Iron-resonant valence band photoemission and oxygen near edge x-ray absorption fine structure study on $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{0.75}\text{Ni}_{0.25}\text{O}_{3-\delta}$

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Iron resonant valence band photoemission spectra (VB PES) of Sr substituted $\text{LaFe}_{0.75}\text{Ni}_{0.25}\text{O}_{3-\delta}$ have been recorded across the Fe $2p$ - $3d$ absorption threshold to obtain Fe specific spectral information on the $3d$ projected partial density of states. Comparison with $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ resonant VB PES literature data suggests that substitution of Fe by Ni forms electron holes which have mainly O $2p$ character. Substitution of La by Sr increases the hole concentration to an extent that the e_g structure vanishes. The variation in the e_g and t_{2g} structures is paralleled by the changes in the electrical conductivity. © 2010 American Institute of Physics. [doi:10.1063/1.3484960]

The electronic structure of defect regulated materials is important for understanding their functional relationship such as transport properties. The electrical conductivity of oxides with perovskite structure depends on their valence band (VB) characteristic.¹ $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ (LSFO) is a parent compound that can be used in solid oxide fuel cell cathodes,² and the conductivity particularly at high temperature is an important quantity for its functionality as a cathode. Sr substitution of LaFeO_3 , which is an insulator, forms electron holes which are associated with nominally tetravalent Fe having the electronic structure of $3d^5\bar{\downarrow}$, $\bar{\downarrow}$ denoting the electron hole from the oxygen. Substitution by 50% ($\text{Fe}^{3+}/\text{Fe}^{4+}=1/1$) warrants that the electron hopping across the $\text{Fe}^{3+}-\text{O}-\text{Fe}^{4+}$ superexchange unit occurs with maximum probability. It has been shown that Fe substitution of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ on the B-site by Ni (Ref. 3) or Co improves the conductivity, with a conductivity maximum at temperatures around 650–750 K, making them attractive for intermediate temperature proton conducting ceramic fuel cells.⁴ The structural and transport properties of $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{1-y}\text{Ni}_y\text{O}_{3-\delta}$ have been studied for different stoichiometries (x , y).^{5–7} It has also been explained how the electronic structure evolves from charge transfer-type insulator LaFeO_3 (2 eV band gap) to the “oxygen-hole metal” SrFeO_3 (Ref. 8) using *in situ* photoemission spectroscopy (PES) on thin films. Out of the rare-earth nickel oxides, LaNiO_3 is the only metallic member.⁹ Chainani *et al.*¹⁰ showed a systematic x-ray photoemission study on bulk LSFO. However, the influences of Ni and Sr substitution on electronic structure, especially for occupied states of Fe, are still not clear.

We employ Fe resonant VB PES to investigate the influence of the Ni-substitution and Sr-substitution with respect to

the Fe, which is the main player for the electrical conductivity via the $\text{Fe}^{3+}-\text{O}-\text{Fe}^{4+}$ superexchange unit.

The A-site substitution of LaFeO_3 by Sr ($\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$) and its impact on the electronic conductivity is well understood. In the oxygen near edge x-ray absorption fine structure (NEXAFS) spectra this substitution manifests in a so called hole doping state with $e_g\uparrow$ symmetry as the leading peak in the O $1s$ pre-edge, preceding the two $t_{2g}\downarrow$ and $e_g\downarrow$ orbital symmetry peaks from the hybridized O $2p$ -Fe $3d$ states. Interestingly, B-site substitution with Ni, too, shows such extra peak. The question naturally arises as to which role Fe and Ni play for the corresponding spectra.

High purity precursors ($\text{La}_2\text{O}_3 > 99.99\%$, SrCO_3 , 99.9% $\text{Fe}_2\text{O}_3 > 99.0\%$, and NiO 99.8%, purities given in weight %) were mixed in stoichiometric proportions, ball milled for 24 h, calcined for 4 h at 1473 K and for 12 h at 1673 K so as to obtain $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{0.75}\text{Ni}_{0.25}\text{O}_{3-\delta}$ (LSFN) with $x=0, 0.50, 0.75$.¹¹ X-ray powder diffractograms confirmed that the samples had rhombohedral symmetry (space group: $R\bar{3}c$, space group number: 167), with a barely noticeable contamination of a tetragonal phase.¹² The four-point dc conductivity shows the same trend like in Ref. 11. For VB PES measurements the fine powders were uniaxially pressed into disks ($\sim \varnothing 13$ mm) at 40 KN and then sintered at 1673 K for 12 h. Photoemission spectra were recorded at end station¹³ at beamline 9.3.2 of the Advanced Light Source, Lawrence Berkeley National Laboratory. The energy resolution of the beamline is $E/\Delta E=3000$.¹⁴ The spectra were recorded in the maximum transmission mode. During measurements the base pressure of the main chamber was maintained at 10^{-9} Torr. The resonant VB PES spectra for Fe metal were measured using photon energies between 704 and 716 eV, leading up to the $2p_{3/2}$ resonance energies. NEXAFS spectra were measured at beamline 8.0.1 in total electron yield mode at 300 K.

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FIG. 1. (Color) Fe 2p-3d resonant VB PES spectra of $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{0.75}\text{Ni}_{0.25}\text{O}_{3-\delta}$. There is on-resonance condition at 710 eV. (a) $x=0$, (b) $x=0.50$, (c) $x=0.75$. (d) Expanded VB PES spectra at Fe 2p-3d on-resonance (710 eV), with an inset showing that the intensity for $x=0.75$ is in between those for $x=0$ and 0.5 .

Figures 1(a)–1(c) show the VB PES spectra of $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{0.75}\text{Ni}_{0.25}\text{O}_{3-\delta}$ for $x=0.0$, 0.50 , and 0.75 obtained by tuning the excitation photon energy across the Fe 2p $\rightarrow$ 3d absorption threshold. The expanded VB PES spectra at Fe 2p-3d on-resonance (710 eV) are shown in Fig. 1(d). Figure 2 shows the normalized Fe L_3 ($2p_{3/2}$) and L_2 ($2p_{1/2}$) x-ray absorption spectra for $x=0$ and $x=0.50$, marked with the energy positions, at which the resonant PES data were recorded. The Fe L edge is split into an L_3 and L_2 multiplet due to the core hole spin orbit coupling. The L_3 and L_2 edges are additionally split by the crystal field into peaks from transitions that arise from states with t_{2g} and e_g orbital symmetry. Visual inspection of the two spectra suggests that the sharp multiplet for $x=0$ corresponds to Fe with predominant Fe^{3+} valence, whereas the more broad multiplet for $x=0.5$ corresponds to Fe with a mixed valence between Fe^{3+} and Fe^{4+} , particularly because of the relatively less intense t_{2g} structure in the L_3 edge. Comparison of simulated spectra based on atomic multiplet theory and measured spectra indeed shows that a very good match is obtained when for x

FIG. 2. (Color) Top panels—Normalized Fe $L_{2,3}$ edge x-ray absorption spectra of $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{0.75}\text{Ni}_{0.25}\text{O}_{3-\delta}$ for $x=0$ and $x=0.50$. Vertical lines denote the energies where VB PES spectra were collected. Bottom panels—atomic multiplet simulation spectra for the same stoichiometries.

$=0$ Fe is entirely Fe^{3+} , and for $x=0.5$ Fe is to equal amounts in Fe^{3+} (50%) and in Fe^{4+} (50%), all of which in the high spin state.¹¹

All spectra are normalized to the photon flux. The resonant enhancement of the spectral intensity at 710 eV (on-resonance), which reflects the Fe 3d partial density of states of LSFN, is clear. It is instructive to enter the discussion of the spectral features of LSFN by referring to the previously discussed VB PES spectra of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$.¹⁵ The VB spectra are known to consist of four principal structures, i.e., an e_g state (A) near the Fermi energy, a state with t_{2g} symmetry (B), the Fe 3d–O 2p bonding state peak (C), and a charge transfer satellite (D).¹⁵ The $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{0.75}\text{Ni}_{0.25}\text{O}_{3-\delta}$ samples studied here are polycrystalline sintered bodies with a finite porosity. Such samples have a larger surface-to-volume ratio than single crystals. It is known that $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ surfaces are slightly under-stoichiometric and oxygen deficient, thus providing the iron atoms near the surface a less than sixfold octahedral coordination. This may be a reason why the VB structures near E_F , particularly the t_{2g} and e_g structures are less pronounced in our sintered polycrystalline samples than those in single crystals.

A comparison of the VB PES spectra for $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ and $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{0.75}\text{Ni}_{0.25}\text{O}_{3-\delta}$ shows that the e_g peak (A) is virtually absent in $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{0.75}\text{Ni}_{0.25}\text{O}_{3-\delta}$; there is a clear t_{2g} feature (B) at around 3.5 eV. As well as the O 2p bonding peak at around 7.5 eV and the satellite at around 11.5 eV. Closer inspection of the on-resonance with $h\nu=710$ eV in Fig. 1(d), which displays the features magnified in the energy range from -1.0 to 4.0 eV, shows that the intensity of the spectrum for $x=0$ is enhanced for $0.20 \text{ eV} < E < 1.70 \text{ eV}$ in comparison to the spectra for $x=0$ and 0.75 , and thus identify the structure at around 0.9 eV as from the e_g symmetry derived transition corresponding to the one known for LaFeO_3 .¹⁵ Upon substitution of Sr by 50% and by 75%, this e_g (A) structure is not noticeable anymore. The next observation is that the energy position of the t_{2g} (B) structure seems to move towards higher binding energy, i.e., from 3.5 eV for $x=0$ to just below 4.0 eV for $x=0.5$, and also for $x=0.75$. This is in contrast to observations made on $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$. It appears also that the relative intensity of the t_{2g} peak decreases when x is increasing. Thus, the general picture is that spectral intensity moves away from the Fermi energy E_F with increasing substitution parameter x , as it is particularly evidenced for the peaks due to transitions from states with the e_g and t_{2g} orbital symmetry. For $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$, the intensity decrease in the e_g (A) structure upon Sr substitution was rationalized by transfer of doped electron holes towards the Fe e_g band.⁸

Since states with e_g orbital symmetry correspond to Fe in octahedral coordination with the oxygen ions, the diminishing of the e_g state can thus be interpreted as a deviation of crystal field effect in octahedral coordination: the crystal field effect increases from 1.80 eV to 1.85 eV by substituting Fe with Ni.¹² We, therefore, conclude that substitution of Fe by Ni, too, leads to formation of electron holes, which move to the Fe e_g bands, and therefore, Ni substitution has the similar effect on the depletion of the e_g structure like Sr-substitution. In addition, as evidenced in our spectra, the established trend that substitution of La by Sr increases the doped hole concentration in $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$, is also recovered in our LSFN samples: The hole states formed upon Sr

FIG. 3. (Color) Normalized O K edge x-ray absorption spectra of $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{0.75}\text{Ni}_{0.25}\text{O}_{3-\delta}$ for $x=0$, and $x=0.50$ with suggested peak deconvolution into Voigt functions. Arrow in top panel spectrum shows the difference between $e_g\uparrow$ peak intensity and normalization level (dashed horizontal line). Spectrum in bottom panel has additional peak at ~ 528 eV.

substitution in $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ and LSFN deplete the e_g states. This suggestion finds further confirmation when looking at the oxygen NEXAFS spectra of $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{0.75}\text{Ni}_{0.25}\text{O}_{3-\delta}$ for $x=0$ and 0.5 , as shown in Fig. 3.

$\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ has an e_g spin up orbital symmetry state from doped holes, and a t_{2g} and e_g spin down doublet from hybridized O $2p$ -Fe $3d$ states as the O $1s$ NEXAFS pre-edge structure. The intensities of the e_g states in $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ scale roughly with the Sr content.¹⁵

Due to the exponential dependence between the relative spectral intensity ratio $e_g\uparrow/(t_{2g}\downarrow+e_g\downarrow)$ and the conductivity was found,¹⁶ it is possible to investigate the transport property of this type material through their pre-edge structures. $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{0.75}\text{Ni}_{0.25}\text{O}_{3-\delta}$ with $x=0$ has a small such leading $e_g\uparrow$ peak, which supports the aforementioned suggestion that Ni substitution has the same effect like hole doping. It has recently been shown that increasing Ni concentration in $\text{LaFe}_{1-x}\text{Ni}_x\text{O}_3$ increases the intensity of prepeak and also shifts it towards E_F .¹⁷ The intensity of the corresponding e_g spin up peak in $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{0.75}\text{Ni}_{0.25}\text{O}_{3-\delta}$ for $x=0.50$ is much higher than the intensity of that for $x=0$, i.e., by a factor of six. In addition we do notice a small shift in the e_g spin up peak energy position toward E_F upon hole doping. We have recently shown that, since the Ni $3d$ states are closer to E_F than the Fe $3d$ states, the doped holes go predominantly to Ni.¹¹ The changes in the electronic structure of the $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{0.75}\text{Ni}_{0.25}\text{O}_{3-\delta}$ upon Sr substitution are qualitatively reflected by the electrical conductivity, as shown in ref. 11. The well known conductivity maximum of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ at $x=0.50$ is also observed for $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{0.75}\text{Ni}_{0.25}\text{O}_{3-\delta}$ for the same x ; this is also corroborated by the $e_g\uparrow$ peak intensity in the oxygen NEXAFS spectra for $x=0$ and 0.50 , see Fig. 3.

The influence of the Ni-when to 25% substituting the Fe in $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ -on the conductivity and on the electronic structure appears clear now. However, the mechanism of

how the Ni interacts in relation to the Fe with oxygen is not yet clear. Quite interestingly, we notice that the e_g intensity for $x=0.75$ in the VB PES is a little yet noticeable larger than that for $x=0.50$. The same holds for the larger extent for the t_{2g} intensity, corroborating how the electrical conductivity depends systematically on the VB PES intensity.

We have performed resonant VB PES, and NEXAFS at the O K edge and Fe $L_{2,3}$ edges on $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{0.75}\text{Ni}_{0.25}\text{O}_{3-\delta}$ ($x=0.0, 0.5$, and 0.75). The spectral weight of occupied e_g and t_{2g} states of Fe is reduced upon electron hole doping up to 50% and then starts to increase which is parallel to changes in electrical conductivity. The spectral weight of the prepeak in the oxygen NEXAFS spectra due to the p-type electron holes created on Ni $3d$ increases with increasing x . With respect to $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$, it is observed that the spectral weight transfers from below E_F to above it across the gap. However, here in $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{0.75}\text{Ni}_{0.25}\text{O}_{3-\delta}$ it is difficult to conclude this since the Ni $3d$ states are located closer to E_F than those of the Fe $3d$ and we do not consider any metal-metal (Fe-Ni and/or Ni-Fe) electron hole transfer.

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