Electronic behavior of three oxygen non-stoichiometric Fe$^{4+}$/Fe$^{3+}$ oxoperovskites

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Received 23 April 2005; received in revised form 6 September 2005; accepted 14 September 2005
Available online 11 October 2005

Abstract

For comparison with the Mn$^{4+}$/Mn$^{3+}$ oxoperovskites at the crossover from localized to itinerant behavior of the $\sigma$-bonding $e$ electrons, the electronic properties of three oxygen non-stoichiometric, mixed-valent Fe$^{4+}$/Fe$^{3+}$ oxoperovskites were explored by measuring their resistivity $\rho(T)$, thermoelectric power $\alpha(T)$, and magnetic susceptibility $\chi(T)$. Oxidation of Ca$_2$Fe$_2$O$_5$ by annealing in ozone progresses by oxygen insertion to give conductive CaFeO$_3$ perovskite clusters in a localized-electron, weakly oxidized brownmillerite Ca$_2$Fe$_2$O$_5^{+\delta}$ matrix. Removal of 0.12 oxygen per formula unit from La$_{1/3}$Sr$_{2/3}$FeO$_3$ lowers somewhat its cooperative disproportionation reaction, and fivefold-coordinated ions neighboring oxygen vacancies in the more ionically bonded slabs act as donors to the covalently bonded Fe(V)O$_6$ planes. Single-crystal SrFeO$_{2.83}$ exhibited bad-metal behavior with superparamagnetic, electron-rich fluctuations below 240 K that, on cooling below 190 K, become progressively trapped by the oxide-ion vacancies as an immobile second phase; long-range antiferromagnetic order is stabilized below a $T_N \approx 60$ K.

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Keywords: Perovskites; Brownmillerite; Bad metals; Disproportionation; Oxygen insertion

1. Introduction

The octahedral-site Mn$^{3+}$ ions of the $RMnO_3$ ($R =$ rare earth) perovskites and the Fe$^{4+}$ ions of the $AFeO_3$ ($A =$ alkaline earth) perovskites each have a high-spin 3$d^5$ manifold. The $\pi$-bonding $t^2$ manifold at each cation is localized with an atomic spin $S = \frac{3}{2}$. The $\sigma$-bonding $e$ electron of the Mn$^{3+}$:$t^2e^1$ ion is also localized as is manifest by a cooperative ordering of the twofold-degenerate $e$ orbitals, but the $e$ electron of an Fe$^{4+}$:$t^2\sigma^*e^1$ ion occupies a narrow, itinerant-electron $\sigma^*$ band of $e$-orbital parentage. An intraatomic exchange field removes the spin degeneracy not only of the localized $e$ orbitals at a Mn$^{3+}$ ion, but also of the orbitally twofold-degenerate $\sigma^*$-band states at an Fe$^{4+}$ ion. In the Mn$^{1+}$/Mn$^{3+}$ and Fe$^{4+}$/Fe$^{3+}$ mixed-valent perovskites, a crossover from localized to itinerant electron behavior may occur. Therefore, a meaningful comparison of the physical properties imparted by localized versus itinerant $\sigma$-bonding electrons in the Mn$^{4+}$/Mn$^{3+}$ and Fe$^{4+}$/Fe$^{3+}$ systems is possible and instructive. We distinguish the single-valent from the mixed-valent situations.

In LaMnO$_3$, which is representative of the single-valent $R MnO_3$ family, a cooperative site distortion below $T_{OCO} = 750$ K removes the degeneracy of the localized $e$ orbitals [1] whereas the orbital degeneracy of the $\sigma^*$ band of Ca$_2$Fe$_2$O$_5$ is removed below 290 K by the formation of molecular $e$ orbitals within Fe(d$^{4+}$e$^0$)O$_6$ complexes that alternate with more ionically bonded Fe(d$^{4+}$e$^0$) ions; $\delta$ approaches unity in an Fe(V)O$_6$ complex at $T = 0$ K [2]. The cost in on-site electron–electron electrostatic energy to form a localized Fe$^{4+}$:$t^2e^1$ configuration is, in this case, less than the gain in bonding energy within the Fe(V)O$_6$ complex. On the other hand, the orbital degeneracy of the $\sigma^*$ band is retained to lowest temperatures in SrFeO$_3$ where a RKKY indirect interatomic exchange interaction via itinerant $\sigma^*$ electrons gives a ferromagnetic spiral-spin configuration propagating along a [111] axis below $T_N = 134$ K [3].

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In the mixed-valent $R_{1-x}A_xMnO_3$ ($A =$ alkaline earth) systems, the introduction of holes into the MnO$_2$ array creates a range of unusual phenomena that vary sensitively with $x$, temperature, and the mean size of the $R_{1-x}A_x$ ions as well as their ionic-size variance [4]. For example, holes introduced into the Mn$^{4+}$/Mn$^{3+}$ couple of the La$_{1-x}$Sr$_x$MnO$_3$ system transform with increasing $x$ from small polarons to two manganese (Zener) polarons that, on lowering the temperature, progressively condense into orbitally disordered, ferromagnetic clusters within an orbitally ordered matrix; these hole-rich, conductive clusters grow to beyond percolation below a global ferromagnetic Curie temperature $T_C$. Above $T_C$, the ferromagnetic clusters grow in an applied magnetic field at the expense of the orbitally ordered, paramagnetic matrix to give a colossal negative magnetoresistance at their percolation threshold. Below $T_C$, a vibronic conduction of the ferromagnetic phase transforms at $x \approx 0.15$ into metallic conduction with $\varepsilon$ electrons occupying a narrow $\sigma^*$ band of $\varepsilon$-orbital parentage.

Oxygen-stoichiometric Fe(IV) oxides are synthesized under high oxygen pressure, and oxidation of the Fe$^{3+}$/Fe$^{4+}$ redox couple is accessible with conventional techniques. However, the introduction of holes or electrons into the Fe$^{4+}$/Fe$^{3+}$ couple is accessible and provides an interesting comparison to the introduction of holes or electrons into the Mn$^{4+}$/Mn$^{3+}$ couple. For example, LaFeO$_3$ is an antiferromagnetic insulator with $T_N = 750$ K [5], and holes introduced into the Fe$^{4+}$/Fe$^{3+}$ couple of the La$_{1-x}$Sr$_x$FeO$_3$ system become trapped as hole pairs within molecular orbitals of Fe(V)O$_6$ complexes [6]. In La$_{1/3}$Sr$_{2/3}$FeO$_3$, Battle et al. [7] have reported and Matsuno et al. [8] have confirmed that below a first-order transition at 198 K, Fe(V)O$_6$ complexes order into every third (111) plane to have confirmed that below a first-order transition at 198 K, Fe$^{4+}$ redox couple is not accessible with conventional techniques. However, the introduction of holes or electrons into the Mn$^{4+}$/Mn$^{3+}$ couple of the Fe$^{4+}$/Fe$^{3+}$ couple of the Fe$^{4+}$/Fe$^{3+}$ couple, respectively. The thermoelectric power $\rho(T)$, the thermoelectric power $\chi(T)$, and the magnetic susceptibility $\chi(T)$ have been used to track the behavior of the charge carriers.

2. Experimental

Polycrystalline Ca$_2$Fe$_2$O$_5$ was prepared by standard solid-state reaction. Stoichiometric mixtures of CaCO$_3$ (99.95%) and Fe$_3$O$_4$ (99.999%) were ground together and calcined in air at 950 °C for 24 h. The sample was then reground, cold-pressed into pellets, and sintered at 1200 °C for another 24 h in air and cooled to room temperature. Then the cold-pressed pellets of the as-prepared, red Ca$_2$Fe$_2$O$_5$ were put into a quartz tube and annealed at 500 °C with flowing ozone gas for 6 days. After this treatment, the color of the pellets changed to black, showing oxidation of the sample to Ca$_2$Fe$_2$O$_5+\delta$.

The seed and feed rods for the growth of single crystals of SrFeO$_{3-\delta}$ and La$_{1/3}$Sr$_{2/3}$FeO$_{3-\delta}$ were prepared by solid-state reaction. Stoichiometric mixtures of SrCO$_3$/La$_2$O$_3$ (99.95%) and Fe$_2$O$_3$ (99.999%) were ground together and calcined in air at 950 °C for 24 h. The sample was then reground and sintered at 1150 °C for another 24 h in air and cooled to room temperature. It was then reground into a powder and pressed in a 6-mm-diameter x 60-mm rod under 400 atm hydrostatic pressure. The rods were finally sintered at 1300 and 1400 °C for 20 h in oxygen for SrFeO$_{3-\delta}$ and La$_{1/3}$Sr$_{2/3}$FeO$_{3-\delta}$, respectively. The crystal growth was carried out in an IR-heated image furnace (NEC) equipped with two halogen lamps and double ellipsoidal mirrors. The feed and seed rods were rotated in opposite directions at 25 rpm during crystal growth at a rate of 2 mm/h. An oxygen pressure of 2.0 bar was applied during growth.

Powder X-ray diffraction patterns for Ca$_2$Fe$_2$O$_5$, Ca$_2$Fe$_2$O$_{5+\delta}$, SrFeO$_{3-\delta}$, and La$_{1/3}$Sr$_{2/3}$FeO$_{3-\delta}$ were recorded with a Siemens 1729 diffractometer equipped with a pyrolytic-graphite monochromator and CuK$_\alpha$ radiation; Si was the internal standard. Data were collected in steps of 0.02° over the range 20 $\leqslant 20 \leqslant 80°$ with a count time of 15 s per step. Peak profiles were fitted with the program JADE. All samples were single-phase to XRD, Fig. 1. The lattice parameters are listed in Table 1.

A Perkin-Elmer TGA-7 thermogravimetric analyzer (TGA) was used to determine the oxygen content of the samples from the weight loss on reduction to Fe$^0$ on heating to 1000 °C in an H$_2$(5%)/Ar flow. The oxygen values were Ca$_2$Fe$_2$O$_{5}$ (1) for the as-prepared Ca$_2$Fe$_2$O$_5$, Ca$_2$Fe$_2$O$_{5+\delta}$ (2) for the oxygen-annealed sample, and SrFeO$_{2.83}$ (1) and La$_{1/3}$Sr$_{2/3}$FeO$_{2.88}$ (2) for the two single crystals.
3. Results and discussion

3.1. Ca$_2$Fe$_2$O$_5$.16

3.1.1. Results

The as-prepared Ca$_2$Fe$_2$O$_5$ sample was orthorhombic $Pcmm$ with $a = 5.604(1)$ Å, $b = 14.782(5)$ Å, $c = 5.432(2)$ Å, and $V = 449.98$ Å$^3$. After being annealed in ozone, Ca$_2$Fe$_2$O$_5$.16 keeps the orthorhombic $Pcmm$ structure, but the lattice parameters changed to $a = 5.554(1)$ Å, $b = 14.912(5)$ Å, $c = 5.402(2)$ Å with a smaller volume $V = 447.40$ Å$^3$.

The as-prepared Ca$_2$Fe$_2$O$_5$ is a good insulator with so large a resistivity that we could not measure it with our apparatus. The resistivity of Ca$_2$Fe$_2$O$_5$.16 was smaller; the measured results are shown in Fig. 2(a). There is a peak around 250 K in the d(ln $\rho$)/d(1/T) vs. $T$ curve, which signals a smooth change of the activation energy from 0.06 to 0.13 eV as the temperature increases. Fig. 2(b) shows the temperature dependences of the magnetic susceptibility $\chi(T)$ and its inverse $1/\chi(T)$; and (c) the thermoelectric power $\alpha(T)$ for Ca$_2$Fe$_2$O$_5$.16. Inset of (c): Temperature dependences of magnetic susceptibility $\chi(T)$ and thermoelectric power $\alpha(T)$ for Ca$_2$Fe$_2$O$_5$.16.
3.1.2. Discussion

Our ozone-annealed sample \( \text{Ca}_2\text{Fe}_2\text{O}_{5.16} \) (\( \text{CaFeO}_{2.58} \)) contains about the same amount of excess oxygen as the \( \text{CaFeO}_{2.56} \) and \( \text{CaFeO}_{2.60} \) samples prepared by Gibb et al. [10,11] by annealing \( \text{Ca}_2\text{Fe}_2\text{O}_3 \) under 10 kbar \( \text{O}_2 \).

The observation of a negative thermoelectric power with 0.16 holes/Fe, Fig. 2(c), shows that the mobile holes are restricted to a subset of Fe atoms. Gibb et al. [10,11] have argued from Mössbauer data that the oxygen insertion into \( \text{Ca}_2\text{Fe}_2\text{O}_3 \) is in stages, oxygen diffusing preferentially into separated planes of tetrahedral sites to convert them into planes of octahedral-site iron. Although we were unable to identify such a staging in our samples with high-resolution electron microscopy, the Mössbauer data suggest segregation of oxygen-rich perovskite clusters three \( \text{FeO}_2 \) planes thick separated by a brownmillerite matrix. This model permits a qualitative explanation for an \( \alpha(T)<0 \). The holes have an octahedral-site preference energy. With two holes per three \( \text{FeO}_2 \) octahedra in an oxygen-rich perovskite clusters, the \( \text{Fe}^{4+}/\text{Fe}^{3+} \) redox couple of a cluster would be one-third filled. Since the \( \text{Fe}^{4+}/\text{Fe}^{3+} \) redox couple is pinned to the top of the O-2p bands, the partially filled e orbitals contain a large oxygen fraction, which allows direct communication between the perovskite clusters. Since the charge carriers belong to the one-third-filled \( \text{Fe}^{4+}/\text{Fe}^{3+} \) redox couple of the clusters, direct communication between clusters would give an \( \alpha(T)<0 \). Moreover, stoichiometric \( \text{CaFeO}_3 \) undergoes a disproportionation reaction below 290 K, and a charge transfer below 250 K from electron-rich perovskite clusters to trap sites in the brownmillerite matrix is consistent with this observation.

The nearly temperature-independent thermoelectric power \( \alpha(T) \) above 250 K in Fig. 2(c) as well as an activated \( \rho(T) \) are consistent with a polaronic conduction of the perovskite electrons having a motional enthalpy in the mobility \( \Delta H_m = 0.13 \text{ eV} \). The sharp increase in the magnitude of \( \alpha(T) \) below 250 K signals a trapping of electronic charge carriers from the perovskite clusters; given the octahedral-site preference of the \( \text{Fe}^{IV} \), we attribute the electron traps to fivefold-coordinated \( \text{Fe}^{IV} \) at isolated interstitial oxygen in the brownmillerite matrix. Transfer of electrons from the perovskite slabs to the brownmillerite \( \text{Fe}^{IV} \) below 250 K would reduce the concentration of electronic charge carriers in the \( \text{CaFeO}_3 \) clusters, thereby increasing \( \alpha(T) \). An associated reduction of the motional enthalpy of the charge carriers to \( \Delta H_m = 0.06 \text{ eV} \) signals an approach to the itinerant character of the e electrons formed in stoichiometric \( \text{CaFeO}_3 \). Note that we do not attribute the activation energy of \( \rho(T) \) above 250 K to an \( E_a = \Delta H_m + (\Delta H/2) \approx 0.13 \text{ eV} \), where \( \Delta H = 0.14 \text{ eV} \) is an acceptor-state trapping energy below 250 K, because \( \alpha(T) \) is temperature-independent above 250 K.

The magnetic data of Fig. 2 are also consistent with this two-phase model. The brownmillerite matrix would become antiferromagnetic well above room temperature, which makes meaningless interpretation of the magnetic susceptibility below room temperature with a paramagnetic Curie–Weiss law. On the other hand, the magnetic data of Fig. 2(b) clearly show an antiferromagnetic transition at a \( T_N = 110 \text{ K} \) with a difference between the FC and ZFC measurements below \( T_N \) that is characteristic of a weak ferromagnetic component due to spin canting. We attribute this Neél temperature to the perovskite clusters; the perovskite \( \text{SrFeO}_3 \), which does not undergo a disproportionation reaction as does stoichiometric \( \text{CaFeO}_3 \), has a \( T_N = 134 \text{ K} \) [3]. Long-range magnetic order between the perovskite clusters would be through the antiferromagnetic brownmillerite matrix. Since the perovskite clusters are also antiferromagnetic with only a weak ferromagnetic component, the situation is different from that of a classic spin glass. Nevertheless, the \( M–H \) hysteresis loop taken at 5 K, Fig. 3, shows only a small remanence and an effective magnetocrystalline anisotropy that is huge. These features signal a magnetic coupling between the magnetic order in the perovskite clusters and that of the brownmillerite matrix.

It is also noteworthy that the \( 1/\gamma(T) \) curve shows a significant bending setting in below 250 K where the \( \rho(T) \) and \( \alpha(T) \) data signal a trapping out of electrons from the perovskite clusters.

3.2. \( \text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_{5.88} \)

3.2.1. Results

Fig. 4 shows the transport and magnetic data for \( \text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_{5.88} \). Fig. 4(b) signals an antiferromagnetic transition at \( T_N \approx 180 \text{ K} \). Above 180 K, the thermoelectric power \( \alpha(T) \) of Fig. 4(c) is essentially temperature-independent with a positive value of 13.5 \( \mu \text{V/K} \); with decreasing temperature, it drops sharply below 180 K to a large negative value. The resistivity \( \rho(T) \) of Fig. 4(a) is consistent with polaronic conduction above 180 K having a motional enthalpy \( \Delta H_m = 0.07 \text{ eV} \). The \( \text{d(ln}\rho)/\text{d}(1/T) \) curve of the
Below 190 K, the Arrhenius plot of resistivity $\rho(T)$ of single-crystal SrFeO$_{2.83}$ shows, inset of Fig. 6(a), a smooth metal-insulator transition near 190 K with a change in slope at ca. 240 K. Below 190 K, the Arrhenius plot of $\rho = \rho_0 \exp(-E_a/\kappa T)$ in Fig. 6(a) gives an activation energy $E_a = 0.02$ eV. Nakanura and Iida [13] reported a similar $E_a = 0.02$ eV for SrFeO$_{2.82}$, but they failed to observe a transition to metallic behavior in their polycrystalline sample.

Above 240 K, the inverse magnetic susceptibility, $1/\chi(T)$, of Fig. 6(b), is linear with a Weiss constant $\theta = 41$ K; below 240 K, the curve flattens in a manner typical of short-range magnetic ordering: long-range antiferromagnetic order sets in below a $T_N \approx 60$ K.

The thermoelectric power $\alpha(T)$ of Fig. 6(c) has a small, nearly temperature-independent negative value above large intraatomic energy $U_{\text{eff}} = U + \Delta_{\text{ex}}$, any electrons introduced would occupy the Fe(V)O$_6/2$ cluster orbitals as Fe(V)O$_6/2$ units formed by cooperative oxygen displacements responsible for the

$$-\text{Fe}^{3+} - \text{O} - \text{Fe}(\text{V}) - \text{O} - \text{Fe}^{3+} - \text{O} - \text{Fe}^{3+}$$

(2)

CDW. As illustrated schematically in Fig. 5(b), the (111) planes within a CDW would have short Fe–O bonds to give rise to a mixed-valent Fe(V)O$_6/2$/Fe(IV)O$_6/2$ level supporting $n$-type conduction. However, the $n$-type carriers would be progressively trapped out at oxygen vacancies in the more ionic regions as the temperature is lowered to give an increasing $|\alpha(T)|$. The transition at 180 K appears to be smooth with a progressive growth of the volume fraction of the CDW phase over the temperature interval $120 \text{K} < T < 180 \text{K}$.

3.3. SrFeO$_{2.83}$

3.3.1. Results

The resistivity $\rho(T)$ curve of single-crystal SrFeO$_{2.83}$ shows, inset of Fig. 6(a), a smooth metal-insulator transition near 190 K with a change in slope at ca. 240 K. Below 190 K, the Arrhenius plot of $\rho = \rho_0 \exp(-E_a/\kappa T)$ in Fig. 6(a) gives an activation energy $E_a = 0.02$ eV. Nakanura and Iida [13] reported a similar $E_a = 0.02$ eV for SrFeO$_{2.82}$, but they failed to observe a transition to metallic behavior in their polycrystalline sample.

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The thermoelectric power $\alpha(T)$ of Fig. 6(c) has a small, nearly temperature-independent negative value above large intraatomic energy $U_{\text{eff}} = U + \Delta_{\text{ex}}$, any electrons introduced would occupy the Fe(V)O$_6/2$ cluster orbitals as Fe(V)O$_6/2$ units formed by cooperative oxygen displacements responsible for the

$$-\text{Fe}^{3+} - \text{O} - \text{Fe}(\text{V}) - \text{O} - \text{Fe}^{3+} - \text{O} - \text{Fe}^{3+}$$

(2)

CDW. As illustrated schematically in Fig. 5(b), the (111) planes within a CDW would have short Fe–O bonds to give rise to a mixed-valent Fe(V)O$_6/2$/Fe(IV)O$_6/2$ level supporting $n$-type conduction. However, the $n$-type carriers would be progressively trapped out at oxygen vacancies in the more ionic regions as the temperature is lowered to give an increasing $|\alpha(T)|$. The transition at 180 K appears to be smooth with a progressive growth of the volume fraction of the CDW phase over the temperature interval $120 \text{K} < T < 180 \text{K}$.

3.3. SrFeO$_{2.83}$

3.3.1. Results

The resistivity $\rho(T)$ curve of single-crystal SrFeO$_{2.83}$ shows, inset of Fig. 6(a), a smooth metal-insulator transition near 190 K with a change in slope at ca. 240 K. Below 190 K, the Arrhenius plot of $\rho = \rho_0 \exp(-E_a/\kappa T)$ in Fig. 6(a) gives an activation energy $E_a = 0.02$ eV. Nakanura and Iida [13] reported a similar $E_a = 0.02$ eV for SrFeO$_{2.82}$, but they failed to observe a transition to metallic behavior in their polycrystalline sample.

Above 240 K, the inverse magnetic susceptibility, $1/\chi(T)$, of Fig. 6(b), is linear with a Weiss constant $\theta = 41$ K; below 240 K, the curve flattens in a manner typical of short-range magnetic ordering: long-range antiferromagnetic order sets in below a $T_N \approx 60$ K.

The thermoelectric power $\alpha(T)$ of Fig. 6(c) has a small, nearly temperature-independent negative value above large intraatomic energy $U_{\text{eff}} = U + \Delta_{\text{ex}}$, any electrons introduced would occupy the Fe(V)O$_6/2$ cluster orbitals as Fe(V)O$_6/2$ units formed by cooperative oxygen displacements responsible for the

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(2)

CDW. As illustrated schematically in Fig. 5(b), the (111) planes within a CDW would have short Fe–O bonds to give rise to a mixed-valent Fe(V)O$_6/2$/Fe(IV)O$_6/2$ level supporting $n$-type conduction. However, the $n$-type carriers would be progressively trapped out at oxygen vacancies in the more ionic regions as the temperature is lowered to give an increasing $|\alpha(T)|$. The transition at 180 K appears to be smooth with a progressive growth of the volume fraction of the CDW phase over the temperature interval $120 \text{K} < T < 180 \text{K}$.
exchange to give a paramagnetic Weiss constant \( \theta > 0 \) [18]. Moreover, trapping of electrons at oxygen vacancies below 240 K would reduce the ferromagnetic coupling, thereby flattening the \( 1/\chi(T) \) curve by lowering the Weiss constant \( \theta \). However, the transition from \( n \)-type to \( p \)-type conduction would require, with this model, a transition from conduction in the matrix to conduction between interacting trap states at the oxygen vacancies, and trapping out of charge carriers should change \( \chi(T) \) in the range 190 K < \( T < 240 \) K, which is not observed.

On the other hand, SrFeO\(_{2.83}\) is a “bad metal,” and the \( \chi(T) \) data above 240 K has little temperature dependence. These features are characteristic of the transport behavior of a mixed-valent perovskite at crossover from localized to itinerant electronic behavior with strong electron-lattice interactions, but no trapping into small polarons [4]. In this situation, an ordering at lower temperatures of the optical-mode lattice vibration that would trap electrons within molecular orbitals of a cluster of Fe atoms would manifest itself as a spinodal phase segregation into electron-rich and electron-poor phases. The simplest such electron-rich cluster would be a two-iron Fe\(^{3+}\)–O–Fe\(^{4+}\) pair corresponding to a Zener polaron; Zener polarons with zero motional enthalpy give rise to ferromagnetic Zener double exchange [19]. Thus bad-metal behavior would also give a paramagnetic Weiss constant \( \theta > 0 \). Moreover, an electron-rich cluster containing fast electron transfer would become superparamagnetic above a long-range ordering temperature.

To apply the Zener polaron model to account for the data of Fig. 6 for SrFeO\(_{2.83}\), we point out that the appearance of short-range ferromagnetic fluctuations below 240 K would not only be responsible for the observed flattening of the paramagnetic \( 1/\chi(T) \) curve, but would also reduce spin-disorder scattering of the mobile electrons so as to account for the sharp change in the slope of \( \rho(T) \) at 240 K. The \( \chi(T) \) data signal that the mobile electrons continue to have access to all the Fe atoms down to 190 K whereas the change from \( \chi(T) < 0 \) to \( \chi(T) > 0 \) on cooling below 110 K suggests a progressive condensation of the mobile Zener polarons into an electron-rich phase that is pinned by the oxygen vacancies to a minority volume fraction of the sample. However, in order for the other percolating volume fraction to be a \( p \)-type polaronic conductor, the electron-rich phase must capture a few electrons from the SrFeO\(_3\) matrix.

### 3.4 Discussion

The \( \sigma \)-bonding \( e \) electrons of the high-spin Fe(IV) ions of SrFeO\(_3\) occupy a narrow \( \sigma^* \) band of itinerant-electron states in which the spin degeneracy is removed by intraatomic exchange with the spin \( S = \frac{3}{2} \) of a localized-electron, \( \pi \)-bonding \( r^3 \) manifold. Removal of 0.17 oxide ions introduces 0.34 electrons into the Fe\(^{4+}\)/Fe\(^{3+}\) redox couple, which would give an electronic conductivity if the electrons have access to all the Fe atoms. Since the oxygen vacancies strongly perturb the periodic potential of the FeO\(_{3−\delta}\) array, the narrow \( \sigma^* \) band of SrFeO\(_3\) would either develop Anderson-localized states at the wings of the \( \sigma^* \) band or be transformed into a polaronic conductor with a trapping out of electronic polarons at the oxygen vacancies as the temperature is lowered. So long as the Fermi energy remains above the mobility edge introduced by Anderson localization, the crystal should exhibit metallic behavior. Moreover, itinerant \( \sigma^* \) electrons would couple nearest-neighbor spins ferromagnetically by de Gennes double

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**Fig. 6.** (a) Temperature dependences of resistivity \( \rho(T) \) and \( \ln \rho \) vs \( 1/T \) curve; and temperature dependences of (b) molar magnetic susceptibility \( \chi \) of SrFeO\(_{2.83}\). Inset of (a): temperature dependences of resistivity \( \rho(T) \) with 150 K < \( T < 300 \) K for SrFeO\(_{2.83}\).
molecular-orbital (or itinerant) electrons and the other localized electrons. On the approach to the transition from the itinerant-electron side, the Mn$^{4+}$/Mn$^{3+}$ perovskites are ferromagnetic metals and cooperative orbital ordering is manifest as the $\sigma^*$ band narrows. In contrast, the Fe$^{3+}$/Fe$^{3+}$ perovskites have $\sigma^*$ bands that either segregate into an electron-rich and an electron-poor phase or, as the band narrows, undergo the disproportionation reaction $2\text{Fe(IV)O}_6/2 = \text{Fe(V)O}_6/2 + \text{Fe}^{3+}$. Covalent bonding in the 2Fe(IV)O$_6/2$ site is too large for Jahn–Teller ordering of localized orbitals.

In this paper, we have explored the transitional domain in iron perovskites made oxygen non-stoichiometric. In those oxides, segregation into oxygen-rich and oxygen-poor phases can occur at relatively low temperatures and electrons are trapped from octahedral sites to sites of lower oxygen stoichiometry at oxygen vacancies below room temperature. Clustering of interstitial oxygen in ozone-oxidized Ca$_2$Fe$_2$O$_5.16$ was argued to provide a CaFeO$_3$ perovskite phase within a brownmillerite matrix that orders antiferromagnetic below 110 K, well below the Néel temperature of the brownmillerite matrix, which contains some isolated interstitial oxygen atoms. A single crystal of La$_{1.5}$Sr$_{2.5}$FeO$_2.88$ was argued to undergo a progressive growth, on cooling below 180 K, of a phase containing a CDW disproportionation reaction. A single crystal of SrFeO$_2.83$ was argued to segregate on cooling into two-iron Zener polarons that become superparamagnetic below 240 K; the Zener polarons become increasingly trapped into an electron-rich phase pinned at oxygen vacancies on cooling below 190 K.

Acknowledgments

The NSF and the Robert A. Welch Foundation of Houston, TX, are thanked for financial support.

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