Valence changes associated with the metal-insulator transition in Bi$_{1-x}$La$_x$NiO$_3$

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Perovskite-type BiNiO$_3$ is an insulating antiferromagnet in which a charge disproportionation occurs at the Bi site. La substitution for Bi suppresses the charge disproportionation and makes the system metallic. We have measured the photoemission and x-ray absorption (XAS) spectra of Bi$_{1-x}$La$_x$NiO$_3$ to investigate how the electronic structure changes with La doping. From Ni 2p XAS, we observed an increase of the valence of Ni from 2+ toward 3+. Combined with the core-level photoemission study, it was found that the average valence of Bi remains $\sim$ 4+ and that the Ni valence behaves as $\sim$ (2 + $x$)+, that is, La substitution results in hole doping at the Ni sites. In the valence-band photoemission spectra, we observed a Fermi cutoff for $x > 0$, consistent with the metallic behavior of the La-doped compounds. The Ni 2p XAS, Ni 2p core-level photoemission, and valence-band photoemission spectra were analyzed by configuration-interaction cluster-model calculation, and the spectral line shapes were found to be consistent with the gradual Ni$^{2+} \rightarrow$ Ni$^{3+}$ valence change.

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I. INTRODUCTION

Perovskite-type 3d transition-metal oxides exhibit various interesting physical properties, such as metal-insulator (MI) transition, colossal magnetoresistance (CMR), and ordering of spin, charge, and orbitals[1]. Among them, the charge-transfer-type RNiO$_3$ ($R$ = rare earth) forms a prototypical system in which an MI transition occurs in a systematic manner, namely, as a function of the radius of the $R$ ion and hence of the one-electron bandwidth[2, 3]. The least distorted LaNiO$_3$ is a paramagnetic metal, whereas more distorted RNiO$_3$ with a smaller $R$ ion becomes an antiferromagnetic insulator. Some RNiO$_3$ with an $R$ ion of intermediate size shows a metal-insulator transition as a function of temperature, too.

In this context, BiNiO$_3$ had been expected to be metallic, if synthesized, because the ionic radius of Bi$^{3+}$ is larger than that of La$^{3+}$. Recently, Ishiwata et al. succeeded in synthesizing BiNiO$_3$ under a high pressure of 6 GPa[4]. Contrary to the above expectation, BiNiO$_3$ was found to be an insulating antiferromagnet with localized spins of $S = 1$. X-ray powder diffraction (XRD) study revealed that the Bi ions were charge-disproportionated into “Bi$^{3+}$” and “Bi$^{5+}$”. Thus the oxidation state of the Ni ion was concluded to be 2+ rather than 3+. To the authors’ knowledge, such a charge disproportionation at the A-site in the perovskite structure has never been reported so far. Since Bi has a deep 6s level, and such a high valence state as “Bi$^{5+}$” at A-site would not be stable from the viewpoint of the Madelung potential[5], the realistic charge configuration of Bi$^{5+}$ may be expressed as Bi$^{5+}$+$\overline{L}$, where $\overline{L}$ denotes a hole in the O 2p band. Subsequently, it was reported that the substitution of La for Bi suppressed the charge disproportionation and made the system conducting[6]. Therefore, an interesting question for this system is how the electronic structure changes from the charge-disproportionated insulating BiNiO$_3$ to the metallic LaNiO$_3$ with La substitution. One possible scenario is that the La substitution suppresses the charge disproportionation and changes the average valence of Bi from 4+ to 3+. If so, the valence of Ni would become 3+, and the Ni atoms become responsible for the metallic conductivity. Another scenario is that the La substitution suppresses the charge disproportionation but the average valence of Bi remains 4+. If so, the valence of Ni becomes (2 + $x$)+, and both the Bi and Ni sites contribute to the metallic conductivity. To settle this question, we have investigated the electronic structure of Bi$_{1-x}$La$_x$NiO$_3$ by photoemission and x-ray absorption spectroscopy (XAS). Our result seems to support the latter scenario.

II. EXPERIMENT

Preparation and characterization of polycrystalline Bi$_{1-x}$La$_x$NiO$_3$ ($x = 0$, 0.05, 0.1, 0.2) are described elsewhere[4, 6]. Figure[1] shows the electrical resistivity of Bi$_{1-x}$La$_x$NiO$_3$[6]. For $x = 0$ (BiNiO$_3$), the system is insulating. Electrical resistivity decreases with La substitution. For $x = 0.05$, 0.075, and 0.1, a broad MI transition occurs as a function of temperature. For $x = 0.2$
and 0.5, the system is metallic. All the experiments except for ultraviolet photoemission spectroscopy (UPS) were performed at BL-2C of Photon Factory (PF), High Energy Accelerators Research Organization (KEK). UPS measurements were performed using a high-flux discharging lamp with a troidal grating monochromator. The photoemission and x-ray absorption measurements were performed under an ultrahigh vacuum of $\sim 10^{-10}$ Torr at room temperature. The photoemission spectra were measured using a Scienta SES-100 electron-energy analyzer. At KEK-PF, the total energy resolution was about 200-500 meV depending on the photon energy, whereas for UPS measurements it was set to about 10 meV and 50 meV for the He I (21.2 eV) and He II (40.8 eV) light sources, respectively. The Fermi level ($E_F$) position was determined by measuring gold spectra. The XAS spectra were measured by the total-electron-yield method. Clean surfaces of the samples were obtained by repeated in-situ scraping with a diamond file.

III. RESULTS AND DISCUSSION

A. Ni 2p x-ray absorption and Ni 2p core-level photoemission spectra

Figure 2 (a) shows the Ni 2p XAS spectra of $\text{Bi}_{1-x}\text{La}_x\text{NiO}_3$. The Ni 2$p_{3/2}$ peak overlaps the La 3$d_{5/2}$ $\rightarrow$ 4$f$ absorption peak. As reported previously [7], the Ni 2p XAS spectra of $\text{RNiO}_3$ (Ni$^{3+}$) are very different from that of NiO (Ni$^{2+}$): The 2$p_{3/2}$ spectrum consists of two peaks labelled as A and B, as shown in Fig. 2 (a). The lower energy peak A is stronger than the higher energy one B for NiO, whereas the two peaks have similar intensities in $\text{RNiO}_3$ (as shown in Fig. 2 (b)). The spectrum of $x = 0$ is similar to that of Ni$^{2+}$, which is consistent with the report that the valence of Ni is 2+ in $\text{BiNiO}_3$ [4]. With increasing $x$, the relative intensity of the higher energy peak increases, indicating that the valence of Ni gradually decreases from Ni$^{2+}$ toward Ni$^{3+}$. Figure 3 shows the Ni 2p photoemission spectra of $\text{Bi}_{1-x}\text{La}_x\text{NiO}_3$. As in the case of XAS, the Ni 2$p_{3/2}$ core level overlaps the La 3$d_{5/2}$ core level. The Ni 2p photoemission spectra do not change with $x$, consistent with the reports that the line shapes of the Ni 2p photoemission spectra of $\text{RNiO}_3$ (Ni$^{3+}$) or Ni$^{2+}$ are almost the same as that of $\text{La}_2\text{NiO}_4$ (Ni$^{2+}$) [10].

In order to confirm that the Ni 2p XAS and photoemission spectra are consistent with the Ni$^{2+}$ $\rightarrow$ Ni$^{3+}$ va-
lence change with La substitution, we have performed a configuration-interaction (CI) cluster-model calculation \[^{11,12}\]. Here, we considered a [NiO\(_6\)]\(^{10-}\) octahedral cluster in the case of Ni\(^{2+}\) and a [NiO\(_6\)]\(^{9-}\) one in the case of Ni\(^{3+}\). In this model, parameters to be fitted are the charge-transfer energy from the O 2p orbitals to the empty Ni 3d orbitals denoted by \(\Delta\), the 3d – 3d on-site Coulomb interaction energy denoted by \(U\), and the hybridization strength between the Ni 3d and O 2p orbitals denoted by Slater-Koster parameters denoted by \((pd\sigma)\) \[^{13}\]. The configuration dependence of the transfer integrals has been taken into account \[^{17}\]. Racah parameters B and C are fixed at 0.142 and 0.527 eV, \(^{−}\)Ref. \[^{12}\]. The Slater integrals between the Ni 2p\(^d\pi\) orbitals and the valence \(p\) orbitals are \(0.1 eV\) in the case of PrNiO\(_3\). The Slater-Koster parameters denoted by \((pd\sigma)\) \[^{13}\]. The ratio of \((pd\sigma)/(pd\pi)\) is fixed to be \(-2.2\) \[^{14,15}\]. The configuration dependence of the transfer integrals has been taken into account \[^{17}\]. Racah parameters B and C are fixed at 0.142 and 0.527 eV, 80% of the atomic Hartree Fock values \[^{17,18}\]. We took into account the intra-atomic multiplet coupling for the Ni 2p XAS spectrum and the valence band spectrum, whereas the multiplet coupling between the core hole and the valence \(d\) electrons was not taken into account for the Ni 2p photoemission spectrum as in the case of Ref. \[^{12}\]. The Slater integrals between the Ni 2p and 3d orbitals are \(F^2 = 6.68, G^1 = 5.07,\) and \(G^2 = 2.88 eV\). The multiplet-averaged 2p-3d Coulomb interaction \(Q(= F^2 - \frac{1}{15} G^3 - \frac{3}{2} G^2)\) is \(\sim 9.3 eV\) in the case of Ni\(^{2+}\) and \(\sim 10 eV\) in the case of Ni\(^{3+}\), satisfying the relationship \(U/Q \sim 0.7\).

The calculated Ni 2p XAS spectra have been broadened by a Gaussian and a Lorentzian. The full width at half maximum (FWHM) of the Gaussian is \(\sim 1.0 eV\), which is determined by the instrumental resolution and the effect of electron-phonon coupling \[^{19}\] and that of the Lorentzian is \(\sim 0.5 eV\), which is determined from the natural width \[^{20}\]. The calculated Ni 2p core-level photoemission spectra have been broadened with an energy-dependent Lorentzian with a FWHM \(2\Gamma = 2\Gamma_0 (1 + \alpha \Delta E)\), where \(\Delta E\) denotes the energy separation from the main peak. We adopted the values \(\alpha = 0.15\) and \(\Gamma_0 = 1.2 eV\). We then used a Gaussian broadening of 1.0 eV to simulate the instrumental resolution and broadening due to the core hole-3d multiplet coupling.

Figure 3 shows that the Ni 2p photoemission spectra thus calculated reproduce the experimental Ni 2p photoemission spectra very well both in the cases of Ni\(^{2+}\) and Ni\(^{3+}\). These calculated spectra have been obtained with \(\Delta = 4.5 eV, \ U = 6.5 eV,\) and \((pd\sigma) = -1.5 eV\) in the case of Ni\(^{2+}\) and \(\Delta = 1.0 eV, \ U = 7.0 eV,\) and \((pd\sigma) = -1.1 eV\) in the case of Ni\(^{3+}\). These values are close to those previously reported: \(\Delta = 4.5 eV, \ U = 7.0 eV,\) and \((pd\sigma) = -1.2 eV\) in the case of La\(_2\)NiO\(_4\) (Ni\(^{2+}\)) \[^{10}\] and \(\Delta = 1.0 eV, \ U = 7.0 eV,\) and \((pd\sigma) = -1.5 eV\) in the case of PrNiO\(_3\) (Ni\(^{3+}\) or Ni\(^{2+}\)) \[^{7}\]. On the other hand, Fig. 2 shows that the calculated Ni 2p XAS spectrum for Ni\(^{2+}\) is very different from that for Ni\(^{3+}\). It should be noted that we have used the same parameter sets as in the case of Ni 2p photoemission spectra. The result thus explains why the Ni 2p XAS spectra change with the Ni valence, whereas the Ni 2p photoemission spectra do not.

In order to evaluate the Ni valence more quantitatively from Ni 2p XAS, we have subtracted the contribution of La 3d\(_{3/2}\) XAS and compared the spectra with those of BiNiO\(_3\) (Ni\(^{2+}\)) and PrNiO\(_3\) (Ni\(^{3+}\)). Figure 4(a) shows the Ni 2p XAS spectra after the subtraction of background and the La 3d\(_{3/2}\) contribution. From the relative intensities of the two peaks, one can estimate the Ni valence as a function of \(x\) as shown in Fig. 4. Here, we have assumed that the spectrum of \(x = 0\) represents pure Ni\(^{2+}\), and adopted that of PrNiO\(_3\) as a reference of Ni\(^{3+}\). Figure 4 shows that the valence of Ni behaves approximately as \((2 + x)^{+}\), rather than \(3^{+}\), the value expected when the average valence of Bi becomes \(3^{+}\) upon La substitution. The result indicates that La substitution does not change the average valence of Bi, while suppressing the charge disproportionation at the Bi site, and the valence of Ni becomes \(\sim (2 + x)^{+}\). The valence of Bi shall be discussed below.

### B. O 1s and Bi 4f core-level photoemission spectra

Figure 5 shows the core-level photoemission spectra of O 1s and Bi 4f. Each O 1s spectrum consists of a single peak with negligible amount of contamination signals on the higher-binding-energy side, meaning that the surfaces of the samples became clean by scraping. The Bi 4f spectrum of BiNiO\(_3\) does not show two components corresponding to Bi\(^{3+}\) and Bi\(^{5+}\), suggesting that the spectrum reflects the average valence of the Bi atom. The absence of a splitting into Bi\(^{3+}\) and Bi\(^{5+}\) components has been reported for BaBiO\(_3\) \[^{21}\], too, which was also thought to exhibit a charge disproportionation into Bi\(^{3+}\) and Bi\(^{5+}\). The peak positions of both core-level spectra change with \(x\). In Fig. 5(a), we have plotted the positions of the O 1s and Bi 4f core levels and their differences as functions of \(x\). Both core levels are shifted downward up to \(x \lesssim 0.1\) and then shifted upward from \(x \sim 0.1\) to \(x = 0.2\).

The shift \(\Delta E_B\) of a core-level binding energy with
both the Ni site (Ni substitution donates holes to the Ni sites. Charge trans-
average valence of Bi remains constant, meaning that La

\[ \Delta E_B = \Delta \mu + K \Delta Q + \Delta V_M + \Delta E_R, \]

where \( \Delta \mu \) is the change in the chemical potential, \( \Delta Q \) is the change in the number of valence electrons on the atom considered, \( \Delta V_M \) is the change in the Madelung potential, and \( \Delta E_R \) is the change in the core-hole screening. The similar shifts of the O 1s and Bi 4f core levels indicate that the change in the Madelung potential (\( \Delta V_M \)) is negligibly small because it would shift the core levels of anions and cations differently. Core-hole screening by conduction electrons is also considered to

Therefore, the result indicates that the chemical potential moves downward with increasing \( x \), that is, hole doping takes place with La substitution from \( x \sim 0.1 \) to \( x = 0.2 \). For \( x \leq 0.1 \), however, the core levels are shifted in the opposite direction, probably reflecting the change of the band structure caused by the considerable change in the lattice constants between \( x = 0 \) and 0.05 \( x \). The O 1s – Bi 4f difference is free from the chemical potential shift and is considered to reflect the valence change of Bi called “chemical shift” denoted by \( K \Delta Q \) in Eq. (1). From Fig. 3(a), the energy difference remains almost the same for all values of \( x \), indicating that the valence of Bi does not change appreciably. Figure 2(b) shows that the valence of Bi calculated from the valence of Ni in Fig. 4 does not change appreciably. Figure 6(b) shows that the lattice constants between band structure caused by the considerable change in the valence of Bi increases with increasing \( x \), while the valence of Bi remains almost unchanged, 4+. Combining these results with the result of Ni 2p XAS, we conclude that the valence of Ni increases with increasing \( x \), while the average valence of Bi remains constant, meaning that La substitution donates holes to the Ni sites. Charge transport in this system is therefore attributed to holes at both the Ni site (\( \text{Ni}^{2+} \) or \( \text{Ni}^{3+} \)) and the Bi site (\( \text{Bi}^{4+} \) or \( \text{Bi}^{3+} \)).

C. Valence-band photoemission spectra

The valence-band spectra of \( \text{Bi}_{1-x}\text{La}_x\text{NiO}_3 \) taken at 600 eV are shown in Fig. 7(a). Considering the photoionization cross-sections [26], most of the contributions come from Ni 3d and contributions from O 2p and Bi 6s are very small. (The relative photoionization cross-sections of the Ni 3d, O 2p, and Bi 6s orbitals are \( \sim 7 : 1 : 1 \) [26].) One can observe three main structures labeled as A (\( \sim -1.7 \) eV), B (\( \sim -3.3 \) eV), and C (\( \sim -6 \) eV) and the satellite structure at \( \sim -11 \) eV. Figure 7(c) shows the photon energy dependence of the valence-band spectrum of \( x = 0.2 \), including the spectra taken at \( h\nu = 21.2 \) eV and 40.8 eV. According to the photon-energy dependence of the photoionization cross-sections, the He I spectrum is dominated by the O 2p contribution (Ni 3d : O 2p : Bi 6s \( \sim 0.37 : 1 : 0.003 \)). The Ni 3d contribution increases with increasing photon energy. Structure A, which is most pronounced at 600 eV, is therefore attributed to the contributions for Ni 3d. On the other hand, structures B and C are due to the O 2p band. This assignment is in agreement with other Ni oxides like NiO [11] and RNiO [2]. We also performed CI cluster-model calculation by using the same parameters as in the case of Ni 2p XAS and photoemission. At the bottom of Fig. 7(a) are shown the calculated spectra for the \([\text{NiO}_6]^{10-}\) cluster (\( \text{Ni}^{2+} \)) and the \([\text{NiO}_6]^{9-}\) cluster (\( \text{Ni}^{3+} \)). The calculated valence-band spectra have been broadened with a Gaussian of 0.8 eV FWHM to account for the combined effects of the instrumental resolution and the d band dispersion, and an energy-dependent Lorentzian (FWHM = 0.2|\( E - E_F \)|) (Ref. [27]) to account for the lifetime broadening of the photohole. Considering the photoionization cross-sections, the Ni 3d emission over-whelms the O 2p emission at \( h\nu = 600 \) eV, where three main structures and the satellite structure are well reproduced in the calculation for both \( \text{Ni}^{2+} \) and \( \text{Ni}^{3+} \).

Spectra in the vicinity of \( E_F \) are shown in Fig. 7(b). There is no \( E_F \) cutoff for the \( x = 0 \) sample, consistent with the insulating behavior. Upon La substitution,
emission appears at $E_F$ and increases with increasing $x$, indicating the insulator-to-metal transition induced by La substitution.

**IV. CONCLUSION**

In conclusion, we have measured the photoemission and x-ray absorption spectra of Bi$_{1-x}$La$_x$NiO$_3$. From Ni 2p XAS, we observed the change of the valence of Ni. Combined with core-level photoemission studies, it was found that the average valence of Bi remains $\sim$ 4+ with increasing $x$, and La substitution causes hole doping into the Ni sites. These results mean that both the Bi and Ni sites contribute to the metallic conductivity. From the valence-band spectra, we observed a Fermi-level cutoff for $x > 0$. The spectra of the Ni 2p XAS, the Ni 2p photoemission, and the valence band have been analyzed by configuration-interaction cluster-model calculation, and good agreement between experiment and calculation was obtained.

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