character. Hole doping introduces new empty localized states in the charge gap region without any spectral weight very close to the Fermi level. The doped carriers are trapped in local bound states

and should therefore locally distort the electronic structure only in the vicinity of their location, giving rise to a possible nonhomogeneous doping at the nanoscopic scale.<sup>7,9</sup> Therefore, the system does not become metallic upon doping, and no charge ordering is observed.

In this paper, we investigate the electronic structure of  $Y_{2-x}Sr_xBaNiO_5$  for  $x=0, 0.1$ , and  $0.2$  by photoemission spectroscopy. By using the photon-energy dependence of the spectral density, we confirm that the first electron removal excitations have mainly a Ni  $3d$  character. Moreover, these measurements illustrate the effect of hole doping in this system by evidencing an increase in the spectral weight of  $d$  symmetry at the top of the valence band. In contrast to most of hole-doped cuprates and nickelates which only present significant spectral modifications for the unoccupied electronic states, a large spectral weight modification is observed in the photoemission spectra of  $Y_{2-x}Sr_xBaNiO_5$  for doping level as low as  $x=0.1$ . This singular behavior probably results from the large Ni  $3d$ -O  $2p$  hybridization along the chain direction and from the inhomogeneous character of the doped system.

## II. EXPERIMENTAL DETAILS

Polycrystalline samples of  $Y_{2-x}Sr_xBaNiO_5$  ( $x=0.0, 0.10$ , and  $0.20$ ) were prepared by standard solid-state reactions and characterized by x-ray powder diffraction, microprobe, and thermogravimetric analysis. Samples are single phased, homogeneously doped, and stoichiometric in oxygen.<sup>11</sup> Photoemission experiments have been carried out on the SU3 beam line of the French synchrotron facilities (LURE). The photon energy used was in the range extending from 60 eV to 200 eV. The sample surfaces were scraped *in situ* with a diamond file to obtain clean surfaces under the ultrahigh vacuum of less than  $10^{-10}$  Torr. The cleanliness of the surfaces was checked by the lack of contaminant in the valence-band spectrum and by x-ray photoemission core level spectra. The Fermi energy was calibrated by measuring the metallic edge of a Cu foil close to the sample. All measurements were carried out at room temperature with an energy resolution better than 50 meV.

## III. RESULTS AND DISCUSSION

In Fig. 1 we present angle-integrated photoemission spectra of  $Y_2BaNiO_5$  for photon energy varying between 60 eV and 200 eV. These spectra exhibit three features at  $E \approx -2.0$  eV,  $E \approx -3.5$  eV and  $E \approx -5.0$  eV, hereafter referred to as A, B, and C, respectively. The peak at  $-10$  eV, usually observed in Ni oxides, could originate from multi-electronic effects and/or impurity features.<sup>12</sup> The spectra are arbitrarily normalized on the C structure. With this normalization, a very strong photon-energy dependence of the A feature intensity is clearly observed. Owing to the different photon-energy dependence of  $d$  and  $p$  states' cross sections, this behavior suggests that the A feature is dominated by the Ni  $3d$  states, whereas the B and C features likely have  $p$  character. This result is in complete agreement with the previous measurements carried out in the Ca substituted oxide

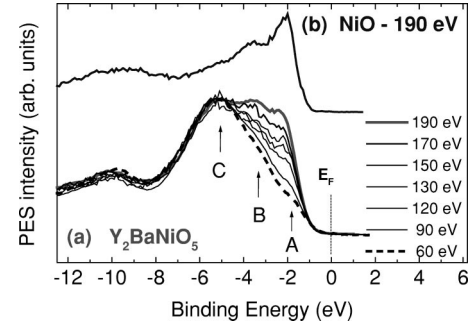


FIG. 1. (a) Angle-integrated photoemission spectra of  $Y_2BaNiO_5$  for several photon energies in the 60 eV–200 eV range. The spectra are arbitrarily normalized on the maximum of the C structure. (b)  $h\nu=190$  eV spectrum of NiO.

( $Y_{2-x}Ca_xBaNiO_5$ ) with HeI ( $h\nu=21.2$  eV) and Mg  $K\alpha$  ( $h\nu=1253.6$  eV) excitations,<sup>12</sup> which exhibit the same trend. Moreover, spin-polarized band calculations in the local-density approximation confirm this statement by showing that the C feature can be associated with O  $2p$ -Ni  $3d$  bonding states with dominant oxygen character, whereas the states in the energy region of the B feature correspond to oxygen  $2p$ - $2p$  interactions with a nonbonding character with respect to Ni  $3d$ -O  $2p$  interactions.<sup>12,13</sup> A satisfactory agreement between band calculation and photoemission spectra is found for these two kinds of states.<sup>12,13</sup> The top of the valence band in the calculations corresponds to antibonding states with a dominant Ni  $3d$  contribution. Recent LSDA +  $U$  calculations, which predict a quite correct energy-gap value, point out the highly hybridized character of these states.<sup>13</sup> A significant disagreement between band calculated density of states and photoemission spectrum is exhibited for these states. This is not surprising since the A structure represents excitations of correlated d states which are poorly described by one-electron (ground-state) approaches. Such a valence spectrum is usually observed in divalent Ni oxides such as NiO,<sup>14</sup> as observed in Fig. 1(b), where the photoemission spectrum of NiO recorded with 190 eV photon energy is presented. In NiO, the main structure close to  $-2$  eV has been interpreted to be due to  $d^8L$  states. The Ni  $3d$  derived structures are less resolved for  $Y_2BaNiO_5$  than for NiO (at the same photon energy) because the transition metal to oxygen atomic ratio is five times larger in the  $Y_2BaNiO_5$  compound. However, an increase in the absolute intensity of this feature can be evidenced by lowering the dimensionality in NiO (3D),  $La_2NiO_4$  (2D) and  $Y_2BaNiO_5$  (1D).<sup>10</sup>

Alternatively, transition metal oxides can be described in many-body approaches.<sup>15</sup>  $Y_2BaNiO_5$  belongs to the charge-transfer regime in the ZSA scheme because the charge-transfer parameter ( $\Delta$ ) is smaller than the Coulomb term  $U$ .<sup>10</sup> In this regime, the ligand  $p$  band is situated between the two Hubbard subbands. However, the photon-energy dependence of the photoemission spectrum clearly shows that Ni  $3d$  symmetry dominates in the first excited states of the photoemission spectrum, in contrast to what is naively expected in the charge-transfer regime for which the first electron removal excitations correspond to the formation of ligand

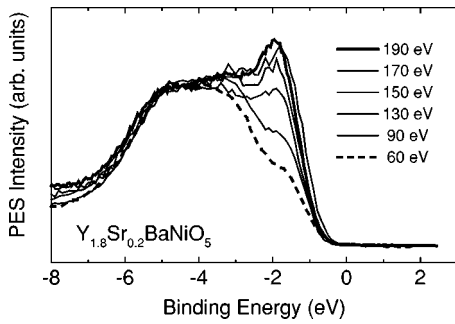


FIG. 2. Angle-integrated photoemission spectra of  $Y_{1.8}Sr_{0.2}BaNiO_5$  for several photon energies in the 60 eV–200 eV range.

holes in the  $p$  band. This behavior results from hybridization effect. Indeed, as shown in the single-impurity model,<sup>15</sup> the hybridization between Ni  $3d$  and O  $2p$  leads to a modification of the simple picture of a O  $2p$  band between the lower and upper Hubbard bands. The filled lower band will hybridize with the O  $2p$  states inducing the appearance of an image Hubbard band at the low-energy side of the  $p$  band<sup>15,16</sup> [Fig. 4(a)]. Cluster calculation shows that the first excitation state has a dominant  $d^8L$  character<sup>10</sup> confirming that the photoemission hole is essentially on the ligand site. Such a behavior is usually encountered in a divalent Ni oxide such as NiO.<sup>14</sup> Figure 2 shows the same photon-energy dependence for the doped  $Y_{1.8}Sr_{0.2}BaNiO_5$  compound. This evolution shows that the spectral feature at low energy significantly increases in intensity with increasing photon energy, confirming that this feature has a Ni  $3d$  character. Comparison with Fig. 1 shows that the main effect of hole doping is to increase the intensity of feature A. Moreover, a narrowing of the bandwidth is also observed. In order to illustrate the increase in intensity, we report in Fig. 3 the photoemission spectra of  $x=0.0, 0.1,$  and  $0.2$  oxides for  $h\nu=190$  eV after subtraction of the standard Shirley background. Note that this photon energy has been chosen in order to emphasize the doping effect on the spectral density. Nevertheless, Figs. 1 and 2 show that this effect is not energy dependent. Figure 3

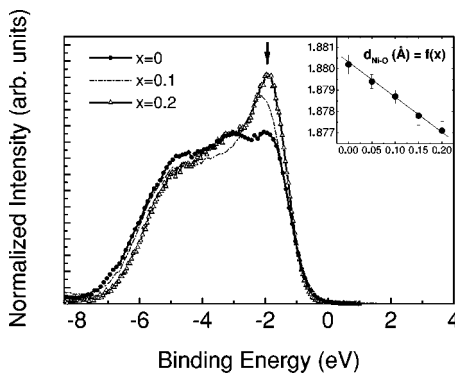


FIG. 3. Angle-integrated photoemission spectra for several dopings after subtraction of the Shirley background and normalized to the area (see explanation in the text). Inset: Ni-O distance as a function of doping  $x$  for Sr substituted samples. Data taken from Ref. 11.

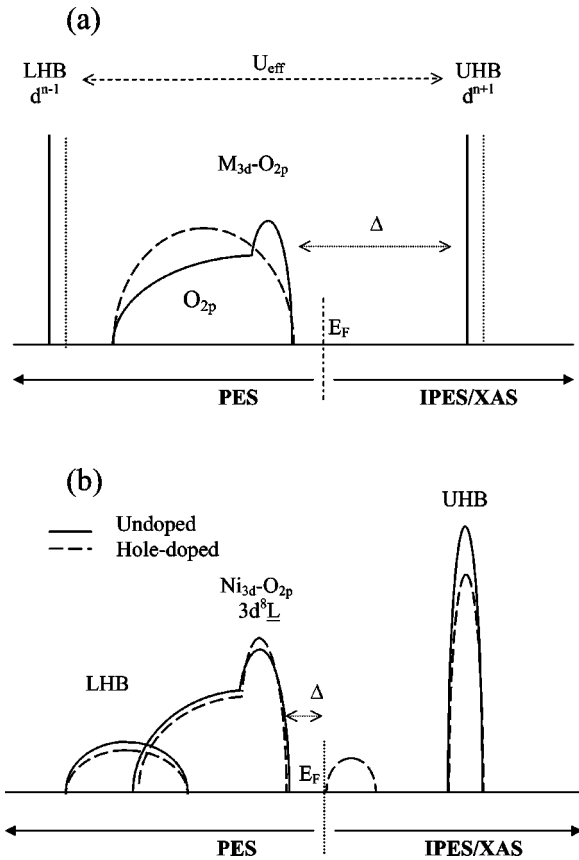


FIG. 4. (a) Effect of hybridization on the spectral density of a nondoped charge-transfer oxide in the impurity approach. From Ref. 15. (b) Schematic view of the situation encountered in  $Y_{2-x}Sr_xBaNiO_5$ . Hole doping leads to a large spectral weight transfer in the electron-addition part and more surprisingly to a spectral weight increase in the first electron-removal states.

illustrates the large effect of hole doping on the photoemission spectral weight in  $Y_{2-x}Sr_xBaNiO_5$ . First, the doping-induced states have a negligible density of states near the Fermi energy and do not yield the formation of a metal. The photoemission-probed part of the gap (400 meV) seems indeed to be not affected by doping. The present data and the optical conductivity of Ref. 9, which evidences a gap of 0.3 eV, confirm that the Fermi level is located immediately below the new unoccupied states induced by doping. The absence of spectral weight at  $E_F$  is corroborated by resistivity measurements, which show that the doped oxides remain insulating.<sup>9</sup> Second, even for low  $x$ , the  $A$  feature exhibits a very large increase in intensity with doping. This behavior contrasts to the usually observed spectral weight modification in hole-doped divalent Ni oxides, and more generally in cuprates and nickelates. In  $La_{2-x}Sr_xNiO_4$ , for instance, no significant increase in the spectral weight intensity is observed for doping levels smaller than  $x=0.5$ .<sup>17</sup> Unfortunately, due to the relative content of O  $2p$  and Ni  $3d$  states, it is not really possible to quantitatively estimate the weight of the  $d^8L$  state. Transfers of spectral weight in hole-doped strongly correlated systems have been previously discussed in detail in the literature.<sup>16</sup> Anomalous spectral weight modifications related to electronic correlations are expected in the

electron-addition part (unoccupied states) of hybridized charge-transfer systems. This trend is indeed observed in the XAS oxygen  $K$  edge of  $Y_{2-x}(\text{Ca,Sr})_x\text{BaNiO}_5$  (Refs. 5 and 11) as well as in inverse photoemission.<sup>10</sup> However the electron-removal part of the spectrum (occupied states) should slightly decrease upon doping within this approach (since some low-energy states are depopulated), in contrast to the spectroscopic behavior. An additional mechanism has to be invoked to explain the evolution of photoemission spectra with Sr content. Interestingly, hole doping in  $Y_2\text{BaNiO}_5$  could result in an increase in the Ni  $3d$ -O  $2p$  hybridization, since, unlike in  $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ ,<sup>18</sup> the average Ni-O distance shortens continuously upon doping (see inset of Fig. 3 for  $Y_{2-x}\text{Sr}_x\text{BaNiO}_5$  and Refs. 19 and 20 for  $Y_{2-x}\text{Ca}_x\text{BaNiO}_5$ ). As the apical Ni-O distance in  $Y_2\text{BaNiO}_5$  is the shortest one observed in nickelates, a small decrease should lead to a large increase in hybridization. This will be emphasized in case of an inhomogeneous doping. If the doped holes are trapped in local bound states, disturbing the electronic states only in their vicinity,<sup>7,9</sup> the real Ni-O bonds in these perturbed parts of the sample should be shorter than the average one measured by x rays. As a consequence, in the photoemission spectra, which are the simple addition of unperturbed parts and doped parts, the  $A$  peak enhancement should originate mainly from the hole-doped regions, where the hybridization strongly increases. Therefore, the  $d$  character of the top of the valence band should be emphasized in the doped compounds due to this strong hybridization enhancement. A similar effect is expected for Ca doped materials and has been observed for highly doped samples in x-ray photoemission<sup>12</sup> in spite of the poor energy resolution.

This scenario of a very large spectral weight modification due to doping-dependent hybridization is in qualitative agreement with the modification of the valence photoemission spectra we observed with Sr content in  $Y_{2-x}\text{Sr}_x\text{BaNiO}_5$ . Figure 4 summarizes the spectroscopic results obtained on hole-doped  $Y_{2-x}\text{Sr}_x\text{BaNiO}_5$ . First, we recall in Fig. 4(a) the effect of hybridization in the impurity approach used to describe qualitatively the spectroscopy of homogeneous charge-transfer transition-metal oxides.<sup>15</sup> Hybridized  $d^8L$  states appear at the top of the O  $2p$  band. Obviously, the  $3d$  character of these states increases with

increasing Ni  $3d$ -O  $2p$  hybridization. Second, Fig. 4(b) illustrates the effect of hole doping in  $Y_2\text{BaNiO}_5$ . In charge-transfer systems, hole doping usually affects the electron-addition spectra by the appearance of the spectral feature just above the Fermi energy associated with the hole states. Hybridization, by introducing  $d$  character in these states, could enhance its spectral weight.

The singular behavior in doped  $Y_2\text{BaNiO}_5$  is the increase in intensity of the first ionization states. This evolution, similar to what is presented in Fig. 4(a), reflects the increase in hybridization within the localized hole-doped regions. We note that a theoretical treatment, based on a multiband Hamiltonian containing the relevant Ni and O orbitals, gives large values of transfer integrals within a hole-doped  $\text{NiO}_6$  cluster.<sup>21</sup> This singular spectroscopic signature, only observed in doped  $Y_2\text{BaNiO}_5$ , could result from the particularly small Ni-O distance characterizing this quasi-1D compound.

#### IV. CONCLUSION

To summarize, we have performed an angle-integrated photoemission investigation of the spectral weight modification by hole doping in the  $Y_{2-x}\text{Sr}_x\text{BaNiO}_5$  oxides. In this Haldane chain compound, hole doping leads to strong modifications in the unoccupied part of the spectral density as usually observed in cuprates and nickelates. However, photoemission spectroscopy exhibits a singular behavior, since a significant spectral weight increase corresponding to final states with  $d$  character is observed. We propose that this surprising behavior could result from an increase in hybridization between Ni  $3d$  and O  $2p$  states induced by the reduction of Ni-O distance in the chain direction by doping. Such an effect is favored by the inhomogeneous character of doping. We hope that reliable calculations will be performed in the future to understand this anomalous spectral weight enhancement.

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