Articles

High Temperature Magnetic Properties of Sr-Doped Lanthanum Cobalt Oxide ($La_{1-x}Sr_xCoO_{3-\delta}$)

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A high-temperature, controlled atmosphere Faraday magnetometer has been used to measure the magnetic susceptibility of $La_{1-x}Sr_xCoO_{3-\delta}$ (LSC) as a function of temperature, Sr content (x), and oxygen nonstoichiometry (δ). Above 800 °C the magnetic susceptibility becomes independent of Co oxidation state and Sr doping, consistent with metallic valance electrons. Under these conditions, conductivity measurements as a function of x, T, and δ exhibit classic metallic behavior, with resistivity scaling linearly with temperature and nonlinearly with defect concentration. However, a large Curie–Weiss susceptibility persists even at high temperatures, suggesting the coexistence of more localized electron configurations. We discuss this behavior in terms of existing theories of electronic and magnetic structure.

Introduction

Perovskite oxides exhibiting high electronic and ionic conductivity have drawn great interest as membrane catalysts, or electrocatalysts in solid oxide fuel cells.[1–5] $La_{1-x}Sr_xCoO_{3-\delta}$ (LSC) has enjoyed particular attention because of its ability to become reduced at moderate P_{O2}, producing high concentrations of oxygen ion vacancies in air. The high-temperature thermodynamic, transport, and catalytic properties of LSC have often been attributed to its high oxygen vacancy concentration, as well as metallic band structure, which appears to prevail at high Sr doping (x) and/or high temperature. Previous electronic conductivity and Seebeck measurements of LSC suggest that it is metallic for $x \geq 0.4$, while for $x < 0.3$ it undergoes a broad semiconductor-to-metal transition as a function of temperature, with the transition temperature being strongly dependent on x.[6,7] The high temperature nonstoichiometry properties of LSC closely obey an itinerant electron model, in which electrons are assumed to have zero entropy, but vary in energy with electron occupation.[8,9]

The metallic state of LSC is generally thought to involve a partially localized σ^* band, an e_g-like band formed by hybridization of oxygen 2p and Co 3d orbitals.[10–13] Some controversy exists as to the origin of the semiconductor-to-metal transition- whether it is driven by changes in occupancy of the σ^* band due to the relative stability of low-spin and intermediate-spin configurations, or involves splitting of the σ^* band within the intermediate spin regime. Nonetheless, one might expect a shift from Curie–Weiss toward Pauli susceptibility as some localized states give way to delocalized magnetic bands.

Prior to the present work, the cobalt spin state has never been measured at high temperature (particularly as a function of Co oxidation state)—most of our current understanding of magnetic properties is based on extrapolation of magnetic properties from low temperature, or ab initio calculations.[10,14,15] The transition to the metallic state appears to be broad and gradual, a difficult observation to rationalize based on current models. High-temperature nuclear magnetic resonance (O-17 NMR)—an indirect measure of Pauli susceptibility through the Knight shift—suggests coexistence of delocalized magnetic bands with localized unpaired spins in similar materi-

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als.[16] More recent work on LSC at lower temperatures based on La-139 NMR[17] shows evidence for local magnetic domains, which may persist at high temperature.

In order to address these issues, we have measured magnetic susceptibility as a function of T and P_{O2}, which allows us to control Co oxidation state via equilibrium with the gas-phase oxygen partial pressure. By quantifying changes in spin state with temperature and oxidation state independently, this technique gives some insight whether electron states (filled or depleted) at the Fermi level are localized or delocalized, as well as the population of unpaired states that remain within the metallic state at high temperatures. We have also extended previous measurements of electronic conductivity as a function of P_{O2} and T so as more clearly delineate changes in electronic structure from changes in carrier concentration.

Theory

Significantly above the magnetic ordering temperature, metallic electrons tend to exhibit weak Pauli paramagnetism (χ_P), which to first approximation is temperature independent. The temperature independence arises because the bandwidth is much greater than kT, and thus magnetic splitting of the band dominates the magnetic moment. Assuming the bandwidth is also much greater than the magnetic splitting, χ_P is proportional to the density of states at the Fermi level:[18]

$$\chi_P = \mu_0 {\mu_B}^2 g(E_F) \tag{1}$$

where $g(E_F)$ is the density of states at the Fermi level, μ_0 is the permeability, and μ_B is the effective magnetic moment of an electron (Bohr magneton). In contrast, systems containing localized unpaired electrons are expected (above the magnetic ordering temperature) to exhibit Curie–Weiss behavior (c_{CW}):

$$\chi_{CW} = \frac{C}{T-\theta}; \quad C = \frac{\mu_0 N p^2 \mu_B^2}{3k} \tag{2}$$

where C is the Curie constant (proportional to the effective number of Bohr magnetons, p) θ is the Weiss constant for magnetic ordering (representing a mean-field correction of the magnetic field due to sample magnetization), and N is the Avogadro's number.

In practice, the Pauli susceptibility is expected to be much smaller than the Curie–Weiss susceptibility, even when significant Stoner enhancements are considered, and thus small in systems with localized paramagnetic centers. For example, the estimated Pauli susceptibility for $La_{1-x}Sr_xCoO_{3-\delta}$ using eq 1 and $g(E_F)$ taken from thermodynamic measurements[9] yields 6×10^{-10} m^3/mol, which is approximately 2 orders of magnitude smaller than typical values we measure. The diamagnetic contribution of core electrons is also negligible compared to the magnitude of paramagnetic susceptibility in these materials.

In systems where localized and delocalized electrons coexist, one expects both Pauli and Curie–Weiss contributions. Hence, measurement of magnetic susceptibility as a function of temperature at fixed oxidation state can be a valuable tool to identifying localized electrons. Likewise, measurements of magnetic susceptibility as a function of oxidation state at fixed temperature helps identify whether valance electrons involve localized or delocalized states.

Experimental Section

Commercially available powders of $La_{0.8}Sr_{0.2}CoO_{3-\delta}$ (LSC-82), $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ (LSC-64), and $La_{0.3}Sr_{0.7}CoO_{3-\delta}$ (LSC-37) from Praxair, Inc., were sintered into porous bars using cornstarch as a pore former. The powders were pressed into 45 mm × 5 mm × 5 mm bars using a uniaxial press with a pressure of approximately 4500 psi. The bars were heated at a rate of 1 °C/min to 1200 °C, held at that temperature for 6 h in air, and cooled down at 1 °C/min to room temperature. The porosity of the sintered samples were found to be in the range of 35–45%, measured using Archimedes method. The use of a porous sample facilitates equilibrium between gas and solid P_{O2} at lower temperatures.[19] The bar was cut into segments approximately 5 mm in length, and notched to accommodate a suspension wire. The porous samples used in the study were confirmed as single-phase perovskite structure by room temperature X-ray diffraction.

Magnetic measurements between 4 K and room temperature were obtained using MPMS SQUID magnetometer. These low temperature measurements showed that LSC samples are paramagnetic at room temperature, with magnetic moments of approximately 4.0 Bohr magnetons per cobalt site. The local paramagnetic moments order ferromagnetically at 198 K, 242 K, and 221 K, respectively, for fully stoichiometric LSC-82, LSC-64, and LSC-37. These values are consistent with previous literature.[12,22] Measurements of saturation magnetization were also made on samples of LSC-64 vs δ. The samples in this case were quenched following annealing at various temperatures and oxygen partial pressures (*to be published*). These measurements ($\theta = 242$ K, 237 K, and 221 K, respectively, for $\delta = 0.000, 0.036, 0.239$) show that the ordering temperature decreases with increasing δ, consistent with increased average M−O bond lengths associated with chemical expansion.[19]

High temperature magnetic force measurements were carried out using a Faraday magnetometer, as described previously.[20] Measurements were made at a uniform magnetic field of 5 T and a gradient field of 1000 Gauss/inch. Oxygen partial pressure in the instrument was controlled using blended gases of oxygen in nitrogen. The flow rate of the feed gas was maintained at 100 sccm by a mass flow controller. Electrical conductivity of LSC-82 and LSC-64 were measured using the AC four probe technique at low frequencies, and corrected for porosity.

Results

Magnetic susceptibility measurements were made as a function of temperature and oxygen partial pressure, $\chi(T, P_{O2})$. To recast our measurement in the form $\chi(T, \delta)$, we used a modified version of Lankhorst's rigid band model[9,19]

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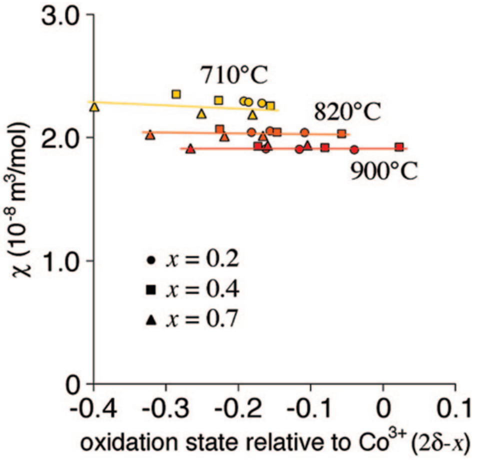

Figure 1. High temperature magnetic susceptibility of LSC as a function of electron occupancy, Sr content (x) (symbols), and temperature (color/grayscale).

to interpolate previously measured oxygen nonstoichiometry properties of $La_{1-x}Sr_xCoO_{3-\delta}$. Our modification adds a parameter that improves overall fit, and for our purposes here should be thought of simply as an empirical interpolation of the data. Accuracy in reproducing $\delta(T, P_{O2})$ is better than ±10% of δ over the range of conditions studied.

Figure 1 shows a plot of magnetic susceptibility versus cobalt oxidation state, expressed in terms of the "electron occupation number", $n_e = 2\delta - x$, as defined by Lankhorst.[9] Increasingly negative values of n_e represent positive deviations of the Co oxidation state from its formal valance of Co^{3+}. Assuming an intermediate spin configuration with delocalized $Co^{3d}-O^{2p}$ σ^* band, n_e also represents the deviation of the band occupancy from half-filled. The data show that as temperature is increased, magnetic susceptibility of LSC collapses to a nearly universal dependence on oxidation state, regardless of Sr doping. Furthermore, at the highest temperatures, magnetic susceptibility is independent of oxidation state.

One might consider two possible explanations for the behavior in Figure 1 at $T \geq 800$ °C. The first is competing effects: As oxidation state increases, magnetic moment increases due to increased occupation of the Co *d*-levels; but at the same time the Weiss field (and thus also θ) decreases due to increased bond length (chemical expansion); the net result being that the numerator and denominator in eq 2 scale equally with oxidation state. Besides being an amazing coincidence, our previous measurements of chemical expansion in LSC family of materials[19] show that bond length scales with *vacancy concentration*, not oxidation state. Thus this theory fails to explain the universality of $\chi(n_e)$ vs x, since materials of differing x would be expected to have different Weiss fields.

This leaves us with a second preferable (perhaps more obvious) explanation for the data in Figure 1 at $T \geq 800$ °C: the electron states associated with changes in oxidation state are itinerant,[7,21] and thus contribute only a small Pauli susceptibility. Since these states do not contribute to χ, no changes in χ are seen with electron occupation. As the temperature is lowered, some dependence of χ on electron occupancy appears, possibly suggesting the onset of localization effects. This dependence becomes stronger with decreasing x, consistent with the fact that LSC undergoes a metal to semiconductor transition with decreasing x in this range of x and T.[7]

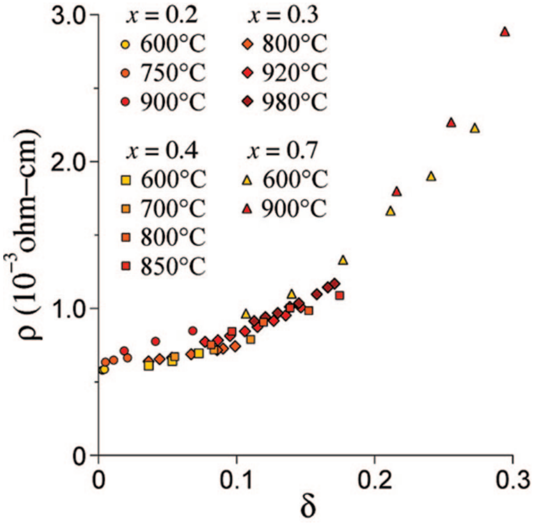

Figure 2. Electrical resistivity of LSC as a function of oxygen vacancy concentration at different temperatures (color/grayscale) and Sr content (x) (symbols). Data for x = 0.3 and x = 0.7 taken from ref 22 and 7, respectively.

Figure 2 shows a plot of electrical resistivity as a function of oxygen nonstoichiometry (δ), Sr content (x), and temperature. In addition to our measurements at $x = 0.2$ and $x = 0.4$, we have also included previously published measurements at $x = 0.3$[22] and $x = 0.7$.[7] The data show that materials of different Sr content exhibit remarkable similarities in the way resistivity scales with δ and T. At a given value of δ, resistivity increases modestly with temperature (consistent with metallic behavior), while at a given temperature resistivity scales strongly (and nonlinearly) with oxygen vacancy concentration.

Discussion

As summarized in the Introduction, there appears to be general agreement that the metallic state of LSC involves a partially occupied delocalized σ^* band, formed by hybridization of oxygen 2p and Co 3d orbitals.[10,11,13,23,24] However, it remains a matter of debate whether the spin state of Co is intermediate spin, or transitional to high spin[14,15,23,25–27] at high temperature. Density functional calculations[10] and thermal expansion studies[28] indicate that Co^{3+} is most likely to be in an intermediate spin configuration at the highest

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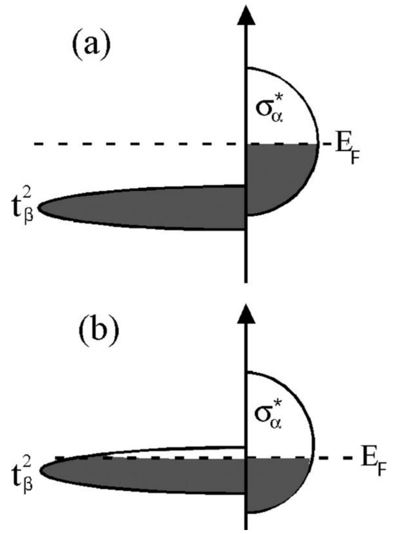

Figure 3. Schematic of the electronic structure of LSC near the Fermi level at high temperatures. (a) Purely intermediate spin (IS) configuration involving a partially filled delocalized s^* band. (b) Partially localized configuration in which the Fermi level overlaps localized t_β^2 states. This figure based on a more complete qualitative diagram in reference.[12]

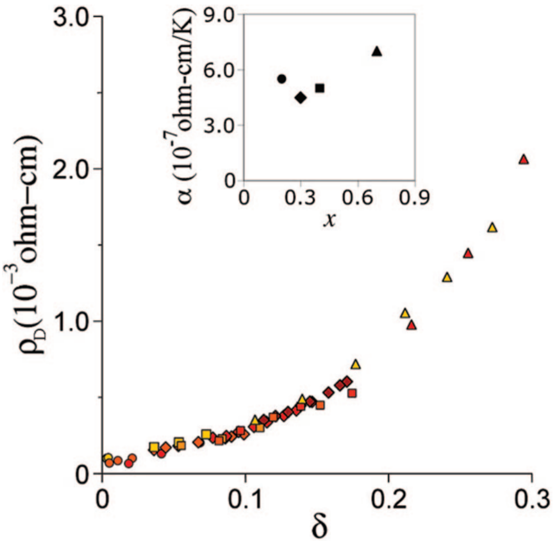

Figure 4. Contribution of defect scattering to electrical resistivity of LSC, calculated from the data in Figure 2 according to eq 4 assuming various values of the thermal resistance coefficient (inset). Symbols and color/grayscale as in Figure 2.

temperatures. However, these calculations generally consider the material to have uniform long-range order with a homogeneous electronic structure.

Assuming LSC is intermediate spin, the resulting electronic structure near the Fermi level is depicted in Figure 3a. At an electron occupation number of zero (i.e., $\delta = x/2$), the Fermi level would be expected reside in the middle of the σ^* band, resulting in metallic properties. Decreasing δ or substitution of Sr^{2+} for La^{3+} would increase the Co oxidation state, resulting in a lowering of electron occupation in the σ^* band. In this scenario, we would expect the magnetic susceptibility to be insensitive to moderate shifts in oxidation state, since the electrons are added or removed from the delocalized σ^* band. Any small changes in Pauli susceptibility due to band curvature would be expected to be small.

In contrast, Figure 3b shows a higher spin electronic structure in which the Fermi level overlaps more localized t_{2g} (t_β^2) states. This situation might prevail, for example, if there were localized Jahn–Teller distortions[10,28] within the overall cubic lattice. In this regime, any change in oxidation state would be expected to involve both localized and delocalized states, and thus measurably influence the paramagnetic susceptibility.

The data in Figure 1 show that above 800 °C the magnetization is almost completely independent of oxidation state over nearly its entire accessible range—up to 1/3 electron per Co atom relative to Co^{3+}. This observation suggests that active valence electrons are part of a purely intermediate spin configuration at the highest temperatures, since even the largest changes in band occupancy are too small to lower the Fermi level into the range of more localized states. In contrast, at 710 °C, the observed dependence of magnetization on electron occupancy appears across the entire range of oxidation states, and an explicit dependence on Sr content also emerges. This effect appears to be most consistent with an upward shift in energy of t_β^2 states relative to σ^* states, resulting in partial localization of the valence electrons at all oxidation states.

The temperature dependence of electrical conductivity may provide further evidence for the arguments presented above. In order to differentiate increases in resistance with temperature from those associated with defect scattering, it is helpful to consider Matthiessen's rule for dilute alloys, which treats the superposition of these effects:[29]

$$\rho = \rho_T + \rho_D \tag{3}$$

where $\rho_T(T)$ is resistance associated with phonon scattering in a normal lattice and ρ_D (assumed independent of temperature), represents additional scattering associated with point defects. Assuming LSC remains metallic with fixed density of states at the Fermi level, $\rho_T(T)$ would be expected to be close to linear (with a coefficient only weakly dependent on Sr content), while $\rho_D(\delta)$ would be expected to be a universal function. Under these assumptions eq 3 can be rearranged as

$$\rho_D(\delta) = \rho - \alpha T \tag{4}$$

where $\alpha(x)$ is the thermal resistance coefficient.

Figure 4 shows a plot of $\rho_D(\delta)$, obtained using eq 4 by assuming various values of $\alpha(x)$ that suppress the T-dependence of $\rho_D(\delta)$ at $\delta = 0$. The values of $\alpha(x)$ so obtained are similar for all materials, as shown in Figure 4 (inset). The resulting plot of $\rho_D(\delta)$ exhibits a nearly universal trend of resistance vs defect concentration, supporting the view that LSC is metallic, with a broad conduction band that sees very little change in density of states at the Fermi level. The universality of this trend is weakest for temperatures below ~800 °C (light colored symbols), consistent with the view that localized states may start to become important at all oxidation states below a certain temperature, accompanied by a breakdown in Matthiessen's rule.

The above explanation of LSC's high-temperature magnetic properties in terms of an approach to a purely IS configuration is only partially satisfying, however. A glaring irregularity is the *magnitude* of Curie–Weiss susceptibility at high temperature. To get an estimate of the number of unpaired spins in the system, eq 2 can be rearranged to give a relation between the number of Bohr magnetons (p) per cobalt ion and magnetic susceptibility:

$$p^2 = \frac{\chi(T-\theta)3k}{\mu_0 N \mu_B{}^2} \quad (5)$$

Equation 5 yields $p \sim 3.5$ Bohr magnetons, consistent with measurements of the saturation moment at low temperatures.[10,12,28] This large value has been previously rationalized in terms of an orbital contribution to the spin-only value (2.83), assuming purely intermediate-spin $Co^{3+}$with all electrons contributing to the total moment.[10] However, if this were the correct explanation, one might expect a much smaller paramagnetic moment at high temperatures, since (according to our measurements here) the valence electrons do not contribute to the localized electron population.

In general the magnitude of Curie–Weiss susceptibility in metallic oxides above their magnetic ordering temperatures is not very well understood.[18] One possible resolution to this paradox is that the material is not homogeneous at a local atomic level. The σ^* electrons participating in changes in oxygen nonstoichiometry may themselves represent only a fraction of the e_g electrons in the system, many of which may be tied up in more localized domains. Evidence for an inhomogeneous electronic structure includes recent ^{139}La NMR measurement showing the coexistence of ferromagnetic and nonferromagnetic phases in LSC for various Sr dopant levels at low temperatures.[17,30] Evidence of phase separation has also been recently observed in a similar perovskite, $Nd_{1-x}Sr_xCoO_3$ using NMR.[31] Thus even though the valence electrons in LSC are itinerant at high temperature (Figure 3a), a significant fraction of the material may possess a more localized high-spin configuration involving fixed Co oxidation state (which does not participate in oxygen exchange). Perhaps, as the temperature is lowered, these localized states become increasingly important for the oxygen nonstoichiometry, leading to a dependence of χ on δ (as in Figure 3b).

Conclusions

Measurements of magnetic susceptibility and electrical conductivity of $La_{1-x}Sr_xCoO_{3-\delta}$ (LSC) at high temperature suggests that above ~800 °C the material possesses itinerant valance electrons. This is consistent with the electrical conductivity, Seebeck coefficient, and oxygen nonstoichiometry properties of LSC. However, the magnitude of the Curie–Weiss susceptibility at these temperatures (~3.5 Bohr magnetons) suggests the coexistence of more localized high-spin domains of fixed oxidation state. As temperature is lowered, the electrons associated with electrical conductivity and oxygen nonstoichiometry appear to become increasingly localized. These conclusions are generally consistent with studies of localized structure and dynamics in highly defective perovskites.

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