2C/2003G149

Valence changes associated with the metal-insulator transition in $Bi_{1-x}La_xNiO_3$

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Introduction

Perovskite-type $RNiO_3$ exhibits a metal-insulator (MI) transition as a function of the ionic radius of the rare-earth R ion. $BiNiO_3$ was expected to be metallic because $LaNiO_3$ remains metallic down to 1.5 K and the ionic radius of Bi^{3+} is larger than that of La^{3+}. Contrary to this expectation, $BiNiO_3$ is an insulating antiferromagnet because the Bi ions are charge-disproportionated into Bi^{3+} and Bi^{5+} and thus the oxidation state of the Ni ion becomes 2+ rather than 3+ [1]. It was also reported that the substitution of La for Bi suppresses the charge disproportionation and makes the system conducting [2]. Therefore, an interesting question is how the electronic structure changes from the charge-disproportionated insulating $BiNiO_3$ to the metallic $LaNiO_3$. To settle this question, we investigated the electronic structure of $Bi_{1-x}La_xNiO_3$ by photoemission and x-ray absorption spectroscopy (XAS).

Experimental

Preparation and characterization of polycrystalline $Bi_{1-x}La_xNiO_3$ ($x = 0, 0.05, 0.1, 0.2$) are described elsewhere [1, 2]. For $x = 0$ ($BiNiO_3$), the system is insulating. Electrical resistivity decreases with La substitution. For $x = 0.05$ and 0.1, a broad MI transition occurs as a function of temperature. For $x = 0.2$, the system is metallic. Experiment was performed at BL-2C of Photon Factory. The photoemission and x-ray absorption measurements were performed under an ultrahigh vacuum of 10^{-10} Torr at room temperature. The photoemission spectra were measured using a Scienta SES-100 electron-energy analyzer. The total energy resolution was about 200-500 meV depending on the photon energy. The Fermi level (E_F) position was determined by measuring gold spectra. The XAS spectra were measured by the total-electron-yield method. All the measurements were performed at room temperature. Clean surfaces of the samples were obtained by repeated *in-situ* scraping with a diamond file.

Results and Discussion

Figure 1 shows the Ni $2p$ XAS spectra of $Bi_{1-x}La_xNiO_3$. The Ni $2p_{3/2}$ peak overlaps the La $3d_{3/2} \rightarrow 4f$ absorption peak. As reported previously [3], the Ni $2p$ XAS spectra of $RNiO_3$ (Ni^{3+}) are very different from that of NiO (Ni^{2+}): The $2p_{3/2}$ spectrum consists of two peaks labeled as A and

B, as shown in Fig. 1. The lower energy peak A is stronger than the higher energy one B for NiO, whereas the two peaks have similar intensities in $RNiO_3$. 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 this material [1]. With increasing x, the relative intensity of the higher energy peak increases, indicating that the valence of Ni gradually increases from Ni^{2+} toward Ni^{3+}. In order to evaluate the Ni valence from Ni $2p$ XAS more quantitatively, 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+}). From the relative intensities of the two peaks, one can estimate the Ni valence as a function of x. 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+}. The valence of Ni is approximately $(2+x)+$ rather than 3+, the value expected when the average valence of Bi becomes 3+ due to the La substitution. The result indicates that La substitution does not change the average valence of Bi appreciably, while suppressing the charge disproportionation at the Bi site, and that the valence of Ni is ~ 2+x. This result is consistent with the core-level photoemission study.
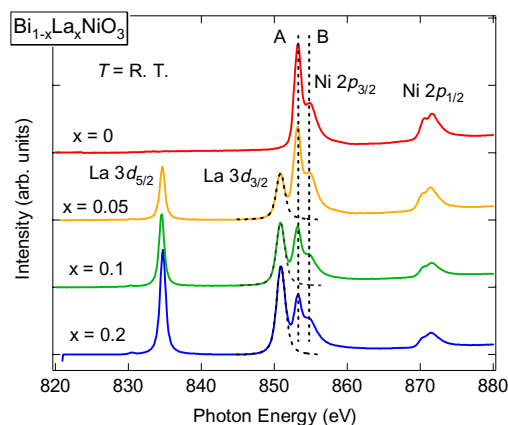

FIG. 1: Ni $2p$ XAS spectra of $Bi_{1-x}La_xNiO_3$. The dashed lines represent the La $3d_{3/2}$ absorption peaks.

References

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