Pre-edges in oxygen (1s) x-ray absorption spectra: A spectral indicator for electron hole depletion and transport blocking in iron perovskites

Artur Braun,^{1,a)} Defne Bayraktar,¹ Selma Erat,^{1,2} Ashley S. Harvey,² Daniel Beckel,² John A. Purton,³ Peter Holtappels,¹ Ludwig J. Gauckler,² and Thomas Graule¹

¹Laboratory for High Performance Ceramics, EMPA–Swiss Federal Laboratories for Materials Testing & Research, CH-8600 Dübendorf, Switzerland

²Department of Nonmetallic Inorganic Materials, ETH Zürich–Swiss Federal Institute of Technology, CH-8053 Zürich, Switzerland

³Synchrotron Radiation Source, Daresbury Laboratory, Warrington WA4 4AD, United Kingdom

(Received 27 December 2008; accepted 30 March 2009; published online 19 May 2009)

The $e_g \uparrow / (t_{2g} \downarrow + e_g \downarrow)$ band ratio in cation-substituted La–Fe oxides is identified in O (1s) x-ray absorption spectra as a linear spectral indicator for conducting electron holes. The $t_{2g} \downarrow$ and $e_g \downarrow$ bands act as a conductivity inhibitor by ferromagnetic double exchange coupling on the $e_g \uparrow$ electron. Disorder induced by substitution appears to modulate the hole conduction such that an exponential relation is found between the conductivity and the $e_g \uparrow / (t_{2g} \downarrow + e_g \downarrow)$ ratio and hole concentration. The quantitative correlation of conductivity and x-ray absorption spectra from heterovalent-substituted LaFeO₃ lets substitution-driven metal insulator transitions appear in a new light. © 2009 American Institute of Physics. [DOI: 10.1063/1.3122926]

Rare-earth transition metal oxides display a manifold of technologically relevant functionalities, which are controlled by the oxygen ion and hybridization of O (2p) states with the transition metal *d* states. Control of transport mechanisms, which are vital for energy materials, can be obtained with cation doping and tuning oxygen stoichiometry. For instance, Ta and Ti in La–Sr–Fe (LSF) oxides are interesting for catalytic oxygen membranes,¹ Ta is a hole depletion agent in photocatalysts,² and Ti suppresses leakage currents in high temperature tantalum capacitors.³

The role of electron holes as charge carriers and their detection in the pre-edge of oxygen x-ray absorption spectra (XAS) has been recognized. But the pre-edges withstood quantitative treatment so far.

Heterovalent substitution of La³⁺ in the charge transfer insulator LaFeO₃ by Sr²⁺ creates electron hole states with O (2p) character near the Fermi energy E_F .^{4–7} In addition to hole doping, the increasing radius from La to Sr decreases the rhombohedral lattice distortion, which in turn increases the hybridization of the O (2p)–Fe(3d) states and, thus, the one-electron band width.⁸

The conductivity of La_{1–x}Sr_xFeO₃ increases with increasing *x*, SrFeO₃ displaying metallic conductivity.^{6,8} Charge balance is maintained by adjustment of the Fe oxidation state and oxygen deficiency δ . While the formal valence is Fe³⁺ in LaFeO₃ (Fe⁴⁺ in SrFeO₃), the actual relative Fe⁴⁺

concentration in SrFeO_{3– δ} may be below 40%. With every Fe⁴⁺ replacing one Fe³⁺, one electron charge carrier hole is created.⁹ Our starting reference La_{0.5}Sr_{0.5}FeO_{3– δ} (LSF50) with maximum conductivity^{7,10} is then doped with 10% Ta, 20% Ta, and 20% Ti. Competition between various mixed valence ions on A(BB*)O₃ type perovskites is attracting increasingly interest.¹¹

The four-point dc conductivity (Burster Resistomat, accuracy 0.03% of reading; resolution 10 $\mu\Omega$) of phase pure LSF50 and substituted LSF with *R*-3c symmetry (Table I) was measured on sintered bars with density >95% of the theoretical density.¹ The polaron activation energy E_a was determined by a least square fit of $\sigma(T) = \sigma_0/T \exp(E_a/kT)$ from 300 to 700 K. For details on structure and properties of LSF see Refs. 7 and 12. LSF50 has an average formal valence of 3.5 on iron and a formal hole concentration of $\tau = \text{Fe}^{4+}/\text{Fe}^{3+} = 1$. The gravimetrically obtained δ served to calculate the actual hole concentration τ (Table I).

Conductivity σ at 307 K and activation energy E_a are listed in Table I. By 20% substitution of Fe with Ta (La_{0.5}Sr_{0.5}Fe_{0.8}Ta_{0.2}O_{3– δ} LSFTa20), σ decreases by three orders of magnitude, while E_a increases by a factor of 2.3. LSF50 has the overall highest conductivity at about 300 K, systematically followed by La_{0.5}Sr_{0.5}Fe_{0.8}Ti_{0.2}O_{3– δ} , La_{0.5}Sr_{0.5}Fe_{0.9}Ta_{0.1}O_{3– δ} , and La_{0.5}Sr_{0.5}Fe_{0.8}Ta_{0.2}O_{3– δ} with

TABLE I. Oxygen deficiency δ , experimental hole concentration τ , conductivity σ , polaron activation energy E_a , branching ratio Q , and spin-orbit splitting Δ .

Stoichiometry	δ	τ	σ (S/cm)	E_a (meV)	Q [$L_3/(L_2+L_3)$]	Spin-orbit splitting Δ (eV)
La _{0.5} Sr _{0.5} FeO _{3–δ}	0.078	0.52	50	180	0.67	12.85
La _{0.5} Sr _{0.5} Fe _{0.8} Ti _{0.2} O _{3–δ}	0.063	0.28	2.28	262	0.68	12.97
La _{0.5} Sr _{0.5} Fe _{0.9} Ta _{0.1} O _{3–δ}	0.058	0.26	0.82	342	0.66	12.86

^{a)}Electronic mail: artur.braun@alumni.ethz.ch.

FIG. 1. (Color online) Normalized Fe *L*-edge spectra.

the lowest σ . Comparison of σ and τ (Table I) reveals direct correlation between σ and substitution level.

Soft XAS were recorded at 300 K and 5×10^{-10} Torr at Daresbury Laboratory Synchrotron Radiation Source (beamline 1.1), United Kingdom. Figure 1 shows the area normalized Fe (*2p*) absorption spectra corrected for the chemical shift. Differences of the overlaid spectra can be made out as a minute variation of the $2p_{3/2}$ t_{2g} shoulder and the height of the e_g peak, and the different height of the $2p_{1/2}$ peak. The multiplet structure of *3d* metals such as iron and its x-ray spectroscopic assessment are generally well understood^{5,13} and provide a unique probe for the local spin moment of magnetic Fe.¹⁴ The degeneracy of the Fe (*2p*) core hole level is lifted by spin-orbit coupling, resulting in the $2p_{3/2}$ and $2p_{1/2}$ multiplets at around 708 and 722 eV. Their centroids are separated by around 13 eV (Table I). The octahedral crystal field lifts the degeneracy of the $2p_{3/2}$ and $2p_{1/2}$ levels so that two levels with t_{2g} and e_g symmetry are created, as indicated by the two structures at about 707 and 708.5 eV and at 720.5 and 722 eV.

The chemical shift of the white lines revealed that the average oxidation state of the Fe varies from sample to sample. LSF-Ta20 contains—due to charge compensation by Ta^{5+} —only Fe^{3+} and thus, has the lowest Fe oxidation state and no holes. With only high spin Fe^{3+} in $3d^5$ configurations LSF-Ta20 has the largest multiplet branching ratio $Q = L_3/(L_2 + L_3) = 0.70$ (Table I).¹⁵ Due to the larger cation size of Ti^{4+} and Ta^{5+} compared to Fe^{4+} , the unit cell of LSF expands upon substitution with Ti and Ta,¹ possibly providing the remaining Fe ions more space for parallel spins. In line with Ref. 5, we find that Fe remains essentially in the ferromagnetic high spin $3d^5$ configuration ($t_{2g}^3 e_g^2$).

The prepeak of oxygen *K*-edge spectra due to doped holes in A-site substituted LaSrMn-oxide correlates well with the conductivity.¹⁶ We extend that study to *B*-site substituted LSF. For deeper insight in the transport mechanism, we recorded O (*1s*) XAS (Fig. 2), which represent to a good approximation the unoccupied oxygen *p* projected density of

states.¹⁷ Since the other orbitals are hybridized with the O (*2p*) orbitals, the spectra also reflect empty Fe (*3d*) and La (*5d*) bands. LaFeO_3 forms spin-down $t_{2g}\downarrow$ and $e_g\downarrow$ peaks at around 528 and 531 eV. They represent mixed O (*2p*)–Fe (*3d*) states subject to the ligand field splitting of $\Delta \approx 1.1$ eV in the FeO_6 octahedra, and hence form $t_{2g}\downarrow$ and $e_g\downarrow$ states in the band-gap.^{5,6,18} The extra peak from hole doping has spin-up $e_g\uparrow$ nature.¹⁹ The pre-edge features between 526 and 531 eV are deconvoluted into the well-known $t_{2g}\downarrow$ and $e_g\downarrow$ bands, and the extra $e_g\uparrow$ band for the doped hole states at around 528 eV (Fig. 2). The sharp peak at 531.6 eV from the carbon tape, on which the samples were dispersed, confirms energy alignment of the spectra. Subtraction of this peak, as exercised for LSF50, brings the pre-edge features back in the well-known shape.¹⁹ With systematic differences depending on the doping situation, we notice considerable variation of the prepeak intensities. The observation that for LSF50 the intensity of one $e_g\uparrow$ hole counts as much as that of the five spin-down holes might be explained by that the doped hole is localized on oxygen (hence close to 100% contributing) and the ten spin-down holes are mainly iron state with some admixture of oxygen character. According to Ref. 5, holes from A-site substitution go to states of primarily oxygen character, and the main component of the ground state in LSF50 is $3d^5\bar{L}$ (ligand hole $\bar{L}$) and not $3d^4$. In their study, and in the study by Wadati *et al.*,¹⁹ the $e_g\uparrow$ peak grows with increasing Sr content and permits quantitative consideration of hole doping by substitution at the A site, which to some extent was already exercised in LSM.¹⁶ Homovalent B-site substitution may cause a mismatch in the lattice, redistributing empty hole states near E_F , thus improving the conductivity.⁴ Here, where the B-site is substituted with the *supervalent* Ta and Ti, we observe the opposite effect: blocking the conductivity. Change in the $e_g\uparrow$ intensity alone does not permit systematic conclusions about the material, much less the conductivity.⁵ As will be shown, the ratio $S = e_g\uparrow / (t_{2g}\downarrow + e_g\downarrow)$ correlates better with τ and σ .

Correlation of σ and S is shown in Fig. 3. Filled circles denote our B-site doping series for Ta, including the non-doped LSF. The conductivity increases exponentially with increasing S , as shown by the fit.

It is interesting to discuss S in terms of τ . The data points (filled circles and squares) show a linear correlation (linear fit) of the dimensionless form $S(\tau) = S_0 + a \cdot \tau$. Due to the mutual relationship between S , σ , and τ we can (not shown here) plot σ versus τ and fit it with an exponential of the form $\sigma \sim \sigma_0 \exp(U\tau)$. Our samples from B-site substitution have nonzero ratio S_0 for vanishing τ . Certainly, LSF-Ti20 has some residual conductivity even in the absence of holes, and the corresponding spectral intensity near E_F and the corresponding conductivity derive not only from hole states. Also, we cannot entirely rule out that this intensity is caused

FIG. 2. (Color online) Deconvoluted O (*1s*) spectra with prepeak near E_F . Numerals indicate peak position and spectral weight.

FIG. 3. (Color online) Correlation and exponential least square fit of σ and S -ratio. Circles are for $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$, $\text{La}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.9}\text{Ta}_{0.1}\text{O}_{3-\delta}$, and $\text{La}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.8}\text{Ta}_{0.2}\text{O}_{3-\delta}$. Squares are data from Ref. 19.

by O ($2p$)–Ta ($5d$) mixed states, as may be the case for other substituted samples. On the other hand, addition of Ti and Ta will slightly expand the unit cell, a situation which will generally not favor an increase in σ and, as observed with 20% Ta, may even shift the pre-edge band to slightly higher energies.

Since the nonsubstituted LSF50 sample fits too in our proposed scheme, we believe that S as an indicator for conductivity is more general than for B -site substitution only. To support this hypothesis, we plotted these S -ratios for published data¹⁹ (an A -site substitution study), i.e. $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_3$, $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_3$, and LaFeO_3 in Fig. 3 as well. These ratios can be expressed as a linear function in τ . Note that we now have a set of A -site and B -site substituted LSF materials with a linear relation of the S -ratio and relative τ (Fig 3). In both cases the unit cell volume increases.⁹ By substitution of the B cation rather than the A cation, we become more sensitive to subtleties of the Fe–O–(Fe,Ta,Ti,...) superexchange unit, which ultimately provides—or blocks—the transport, particularly since A cations usually do not transport).

Why should $t_{2g}\downarrow$ and $e_g\downarrow$, which are more remote from E_F than the $e_g\uparrow$ band, have any relevance to the transport properties? The $t_{2g}\downarrow$ orbitals are localized and do not point toward the neighboring ligands, whereas the more delocalized $e_g\uparrow$ bands do so and hence basically operate as switches for the charge transfer across the superexchange unit. Resolution is provided by Zener's²⁰ double exchange, which ferromagnetically couples the $t_{2g}\downarrow$ spins with the mobile $e_g\uparrow$ electrons. In this context, it is interesting to note that our samples with the highest σ and smallest E_a also have the smallest branching ratios Q (Table I, see also Fig. 6 in Ref. 7). The more remote $e_g\downarrow$ peak in the $t_{2g}\downarrow$ and $e_g\downarrow$ pair seems to be of little influence for σ within the accuracy of our data.

Fe^{4+} with $3d^5L$ configuration⁵ has octahedral d^2sp^3 coordination, whereas Fe^{3+} with a $3d^5$ configuration prefers tetrahedral coordination. Depletion of Fe^{4+} with increasing Ta or Ti substitution, and resulting enrichment of Fe^{3+} , causes coordination from octahedral to tetrahedral, which consequently manifests in a depletion of the conducting $e_g\uparrow$ bands, which require octahedral coordination.⁷

The observed exponential relation between τ and σ , and the linear relation between τ and S , can be written in simple mathematical terms, $\sigma \sim \exp\{U[e_g\uparrow/(t_{2g}\downarrow + e_g\downarrow)]\}$, with specific constant U .

The fact that the decrease of σ is exponential, while the hole variation and the spectral changes are linear, suggests that the hole concentration *per se* cannot account for the entire conductivity loss. Such is found for Ta doping on Na_xWO_3 ²¹ and for Ni/Fe substitution on $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_3$.²²

We speculate that substitution disorder and consequential percolation may be an additional cause for the conductivity decrease. Okunev *et al.*²³ find an exponential relationship between σ and the distance of nonconducting clusters on LaSrMn -oxide, for example. We envision a similar situation here, with a ratio of more conducting $e_g\uparrow$ and less conducting $t_{2g}\downarrow$ species, which is the argument of and modulated by an exponential. Since $e_g\downarrow$ is remote from E_F , its influence on the conductivity is negligible.

This study provides quantitative results that clarify and unify our understanding of substitution mechanisms. The combination of transport measurements and x-ray spectroscopy, particularly that of O ($1s$) for unoccupied states, holds promise to tell whether conductivity changes are related to hole doping or depletion, or to changes in the band structure due to lattice structure alterations.

Financial support by the Swiss National Science Foundation Project No. 200021-100674/1 and the European Commission under Grant No. MIRG-CT-2006-042095. The Science and Technology Facilities Council of the U.K. are acknowledged for beamtime at the Synchrotron Radiation Source, Project No. 47093.

¹D. Bayraktar, S. Diethelm, P. Holtappels, T. Graule, and J. Van herle, *J. Solid State Electrochem.* **10**, 589 (2006).

²T. Ishii, H. Kato, and A. Kudo, *J. Photochem. Photobiol., A* **163**, 181 (2004).

³W. S. Lau, T. S. Tan, and P. Babu, *Appl. Phys. Lett.* **90**, 112903 (2007).

⁴D. D. Sarma, O. Rader, T. Kachel, A. Chainani, M. Mathew, K. Holldack, W. Gudat, and W. Eberhardt, *Phys. Rev. B* **49**, 14238 (1994).

⁵M. 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).

⁶H. Wadati, D. Kobayashi, H. Kumigashira, K. Okazaki, T. Mizokawa, A. Fujimori, K. Horiba, M. Oshima, N. Hamada, M. Lippmaa, M. Kawasaki, and H. Koinuma, *Phys. Rev. B* **71**, 035108 (2005).

⁷J.-C. Grenier, N. Ea, M. Pouchard, and M. M. Abou-Sekkina, *Mater. Res. Bull.* **19**, 1301 (1984).

⁸S. K. Park, T. Ishikawa, Y. Tokura, J. Q. Li, and Y. Matsui, *Phys. Rev. B* **60**, 10788 (1999).

⁹X.-D. Zhou, Q. Cai, J. Yang, M. Kim, W. B. Yelon, W. J. James, *J. Appl. Phys.* **97**, 10C314 (2005).

¹⁰M. V. Patrakeev, J. A. Bahteeva, E. B. Mitberg, I. A. Leonidov, V. L. Kozhevnikov, and K. R. Poeppelmeier, *J. Solid State Chem.* **172**, 219 (2003).

¹¹J.-S. Kang, H. J. Lee, G. Kim, D. H. Kim, B. Dabrowski, S. Kolesnik, Hangil Lee, J. -Y. Kim, and B. I. Min, *Phys. Rev. B* **78**, 054434 (2008).

¹²S. E. Dann, D. B. Currie, M. T. Weller, M. F. Thomas, and A. D. Al-Rawwas, *J. Solid State Chem.* **109**, 134 (1994).

¹³F. de Groot and A. Kotani, *Core Level Spectroscopy of Solids* (CRC, Boca Raton, 2007).

¹⁴C. S. Fadley, D. A. Shirley, A. J. Freeman, and P. S. Bagus, *Phys. Rev. Lett.* **23**, 1397 (1969).

¹⁵B. T. Thole and G. van der Laan, *Phys. Rev. B* **38**, 3158 (1988).

¹⁶H. L. Ju, H. -C. Sohn, and K. M. Krishnan, *Phys. Rev. Lett.* **79**, 3230 (1997).

¹⁷F. M. F. de Groot, M. Grioni, J. C. Fuggle, J. Ghijsen, G. A. Sawatzky, and H. Petersen, *Phys. Rev. B* **40**, 5715 (1989).

¹⁸Z. Y. Wu, S. Gota, F. Jollet, M. Pollak, M. Gautier-Soyer, and C. R. Natoli, *Phys. Rev. B* **55**, 2570 (1997).

¹⁹H. 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**, 054704 (2006).

²⁰C. Zener, *Phys. Rev.* **82**, 403 (1951).

²¹A. K. Raychaudhuri, *Phys. Rev. B* **44**, 8572 (1991).

²²D. D. Sarma, D. D. Sarma, A. Chainani, S. R. Krishnakumar, E. Vescovo, C. Carbone, W. Eberhardt, O. Rader, Ch. Jung, Ch. Hellwig, W. Gudat, H. Srikanth, and A. K. Raychaudhuri, *Phys. Rev. Lett.* **80**, 4004 (1998).

²³V. D. Okunev, R. Szymczak, M. Baran, H. Szymczak, and P. Gierlowski, *Phys. Rev. B* **74**, 014404 (2006).