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THE LOCAL ATOMIC STRUCTURE OF $La_{1-x}Sr_xCoO_3$: EFFECTS INDUCED BY THE SPIN-STATE AND NON-METAL TO METAL TRANSITIONS

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ABSTRACT

The pair density function (PDF) used in the analysis of pulsed neutron diffraction data of $La_{1-x}Sr_xCoO_3$ revealed new structural effects which are correlated to the susceptibility and transport transitions. The transition in the spin configuration of the Co ions from the low-spin (LS) to the high-spin (HS) state in the Co perovskite oxides can potentially induce structural distortions due to the coupling of the spin to the lattice and charge. The ground state of the pure compound, $LaCoO_3$, is in the LS state and is non-magnetic. A transition occurs to the HS state at ~ 50 K as indicated from the susceptibility measurements due to the thermal excitation of electrons to the e_g level. The $Co_{LS}O_6$ octahedra associated with the Co ions in the LS configuration are distinguished from the $Co_{HS}O_6$ octahedra with the Co in the HS configuration because the Co_{LS}-O bond length is shorter than the Co_{HS}-O distance due to the different size of the corresponding Co ions. Such bond lengths are clearly identified in the local structure between 15 - 300 K. This finding is in contrast to the average structure which shows only one type of bond length in this temperature range but two types of bond lengths are suggested at considerably higher temperatures. This suggests that whereas the LS and HS CoO_6-octahedra coexist, they are randomly distributed in the crystal lattice at lower temperatures and become ordered at higher temperatures. The introduction of charge carriers in the structure does not eliminate the coexistence of both the LS and HS states, indicating that with the transition to the ferromagnetic metallic state, the spin configuration is not entirely of the HS character and structural inhomogeneities are present.

INTRODUCTION

Crystals with the perovskite structure have been extensively studied in part due to their superconducting and magnetoresistive properties. The coupling of the charge to the spin and lattice degrees of freedom yields interesting phenomena such as the colossal magnetoresistance (CMR) [1] and high temperature superconductivity (HTSC) [2] where the underlying mechanisms are still under investigation. The Co perovskite system is yet another example that exhibits several magnetic and transport transitions. In addition, doped cobalt compounds of the $La_{1-x}A_xCoO_3$ composition where A is a divalent atom, are commonly used as cathode materials in solid oxide fuel cells (SOFC) and as a catalyst for controlling the emission of carbon monoxide in automotive combustion engines [3]. The transport is brought about by mixed oxygen and electron conduction.

The pure $LaCoO_3$ is a non-magnetic insulator with an average rhombohedral structure ($R\bar{3}C$). The low spin (LS) state ($S = 0$) is the ground state of this system with the Co ions in the nominal $3d^6$ configuration. Raising the temperature induces a spin transition to a high-spin (HS) configuration of the Co ions. The temperature at which this occurs is about 50 K as indicated by magnetic neutron scattering measurements [4] and susceptibility measurements.

The high temperature phase undergoes a structural as well as a transport transition. At about 400°C, a transition to an $R\bar{3}$ symmetry occurs [5, 6] and at 940°C, a semiconductor-metal transition occurs [6]. It was proposed early on by Raccah and Goodenough [5] that the octahedra corresponding to the LS and HS Co ions coexist and begin to order along the [111] plane above 375°C. This calls for a short range ordering below this temperature. In addition, an intermediate spin (IS) transition is suggested by photoemission [7-9]. The IS state could induce a structural distortion of the Jahn-Teller (JT) type because of the single occupancy of the e_g level. The temperature at which the IS state appears is controversial.

Hole doping in the LS ground state of the pure compound is believed to lead to the formation of localized magnetic polarons with unusually high spin numbers (S = 10-16) [10]. The doped holes induce a local transition from the LS to HS state and create a high spin polaron. The transition from an LS to HS state through doping has been confirmed by NMR studies of ^{59}Co and ^{139}La [11]. The FM state is presumably composed of mobile high-spin polarons. The formation of these magnetic polarons creates a precursor state to the doping-induced FM metallic state which occurs at about $x = 0.18$ in $La_{1-x}Sr_xCoO_3$. It is possible that ferromagnetism in the hole-doped Co oxides is mediated by the double exchange (DE) interaction similar to the CMR manganites via the coupling of the carriers to the local spins. However, the cobaltates can be more complicated because of the transition between the LS and HS states in addition to the stronger hybridization of the Co 3d orbital with the oxygen 2p orbital in comparison to the manganites. All these effects strongly suggest a strong lattice contribution which could change with doping and temperature.

The cobaltates are related to the manganites with regard to their properties but the Co system does not exhibit the CMR effect. In the case of the manganites, it has been shown that the lattice is actively involved in the mechanism that results in the magnetic and transport transitions [13-15] whereas the role of the lattice in cobaltates is not well defined. In the present work, by using pulsed neutron diffraction, we investigated how the structure responds to the change from a non-magnetic to a magnetic state, either paramagnetic (PM) or ferromagnetic (FM), and from an insulating to metallic conductivity. These preliminary results indicate a strong lattice response that is coincident with the change in the electrical and magnetic properties. The local atomic structure of the $La_{1-x}Sr_xCoO_3$ perovskite was studied as a function of temperature using the atomic pair density function (PDF) analysis.

EXPERIMENT

The $La_{1-x}Sr_xCoO_3$ powder samples were prepared by a standard ceramic method from La_2O_3, Co_3O_4 and $SrCO_3$, fired several times at 1100°C to achieve a single phase with intermediate grinding. Their final firing occurred at 1300°C in air for a day and were quenched from this temperature. The pure sample was additionally annealed in nitrogen at 900°C for a day. The samples were characterized by XRD and magnetic measurements. The neutron diffraction data were collected using the Glass Liquid and Amorphous Materials Diffractometer (GLAD) at the Intense Pulsed Neutron Source (IPNS) of the Argonne National Laboratory. Data were collected from room temperature (RT) down to 15 K. The structure function, S(Q), was determined up to 33 Å^{-1} and was corrected for background, absorption, incoherent scattering, multiple scattering as well as for inelastic scattering (Placzek correction [16]). The multiple scattering correction procedure for the GLAD spectrometer was carefully calibrated so that it gives a correct PDF for crystalline Ni and $SrTiO_3$ powders [17]. The PDF, $\rho(r)$, (Eqn. 1) is a real space representation of atomic density correlation and is obtained by Fourier transforming the structure function as follows:

$$\rho(r) = \rho_0 + \frac{1}{2\pi^2 r}\int_0^\infty Q\left[S(Q) - 1\right]\sin(Qr)dQ\,. \qquad (1)$$

ρ_o is the average number density of the material and Q is the momentum transfer. The PDF analysis provides direct information with regard to the local structure without a requirement of long range structural periodicity. Its application extends beyond the amorphous materials, to crystalline solids as well [18, 19].

RESULTS

In Fig. 1, the magnetic susceptibility for $LaCoO_3$ is plotted as a function of temperature and is measured at two fields where data were collected on warming after being cooled in almost zero field (1 Gauss). The top panel shows the high field measurement where a transition begins to occur at ~ 25 K and is complete by 80 K. This corresponds to the excitation from the LS to the HS configuration of the Co ions and is thermally activated in this system. The negative slope of the susceptibility at high temperature is an indication of the paramagnetic state of this system. Below 25 K, an upturn in the magnetization is observed which is present in the low field measurement as well (bottom panel). The origin of the low-temperature increase in the susceptibility is unclear at present. It is suggested that this could be due to frozen-in ferromagnetic domains which are trapped at lower temperatures. Another possibility would be due to the presence of impurities or due to a non-stoichiometry of the sample. However, annealing the sample in an inert atmosphere, N_2, did not change the results. Further investigation is under way to understand this phenomenon.

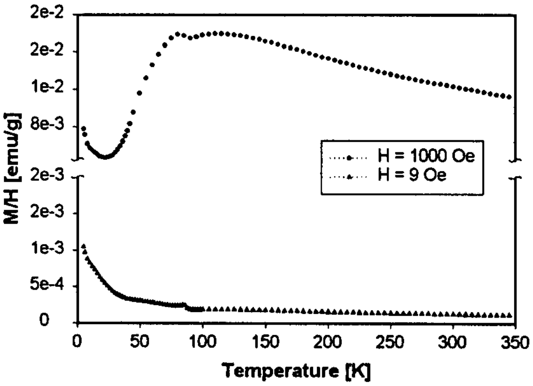

Figure 1: The susceptibility as a function of temperature at two fields, 1000 and 9 Oe. In the high field case, the magnetization increases between 25 and 80 K in going from the low-spin to the high-spin state. Above this temperature, the spin ordering becomes paramagnetic. Below 25 K, an upturn in the susceptibility is observed in both fields which could be due to frozen-in ferromagnetic domains.

The PDF analysis of the $LaCoO_3$ compound revealed interesting structural changes with temperature that have not been observed in previous crystallographic studies. The local atomic structure of $LaCoO_3$ changes as a function of temperature in the way shown in Fig. 2 for the data collected at 15 and 300 K. Note that the local structure determined at the two temperatures changes significantly in the short range region, particularly in the Co-O distance, the shortest distance in the crystal structure. The changes in the Co-O peak are a reflection of the changes of the octahedron. These are in turn associated with the transition from the LS to HS state. As seen from the PDF, two Co-O peaks are present. These correspond to two types of bond lengths, one associated with the LS Co ion (Co_{LS}) and the other with the HS configuration of the Co ion (Co_{HS}). The Co_{HS} ion is of a larger radius and the average Co_{HS}-O distance is 2.01 Å while the Co_{LS}-O distance is 1.95 Å [20]. However, the local structure shows that the actual longest bond length is at 2.15 Å and the shortest at 1.9 Å with possibly an even shorter distance at 1.75 Å. These results are in agreement with the results of Raccah and Goodenough [5] for the high temperature ordered state of the octahedra.

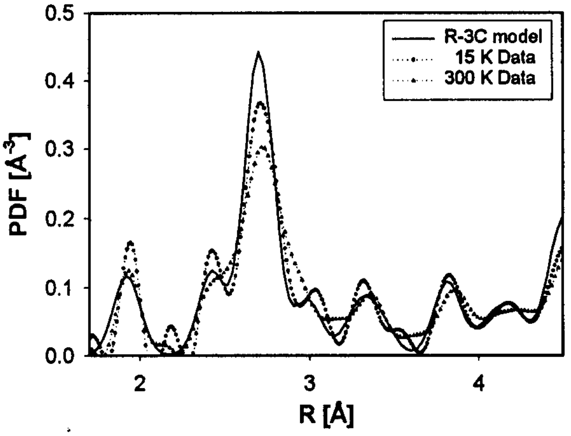

Figure 2: The PDF's of the pure $LaCoO_3$ determined at two temperatures is compared to the model PDF for the known crystallographic structure with R-3C symmetry. Note that although the intermediate local structure resembles that of the average structure, the short range structure differs significantly. At 15 K two types of Co-O distances are observed.

A model PDF calculated from the $R\bar{3}C$ structure of $LaCoO_3$ is also shown in Fig. 2 (solid line) and is compared to the PDF determined from the experiment. The model PDF is calculated in the following way:

$$\rho(r)=\frac{1}{N}\sum_{i,j=1}^{N}\frac{b_ib_j}{\langle b\rangle^2}\delta\left(r-r_{i,j}\right), \qquad (2)$$

where N is the total number of atoms, <b> is the compositionally averaged neutron scattering length and the distance between the atoms is given by $r_{i,j} = |r_i - r_j|$. The model PDF is constructed of δ-functions corresponding to interatomic distances in the structure. The parameters for the model are obtained from the known structure of the compound [5]. The sum of the partial PDF's for each atom gives rise to the total PDF of the crystal which is convoluted with a gaussian function to simulate thermal and quantum zero point vibrations. Although deviations from this model are observed at both temperatures, the PDF determined from the 300 K data is in closer agreement with the model PDF at the first nearest neighbor distance which is the Co-O distance. The Co-O peak in the model is very wide. The 15 K data, on the other hand, are actually quite different from the model, particularly in the first and second nearest neighbor distances. The experimental PDF clearly shows the presence of two peaks, whereas only one peak is evident in the model for the average structure. The two peaks establish the presence of both HS and LS Co ions. This is consistent with the magnetic measurements performed on this sam-

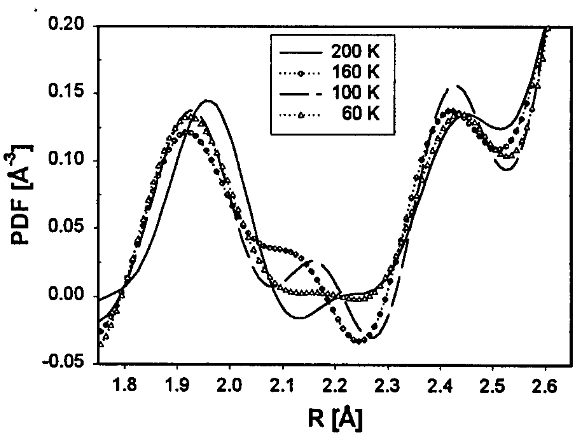

Figure 3: The temperature dependence of the Co-O PDF peaks in $LaCoO_3$. Note how both peaks change position with temperature. The shift in the peak position could be dynamic in origin.

ple which indicate that the spin state changes with temperature in this system.

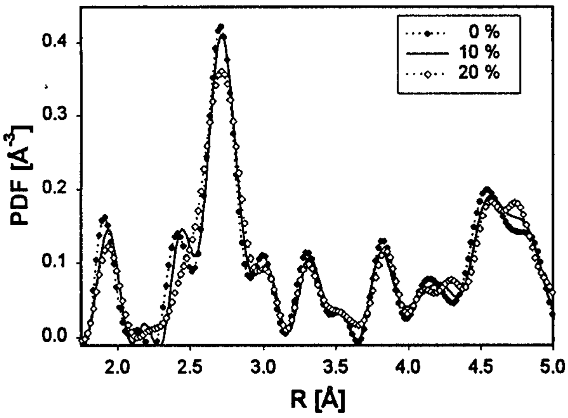

Figure 4: The PDF's of La$_{1-x}$Sr$_x$CoO$_3$ at x = 0, 0.1 and 0.2. The data were collected at 15 K. At this temperature, the peak at 2.15 Å is present at all compositions but is reduced at 20 % of doping.

The temperature dependence of the Co-O peaks of LaCoO$_3$ for intermediate temperatures is shown in Fig. 3. As the temperature is raised which corresponds to the transition from the LS to the HS state, the local structure shows a lot of changes. In particular, the peak at 2.15 Å is present at all temperatures. The nature of this peak could be dynamic due to the thermally excited spin fluctuations. An intermediate spin (IS) state has been proposed possibly at temperatures higher than room temperature [5, 7]. Such an IS state, which resembles a Jahn-Teller type of distortion, induces a bond length of longer than the average Co-O bond length of ~ 2.1 Å, longer than the average Co-O bond (1.95 Å). More experiments are under way to investigate the details of this state.

Doping with Sr changes the local structure as shown in Fig. 4. At 15 K and with 10% Sr, it has been proposed [21] that the system is in a spin-glass state, whereas with 20% of Sr, a ferromagnetic transition occurs. Although the average structure is rhombohedral for all compositions, the local structure changes with doping as indicated by the comparison of the 10 and 20% samples to the pure compound. At this temperature, it is expected that with 20% Sr, the Co ions would all be in the HS state but two Co-O peaks are observed, suggesting that the ferromagnetic metallic state is not made of a uniform HS state.

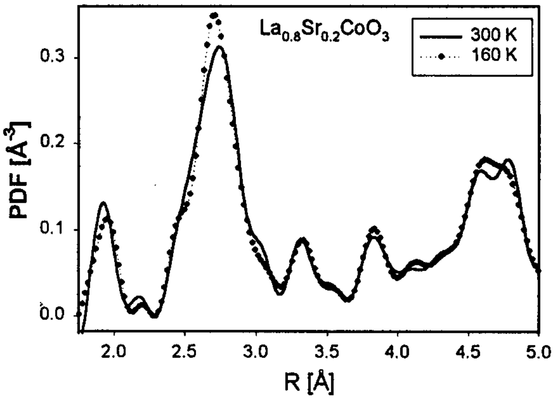

Figure 5: The PDF's of La$_{.8}$Sr$_{.2}$CoO$_3$ at two temperatures, 160 and 300 K. Note that even at this composition, two types of Co-O bonds are present as in the undoped compound.

A similar temperature dependence of the PDF is observed in the doped samples as in the pure compound. The local structure of La$_{0.8}$Sr$_{0.2}$CoO$_3$ changes with temperature as shown in Fig. 5. The long Co-O peak is present in the local structure, similar to LaCoO$_3$, indicating that both LS and HS octahedra are present in the insulating and metallic states of this compound.

DISCUSSION

The PDF analysis has shown that two types of Co-O bonds are present in the local structure despite the fact that the average crystallographic structure indicates the presence of a single type of Co-O bond in the temperature range we investigated. However, x-ray studies at higher temperature demonstrate the existence of such bond lengths due to the ordering of the octahedra [5]. This suggests that the LS and HS octahedra are present even at temperatures where average techniques become insensitive to their presence, and they are randomnly distributed in the crystal structure. Further studies are underway to understand the differences between the local and average structures which might be important in order to understand the mechanism of the spin-state transition in these compounds.

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