High temperature oxygen near edge x-ray absorption fine structure valence band spectra and conductivity of $\text{LaFe}_{3/4}\text{Ni}_{1/4}\text{O}_3$ from 300 to 773 K

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$\text{LaFe}_{3/4}\text{Ni}_{1/4}\text{O}_3$ was subjected to oxygen near edge x-ray absorption fine structure spectroscopy for $300\text{ K} < T < 773\text{ K}$. The spectra show in the pre-edge a small hole doped peak originating from Ni substitution. The relative spectral weight of this transition to the weight of the hybridized $\text{O}(2p)\text{-Fe}(3d)$ transitions scales with T and has a maximum at around 600 K. The characteristic energies of the thermal activated spectral intensity and conductivity suggest that the concentration of charge transferred electrons from $\text{O}(2p)$ to $\text{Ni}(3d)$ increases and that the pre-edges account in part for the polaron activated transport. © 2011 American Institute of Physics. [doi:10.1063/1.3662970]

The electronic structure of materials for solid oxide fuel cell (SOFC) cathodes such as $\text{La}_{1-x}\text{Sr}_x\text{MeO}_3$ ($\text{Me} = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$) is subject of increasing interest in the last decades.¹ Electronic structure studies are limited to ambient temperature in the context of SOFC and even lower temperatures in the context of condensed matter theory. There are numerous high temperature ($T \rightarrow 1200\text{ K}$) transport and crystallographic structure studies as a function of stoichiometry, temperature, and oxygen partial pressure, but virtually not for electronic structure.

We recently reported valence band photoemission spectroscopy (VB PES) studies on LaSrFe -based and LaSrFeNi -based perovskites in ultra-high vacuum (UHV) for T up to 673 and 831 K. The correlation of spectral and conductivity characteristic suggested that VB PES is adequate to study the transport properties of ceramics at high T at the molecular level.²⁻⁴

Because the VB and the density of states (DOS) near the Fermi energy E_F are relevant for the functionalities of materials, we employed near edge x-ray absorption fine structure (NEXAFS) spectroscopy at the oxygen K-edge. Encouraged by the finding that the ratio of spectral weight of electron hole states and hybridized states in the pre-edges of the oxygen NEXAFS spectra of LaSrFe -based materials scale quantitatively with their electronic conductivity,⁵ we performed NEXAFS for LaFeNi -oxide from 300 to 773 K. We find that the intensity of the Ni derived states increases with T .

From an Arrhenius plot of the conductivity and spectral intensity we derive activation energies, which are $151.7\text{ meV} \pm 1.3\text{ meV}$ for the conductivity and $66\text{ meV} \pm 34.5\text{ meV}$ for the spectral weight. In the spirit of a recent presentation of

the T -dependency of VB PES (Ref. 6) and NEXAFS data between low temperature and 300 K in a sketch of the DOS,⁷ we combine high temperature VB PES and NEXAFS data of the present study in order to sketch changes of the DOS at E_F from 300 to 773 K.

Polycrystalline $\text{LaFe}_{0.75}\text{Ni}_{0.25}\text{O}_{3-\delta}$ was prepared by solid state reaction according to Ref. 8. Precursors were calcined at 1473 K for 4 h, sintered at 1673 K for 12 h and pressed to bars and sintered at 1673 K for 12 h with the 5 K/min heating/cooling rates.⁸ The crystallographic structure has been determined by x-ray diffraction at 300 K: $\text{LaFe}_{0.75}\text{Ni}_{0.25}\text{O}_3$ has orthorhombic symmetry with space group $Pbnm$ (62).⁹ The 4-point DC conductivity was measured in a furnace in air from 300 to 1273 K.⁸

T dependent NEXAFS spectra were recorded at beamline UE56/2-PGM1 at BESSY II using the BESSY/HU chamber, with the samples mounted on aluminum sample holders and measured in UHV with a base pressure of about 10^{-8} mbar. Signal detection was carried out in the total electron yield (TEY) mode. Temperature was controlled by resistive heating of the sample holder and passive cooling and measured with a thermocouple in direct contact with the sample. Background subtraction and normalization of spectra was performed by subtracting linear least square fits for energies lower than 525 and higher than 550 eV. Relative uncertainties in the peak height ratios, as determined by deconvolution of the spectra into Voigt functions with WinXAS,¹⁰ served as input for error propagation in order to obtain the uncertainty for the relative spectral weight S . The crystallographic and electronic structure¹¹ and the NEXAFS spectrum at the oxygen K-edge of the charge transfer insulator LaFeO_3 are well understood.^{5,12} Figure 1 shows the spectrum of LaFeO_3 as reproduced after Ref. 12 and our deconvoluted $\text{LaFe}_{3/4}\text{Ni}_{1/4}\text{O}_3$ spectrum. LaFeO_3 has a characteristic doublet in the VB from $\text{Fe}3d\text{-O}2p$ hybridized states

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FIG. 1. (Color online) O 1s spectrum of $\text{LaFe}_{3/4}\text{Ni}_{1/4}\text{O}_3$ at 300 K (bottom) with peak assignment and deconvolution, and spectrum of LaFeO_3 (top) after Ref. 12.

with spin up t_{2g} and e_g symmetry at around 529 and 530 eV. Substitution on the A-site with Sr forms holes which manifest in an extra transition with spin up e_g symmetry just before this doublet.¹³ Similar holds for B-site substitution with Ni (Refs. 14 and 15), in Fig. 1 (bottom), where we see an extra small peak at about 527 eV which is absent in LaFeO_3 (top). The relative spectral weight $S = \frac{e_g\uparrow}{t_{2g}\downarrow + e_g\downarrow}$ of the hole peak and the doublet in LSF-based perovskites are quantitatively correlated with the conductivity; this is particularly evident in systematic substitution studies such as in Ref. 5.

The spectra of $\text{LaFe}_{3/4}\text{Ni}_{1/4}\text{O}_3$ in Fig. 2 were recorded from 300 to 773 K and precisely deconvoluted so as to be able to accurately determine S . The $e_g\uparrow$ peak at 300 K with an intensity of 0.08 is barely visible. The relative intensities of the $t_{2g}\downarrow$ and $e_g\downarrow$ peaks are 1.600 and 1.338. S thus ranges from 0.027 to 0.076 between 300 and 773 K. The upper temperature range is relevant for intermediate temperature SOFC.¹⁶ In addition to changes in peak heights, we notice changes of line shape and widths due to thermal broadening

FIG. 2. (Color online) O 1s spectra recorded for 300–773 K. Spectra are off-set for better comparison. Numbers on the left show relative peak height of $e_g\downarrow$; numbers on the right denote T .

with increasing T . This affects also the fine features at the $t_{2g}\downarrow$ and $e_g\downarrow$ peaks, particularly, at 773 K.

The conductivity in LaSrFe -oxides¹⁷ and LaSrFeNi -oxides is rationalized as thermal activated small polaron hopping,^{18,19} which involves trapping of an electron or hole at one site by the local lattice polarization which it causes.²⁰ The T -dependent conductivity $\sigma(T)$ for small polaron hopping conductors is given by an exponential $\sigma \cdot T \propto \exp(E_a/k_B T)$ with activation energy E_a and Boltzmann's constant k_B .^{21–24} Figure 3 (top) shows the Arrhenius plot of σ and S . Both increase upon temperature increase at intermediate temperatures. σ decreases at $T > 895$ K whereas S decreases at around $T > 600$ K. E_a was determined for $305 \text{ K} \leq T \leq 555 \text{ K}$ to around 151.7 meV.

$\text{LaFe}_{0.75}\text{Ni}_{0.25}\text{O}_3$ has distorted orthorhombic symmetry in which the super exchange angle deviates from 180° . In addition, it has completely Fe^{3+} configuration $3d^5$ at 300 K, where the hopping mechanism takes place in the super exchange unit $\text{Fe}^{3+}-\text{O}-\text{Fe}^{3+}$ with antiferromagnetic super exchange interaction.⁸ Since the hopping mechanism occurs via O bridges, oxygen vacancies decrease the conductivity. The symmetry of the lattice increases with T and results in an increase in the super exchange angle and enhances the overlap between $\text{Fe/Ni}(3d)$ and $\text{O}(2p)$ orbitals. This decreases the electron-electron interaction which is one of the reasons for resistivity.

Hybridization between $\text{Ni}(3d)$ and $\text{O}(2p)$ creates $e_g\uparrow$ states, and the $e_g\downarrow + t_{2g}\downarrow$ states are due to $\text{Fe}(3d)-\text{O}(2p)$ hybridization. Their relative spectral weight S increases with T up to 600 K and then decreases. As we see in Fig. 2, the Ni derived empty $e_g\uparrow$ states are closer to E_F than the two Fe derived states. The Ni states are hence more favourable for charge transfer and thus higher conductivity. This is the rational why LaFeO_3 is an insulator with 2 eV charge transfer band gap⁶ whereas $\text{LaFe}_{0.75}\text{Ni}_{0.25}\text{O}_3$ is a semiconductor. Since S increases with T , we conclude that the concentration of charged transferred electrons from $\text{O}(2p)$ to $\text{Ni}(3d)$ (creating an electron hole on the O site) is increased up to 600 K. However, at higher T that concentration is reduced most likely because of emerging oxygen vacancies. It is not surprising that the variation of S and σ is not parallel since $\text{LaFe}_{0.75}\text{Ni}_{0.25}\text{O}_3$ has two different conductivity mechanisms: electron hopping and charge transfer.

In Fig. 4, we sketch the DOS for LaSrFeNi -oxide for 300 to 773 K as derived from VB PES (Refs. 1 and 2) and oxygen NEXAFS. The occupied (PES) and unoccupied states (NEXAFS) are affected by temperature. Interestingly,

FIG. 3. (Color online) Arrhenius plot for σ (top, right axis) and S (bottom, left axis) with error bars, with least square fits for determination of E_a .

FIG. 4. (Color online) Schematic for DOS of LaSrFeNi-oxide for 300–773 K. The right bold arrow represents increasing T . Other bold arrows show whether a state increases or decreases, or whether it shifts along energy axis.⁷

Sr substituted LaFeO₃ and Ni substituted LaFeO₃ show the $e_g\uparrow$ peak just above E_F , virtually at the same energy. In the former case (heterovalent substitution of La³⁺ by Sr²⁺), new “empty states” or “hole states” are created. In the latter case (homovalent substitution), Ni affects the unoccupied states and redistributes these states towards E_F . Furthermore, the density of these “redistributed states” increases up to 600 K.

Ni-doped LaFeO₃ shows an extra NEXAFS pre-peak due to Ni(3d)-O(2p) hybridization. Its intensity increases with T . In contrast to Sr doping, Ni doping does not create new hole states but causes redistribution of empty states. The conductivity of LaFe_{0.75}Ni_{0.25}O₃ is explained by two different thermally activated mechanisms: hopping in Fe³⁺-O-Fe³⁺ chains and charge transfer from O(2p) to mainly Ni(3d). The T dependent spectral weight and conductivity show similar yet not the same trend, which leads us to conclude that the difference results from the hopping process. The subsequent decrease in S occurs at around 600 K, prior to the transition from semiconducting to metal like conductivity at around 900 K (Fig. 3). This can be attributed to the differences in the measurement environment: NEXAFS was done in UHV whereas the conductivity was measured in ambient air. The differences in the oxygen partial pressure, particularly at high T , affect the concentration of oxygen vacancies, which are more easily created in vacuum.

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¹R. Chiba, F. Yoshimura, and Y. Sakurai, *Solid State Ionics* **152–153**, 575 (2002).

²A. Braun, J. Richter, A. S. Harvey, S. Erat, A. Infortuna, A. Frei, E. Pomjakushina, B. S. Mun, P. Holtappels, U. Vogt, K. Conder, L. J. Gauckler, and T. Graule, *Appl. Phys. Lett.* **93**, 262103 (2008).

³A. Braun, X. Zhang, Y. Sun, U. Müller, Z. Liu, S. Erat, M. Ari, H. Grimmer, S. S. Mao, and T. Graule, *Appl. Phys. Lett.* **95**, 022107 (2009).

⁴A. Braun, B. S. Mun, Y. Sun, Z. Liu, O. Groning, R. Mader, S. Erat, X. Zhang, S. S. Mao, E. Pomjakushina, K. Conder, T. Graule, *Electron Spectrosc. Relat. Phenom.* **181**, 56 (2010).

⁵A. Braun, D. Bayraktar, S. Erat, A. S. Harvey, D. Beckel, J. A. Purton, P. Holtappels, L. J. Gauckler, and T. Graule, *Appl. Phys. Lett.* **94**, 202102 (2009).

⁶H. Wadati, D. Kobayashi, Z. Chikamatsu, R. Hashimoto, M. Takizawa, K. Horiba, H. Kumigashira, T. Mizokawa, A. Fujimori, M. Oshima, M. Lippmaa, M. Kawasaki, and H. Koinuma, *J. Electron Spectrosc. Relat. Phenom.* **144–147**, 877 (2005).

⁷H. Wadati, A. Chikamatsu, R. Hashimoto, M. Takizawa, H. Kumigashira, A. Fujimori, M. Oshima, M. Lippmaa, M. Kawasaki, and H. Koinuma, *J. Phys. Soc. Jpn* **75**(5), 054704 (2006).

⁸S. Erat, A. Braun, A. Ovalle, C. Piamonteze, Z. Liu, T. Graule, and L. J. Gauckler, *Appl. Phys. Lett.* **95**(17), 174108 (2009).

⁹S. Erat, A. Braun, C. Piamonteze, Z. Liu, A. Ovalle, H. Schindler, T. Graule, and L. J. Gauckler, *J. Appl. Phys.* **108**, 124906 (2010).

¹⁰T. Ressler, *J. Synchrotron Radiat.* **5**(2), 118 (1998).

¹¹J.-C. Grenier, N. Ea, and M. Pouchard, *Mater. Res. Bull.* **19**, 1301 (1984).

¹²Z. Y. Wu, M. Benfatto, M. Pedio, R. Cimino, S. Mobilio, S. R. Barman, K. Maiti, and D. D. Sarma, *Phys. Rev. B* **56**(4), 2228 (1997).

¹³M. Abbate, F. M. F. de Groot, J. C. Fuggle, A. Fujimori, O. Strebel, F. Lopez, M. Domke, G. Kaindl, G. A. Sawatzky, M. Takano, Y. Takeda, H. Eisaki, and S. Uchida, *Phys. Rev. B* **46**, 4511 (1992).

¹⁴A. Chainani, M. Mathew, and D. D. Sarma, *Phys. Rev. B* **48**, 14818 (1993).

¹⁵D. D. Sarma, O. Rader, T. Kachel, A. Chainani, M. Mathew, K. Holldack, W. Gudat, and W. Eberhardt, *Phys. Rev. B* **49**, 14238 (1994).

¹⁶E. Maguire, B. Gharbage, F. M. B. Marques, and J. A. Labrincha, *Solid State Ionics* **127**, 329 (2000).

¹⁷M. V. Patrakeeva, I. A. Leonidova, V. L. Kozhevnikova, and K. R. Poeppelmeier, *J. Solid State Chem.* **178**, 921 (2005).

¹⁸K. Swierczek, J. Marzec, D. Palubiak, W. Zajac, and J. Molenda, *Solid State Ionics* **177**, 1811 (2006).

¹⁹E. V. Tsipis, E. A. Kiselev, V. A. Kolotygin, J. C. Waerenborgh, V. A. Cherepanov, and V. V. Kharton, *Solid State Ionics* **179**, 2170 (2008).

²⁰P. A. Cox, *Transition Metal Oxides* (Oxford Science Publications, Oxford, UK, 1992).

²¹W. H. Jung, *J. Mater. Sci.* **41**, 3143 (2006).

²²W. H. Jung, *J. Phys. Condens. Matter* **10**, 8553 (1998).

²³W. H. Jung, *J. Mater. Sci. Lett.* **17**, 1317 (1998).

²⁴W. H. Jung and E. Iguchi, *J. Phys. D: Appl. Phys.* **31**, 794 (1998).