Electron hole–phonon interaction, correlation of structure, and conductivity in single crystal $\text{La}_{0.9}\text{Sr}_{0.1}\text{FeO}_{3-\delta}$

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The conductivity and structure of the hole-doped polaron conductor $\text{La}_{0.9}\text{Sr}_{0.1}\text{FeO}_{3-\delta}$ are reported for elevated temperatures. The conductivity increases exponentially with temperature to a maximum and decreases for $T > 700$ K following a power law, accompanied by a shift of spectral weight in the photoemission valence band. The conductivity decrease is accompanied by a phase transformation, due to the reduction of Fe, as evidenced by x-ray absorption spectra. Additional fine structures in the conductivity are correlated with a strong decrease in valence band intensity near E_F and with the onset of a corresponding structural transition. © 2008 American Institute of Physics.

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Properties of strongly correlated fermion systems are rarely studied at high temperatures, although such temperatures are relevant for solid oxide fuel cells and sensors, for example. We report on single crystal $\text{La}_{0.9}\text{Sr}_{0.1}\text{FeO}_{3-\delta}$ (LSF10), which comes close in properties to the insulating parent compound LaFeO_3 . LaFeO_3 is an antiferromagnetic (AFM) charge transfer insulator with a band gap energy E_g of 2 eV and Néel temperature of 750 K and has orthorhombic symmetry with four distorted pseudocubic cells in the space group $Pbnm$. The Fe has its spin antiparallel to its six nearest neighboring Fe atoms, with parasitic ferro- and ferrimagnetism^{1,2} for low Sr doping. *Heterovalent* substitution of La^{3+} with Sr^{2+} (hole doping) creates conducting electron hole states with O ($2p$) character near E_F ,³ accompanied by a decrease of T_N . SrFeO_3 is an AFM metallic conductor.⁴

La and Sr are considered to retain their formal valence La^{3+} and Sr^{2+} . Charge balance is maintained by adjustment of the valence of the Fe and by oxygen deficiency δ in the $\text{La}_{(1-x)}\text{Sr}_x\text{FeO}_{3-\delta}$. The formal valences of Fe in LaFeO_3 and SrFeO_3 are Fe^{3+} and Fe^{4+} , respectively. The Fe^{4+} ions provide the electron holes and control the conductivity, whereas Fe^{3+} controls via its spin structure and double exchange the magnetic properties.⁵

LSF10 was prepared by solid state synthesis and phase purity confirmed by x-ray diffraction (XRD).^{1,6,7} The gravimetrically obtained δ is 0.01. A single crystal (SC) was grown in an optical floating zone furnace and its dc conductivity determined by the four-probe technique. Laue XRD confirmed orthorhombic symmetry with space group $Pbnm$

62 and lattice constants $a=5.543$ Å, $b=5.568$ Å, and $c=7.846$ Å. A 1 mm thick SC disk in $[111]$ orientation was cut and high-quality surface finished. Part of the SC was pulverized and analyzed with XRD (wavelength of 1.936 040 Å), at a heating rate of 25 K/min.

The SC was subject to x-ray photoemission spectroscopy (PES) at 450 eV excitation energy (Beamline 9.3.1, Advanced Light Source, Berkeley, California) after Ar^+ bombardment at 500 eV for 30 min, a heating cycle to 500 K, and a scan for residual carbon. This procedure was repeated twice, and no carbon signal was detected. Temperature dependent x-ray absorption spectra (XAS) of the Fe K edge were recorded at beamline BM29 of the European Synchrotron Radiation Facility, Grenoble, France.

LSF10 undergoes a transition from orthorhombic to rhombohedral at about 700 K.^{1,2,6} The split of the (020) reflex at 41.5° during temperature change suggests structural changes (Fig. 1). The slight shoulder at about 573 K around

FIG. 1. (Color online) X-ray diffractogram of LSF10 powder from SC for $313 < T < 773$ K in ambient atmosphere.

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FIG. 2. (Color online) Valence band PES spectra of LSF10 SC for 323–723 K. The inset in the left figure shows a magnification of the intensity near E_F . The right figure shows a magnification of the energy range of $-2 < E < 1$ eV.

41.35° matches with tetragonal $\text{Sr}_3\text{Fe}_2\text{O}_7$ (00-45-0398), possibly a transitional contamination, and becomes more pronounced with increasing T . At 773 K, the reflex is split into peaks, separated by 0.2° . The general trend is that the diffracted intensity shifts towards larger angles, suggesting a decrease of the unit cell.

The assignment of the valence band features in the photoemission spectra (VB PES) in Fig. 2 is in accordance with Refs. 8–10. Upon heating, the intensity of the t_{2g} band (-3.5 eV) and the e_g band decrease, which is developed as a shoulder at about -1.5 eV below E_F . However, the intensity near E_F increases slightly, i.e., intensity is redistributed towards E_F . The inset in Fig. 2 shows a magnification of the relevant range near E_F . First, the spectral weight at 373 K near E_F is smaller than for the lower temperature of 323 K. Second, the intensities for the following T do increase, except for $T=723$ K, where the intensity is just below that of 473 K, and above that of 323 K. The spectrum at 673 K has thus the highest intensity near E_F . In order to quantify the intensity redistribution near E_F , we determined the intensity at E_F , and 100 meV above and below E_F , and plotted these versus T (Fig. 3, bottom). The three solid lines corresponding to the three energy positions show basically the same variation. Close inspection of the PES intensity variation curves reveals a correlation with features of the conductivity, which for comparison is plotted on the top in Fig. 3.

The increasing conductivity is typical for thermally activated small polaron hopping, where here with an activation energy of $E_p=317$ meV.¹¹ The conductivity attains its maximum at about 700 K. On very close inspection, we notice two peculiarities: First is a reversible small jump at 357 K with a small hysteresis; the conductivity drops (jumps) upon heating (cooling) by about 0.025 S/cm. The inset in Fig. 3 (top) on the left magnifies the conductivity variation near this jump. The conductivity jump effect coincides with the valence band PES spectrum recorded at 373 K in Fig. 3, which shows a remarkable decrease in intensity near E_F .

The second peculiarity is a slight increase in the slope in the conductivity, i.e., an increase of E_p to 332 meV at about 573 K. This observation is paralleled in the diffractogram at 573 K (Fig. 1), above which a clear transition from orthorhombic to rhombohedral is observed, suggesting that the rhombohedral structure is less conductive. Here we notice enhanced scattering of the conductivity, suggesting a struc-

FIG. 3. (Color online) Variation of conductivity (top) and the conduction e_g band height (bottom) as a function of temperature. Data are considered for E_F , and 100 meV above and below E_F . The red circle region is magnified in the lower left part of the right figure and shows two tilted set (red for high, blue for low temperatures) of parallel lines.

turally poorly defined transitional stage. This behavior is to some extent reflected in the magnetic properties. We recollect that LSF is predominantly AFM, but may have canted ferromagnetic (FM) structure. The SC shows FM behavior at 300 and 400 K, as evidenced by rectangular magnetization curves (not shown here). Out of the LSF series, LSF10 has the highest internal magnetic field at ambient T and a Néel temperature of around 600 K.^{1,12} The FM Curie point may be below 600 K. Summarizing for $T \geq 573$ K, we believe that the structural transition increases the lattice distortion, impairing the $\text{Fe}(3d)\text{-O}(2p)$ hybridization via the double-exchange angle θ , and thus increasing the band width $W \sim \cos(2\theta)$ and E_g .⁴ We speculate that at this temperature the FM Curie point is already passed, and that no double-exchange-related conductivity decrease occurs.

The conjugated PES intensity increase near E_F with increasing T shows two extra features, having smaller spectral weight at 373 K than at 323 K, and, subsequently, increasing spectral weight, with a maximum at about 700 K, where σ is maximal. The back-switching spectral weight at this temperature is hence paralleled by the maximum conductivity.

The T dependent Fe K edge XAS spectra (Fig. 4) point to the physical origin for the decrease of σ and the cross-over in the conductivity mechanism above 700 K. They show noticeable changes at 310, 423, and 573 K. However, the spectra at 573 and 673 K differ insofar as the 673 K spectrum has a smaller chemical shift and hence represents a more reduced Fe species than those at lower T . With the exception for 773 K, the white lines all coincide at 7127 eV. The 773 K spectrum has pronounced e_g and t_{2g} prepeaks at 7104 and 7112 eV, indicative of Fe^{3+} . This conclusion is supported by the position of the absorption edges at 7117.5 eV for 773 K and 7121 eV for 310 K. The average nominal va-

FIG. 4. (Color online) XAS of the Fe K edge for $T=310\text{--}773$ K.

lence of Fe is 3.1, brought about by 10% Fe^{4+} and 90% Fe^{3+} . The chemical shift upon heating to 773 K is 3.5 eV, which accounts for about 0.75 valence formula units.¹³ Thus, the Fe is reduced from average $\text{Fe}^{3.10}$ at 300 K to $\text{Fe}^{2.35}$ at 773 K. The XAS thus resemble to a large extent the Fe^{3+} features, as evidenced by the pre-edge peaks of Fe^{3+} . The width of the white line at 773 K is larger than for lower T . White lines from ionic and covalent compounds are typically sharper than those from metals. This indicates that the ionic bond strength structure is softened during annealing and suggests a more metallic bonding, in line with the observed chemical shift towards lower energies. The decrease of the average iron valence is caused by oxygen loss during annealing, and, consequently, decreases the number of conducting holes. This manifests in decreasing conductivity and decline of the VB PES intensity at $T > 700$ K.

This work is a high temperature application of VB PES on a rare-earth transition metal oxide perovskite. Ambient temperature studies on related materials were published recently. Matsuno *et al.*¹⁴ found a decrease of spectral weight near E_F towards $x=0.67$ (charge ordering state). SrFeO_3 has the highest spectral weight at E_F , compared to LSF. Their studies¹⁴ from 130 to 210 K indicated that changes are most pronounced for $x=0.67$ at 190 K. Wadati *et al.*⁹ identified in the PES three main structures as from $\text{Fe}(3d)\text{--O}(2p)$ bonding states, and t_{2g} and e_g states from Fe, the latter of which is next to the E_F . In the spectra at room temperature, the e_g band next to E_F became weaker but moved toward E_F as x increased towards better conducting compositions. They¹⁰ found for 10–260 K hole doping induced spectral weight transfer from below to above E_F across the band gap in a highly non-rigidlike-band-manner. With increasing T , the weight of the e_g band at -1.5 eV from E_F decreased noticeably, with a corresponding weight increase at about -0.2 eV from E_F .⁸

The three parallel dotted lines in the bottom of Fig. 3 reflect the global trend of the weight increase around E_F with increasing T . The spectral weight maximum at about 700 K coincides with the conductivity maximum, and the two spectral weight minima coincide with the change of E_p and the jump of σ at about 573 and 357 K, respectively. The intermediate PES maximum at about 463 K represents not a maximum that would correspond to a particular high conductivity, but the continuation of the overall linear increase of the spectral weight along with the temperature increases. It is noteworthy that the minute conductivity jump and the increase of E_a cause significant changes in the trend of the spectral weight evolution during temperature change, whereas the global linear increase of the spectral weight is

unspectacular. The overall linear behavior therefore accounts for the excitation of polarons as a primary response to thermal activation, while the distinct minima account for direct structural changes, which are secondary effects with respect to the temperature change. Comparison with calorimetry data confirms subtle yet systematic correlation between structural, spectral, and transport properties. The cause for the conductivity jump remains open.

The lightly Sr doped $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ has a thermally activated conductivity up to 673 K from polaron hopping of holes created by the Fe^{4+} . The conductivity increase is reflected by the PES, i.e., spectral weight shift from the Fe e_g band towards E_F . The density of states near E_F is thus filled by the Fe^{4+} holes. Upon further heating, LSF10 adopts rhombohedral symmetry. Since La and Sr are virtually redox inert, the Fe valence adjusts to maintain charge balance, i.e., the Fe^{4+} is reduced, and the hole concentration decreases accordingly. This stage is met at about 700 K, with maximum conductivity and its subsequent decrease. The temperature dependent XAS display significant changes, including the chemical shift towards smaller energies, confirming a reduction of the Fe. The PES spectrum at 723 K shows, consequently, a smaller spectral weight at E_F than the other high temperature spectra. Since the attenuation length for 7210 eV photons of around $3.5\text{ }\mu\text{m}$ and the conductivity measurements are bulk representative, and the PES probing depth as applied here is below 20 Å, our study suggests that surface sensitive VB PES can be meaningful applied at high T for LSF studies and permits correlation with bulk representative transport properties.

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