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Density of states, magnetic and transport properties of Nd doped two dimensional perovskite compound Sr_2CoO_4

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Structures, transport, magnetic properties, and first principle calculation results will be reported for the two dimensional layered structured perovskite compounds $Sr_{2-x}Nd_xCoO_4$ (x = 0.5, 0.75, 1, 1.25). Structure refinement results revealed that these compounds crystallized in K_2NiF_4-type structures with space group $I4/mmm$. The temperature dependence of resistivity showed semiconductor like behavior for these samples. It was found that the lattice parameter c decreases as the doping level x increases. The compounds exhibited a paramagnetic to ferromagnetic transition at temperatures of about 170, 125 K for the x = 1 and 0.75 samples, respectively. The temperature dependence of resistivity for the samples can be well fitted by the 2D variable hoping (VRH) model $\rho = \rho_o \exp(T_0/T)^{1/3}$ (where ρ_o is a material specific characteristic conductance, with unit Ω^{-1}, T_0 is a material specific characteristic temperature in K) over the whole measured temperature range. First principles calculations indicated that the Nd doped Sr_2CoO_4 compounds show high spin polarization. © *2012 American Institute of Physics*. [doi:10.1063/1.3672825]

Two dimensional compounds with the K_2NiF_4-type structure has generated great interest in recent years,[1–5,8–14] due to their well known interesting properties, such as superconductivity, ionic and electronic conductivity, magnetoresistance, catalysis, spin/charge stripes in nickelates and manganites. It has been reported that Sr_2CoO_4 polycrystalline samples prepared by high temperature and high pressure, as well as single-crystalline thin films prepared by pulsed laser deposition are metallic ferromagnets with a fairly high Curie temperature (T_C) of 255 K.[1,2,16] So far, the $Sr_{2-x}Nd_xCoO_4$ ceramic compound's magnetic, transport and density of states properties has not been subjected to much study. Based on our study, the Nd doped Sr_2CoO_4 ceramic compounds was found to be ferromagnetic semiconducting. Its magnetic, transport and density of states properties will be discussed in this report.

Polycrystalline samples $Sr_{2-x}Nd_xCoO_4$ (x = 0.5, 0.75, 1, 1.25) were synthesized using conventional solid-state reaction. Fine and pure powders of Nd_2O_3, $SrCO_3$, and Co_3O_4 were mixed in the appropriate stoichiometries, pelletized, and sintered in air at 1000 °C for 12 h with several intermediate grindings. The resultant phases and structures were studied using the powder x-ray diffraction (XRD). Rietveld refinements were carried out using the Rietica program.[6] Magnetic and electrical transport properties were investigated using a commercial quantum design magnetic property measurement system (MPMS) and physical property measurement system (PPMS) between 5 and 330 K in magnetic fields up to 8 T (T). First principles calculations were performed using the WIEN2k package.[7] The generalized gradient approximation was adopted, with the Perdew-Burke-Ernzerhof functional 96 (PBE-GGA).

XRD measurements of the $Sr_{2-x}Nd_xCoO_4$ samples for the 2θ range from 20 to 75 deg were taken at room temperature. It was found that the diffraction peaks of all the samples fit well with the XRD profile of the Sr_2CoO_4 single phase. Figure 1 shows one of the Rietveld refinement result (for $Sr_{0.75}Nd_{1.25}CoO_4$). It can be seen that the calculated results matched well with the corresponding experimental data for the sample. The refined results for lattice parameters a and c were obtained through the refinements for all samples. The lattice parameter a was found to be not sensitive to the doping level of Nd (or the value of x) and remains around 3.7 Å for all samples, while the lattice parameter c decreases as the doping level x increases. This is in agreement with the fact that the Pauling ionic radius of Nd^{3+} (0.98 Å)[18] is smaller than the ionic radius of Sr^{2+} (1.32 Å).[19] The temperature dependence of the electrical resistivity in a temperature range of 5 to 340 K for the samples with x = 0.75 and 1 is shown in Fig. 2. The resistivity of the x = 1 sample is always greater than the resistivity of the sample with x = 0.75 for the same temperature. This clearly indicates that the Nd doping increases the resistivity. The log of the resistivity (ρ) vs $\exp(1/T)^{1/3}$ (where T is the measured temperature) for the samples with x = 0.75 and 1 is shown in Fig. 3. Both samples can be well fitted by the VRH model $\rho = \rho_o \exp(T_0/T)^{1/3}$. This suggests that the 2D variable-range hopping (VRH) mechanism could be used to account for the conducting mechanism for these samples. Figure 4 shows the temperature dependence for field-cooled and zero-field-cooled magnetization from 5 to 340 K for the $Sr_{2-x}Nd_xCoO_4$ samples with x = 0.75 and 1, measured in a magnetic field of 0.2 T. It

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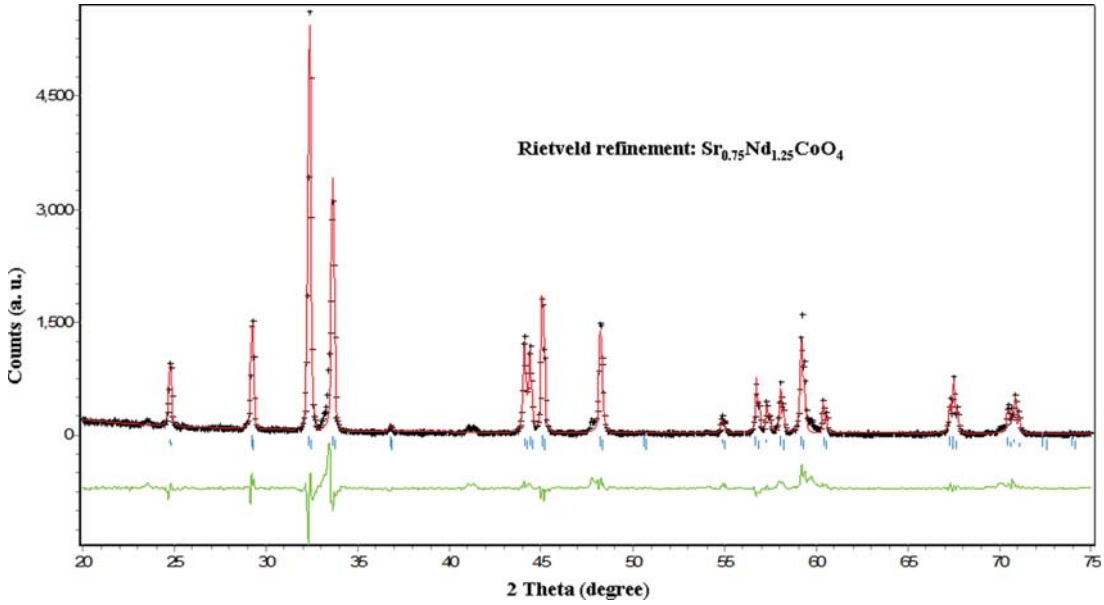

FIG. 1. (Color online) Rietveld refinement for $Sr_{0.75}Nd_{1.25}CoO_4$ showing the observed (crosses), calculated (solid line) and differences (bottom line) profiles at 300 K.

is obvious that both of the samples are ferromagnetic in the low temperature range. Through the Curie Weiss fitting (see the inset in Fig. 4), it was found that samples exhibited a paramagnetic to ferromagnetic transition at temperatures of about 250, 170 K for the $x = 1$ and 0.75 samples, respectively. It is observed that the Nd doping in $Sr_{2-x}Nd_xCoO_4$ drives the critical temperature to a higher value for the compound. It should be noted that the resistivity monotonically increases with decreasing temperature from 340 to 5 K (Fig. 2), and no anomaly occurs at magnetic transition temperatures for either of the samples with $x = 0.75$ and 1, and both show a semiconducting character. This reveals that the variation in the resistivity with temperature for these compounds is not dominated by spin-dependent scattering of carriers, but by carrier concentration.[15]

First principles calculations have been performed using the WIEN2k package. Lattice parameters and atomic positions obtained from Rietveld refinements for the compounds were used as the structural parameters for calculations. For the compound $Sr_{1.5}Nd_{0.5}CoO_4$, a $2 \times 2 \times 1$ k mesh was used for Brillouin sampling. A calculation for the pure Sr_2CoO_4 was also performed as a comparison. Figure 5 shows the total density of states for the $Sr_{1.5}Nd_{0.5}CoO_4$ and the Sr_2CoO_4 compound (with the Fermi energy set at zero). Our DOS results for the Sr_2CoO_4 compound is in good agreement with the previously reported results in this compound.[16,17] No previous report was found on the DOS for the $Sr_{1.5}Nd_{0.5}CoO_4$ compound. Upon closer observation, the DOS of the $Sr_{1.5}Nd_{0.5}CoO_4$ compound shows a slightly stronger polarized state, with 7 states/eV/f.u. (f.u. stands for per formula unit) spin down and 2 states/eV/f.u. spin up at Fermi level, compared with the Sr_2CoO_4 compound which was about 3.8 stats/eV/f.u. spin down and 0.4 states/eV/f.u. spin up. The partial density of states of Co and O of the compound Sr_2CoO_4 are shown in Fig. 6. It can be seen that Co was highly polarized (spin down) at Fermi level, and the Co's density of state comes mainly from the 3*d* electrons, as evidenced by the fact that the density of states of the 3*d* electrons (blue and thin line, upper panel) for Co is basically overlapping with Co's total density of states (orange and thick line, upper panel). It should be noted that the metallic nature of this undoped compound is also determined by the Co's 3*d* electrons. The DOS of Os in the lower panel in Fig. 6 shows that planar O and apical O contributing approximately the same

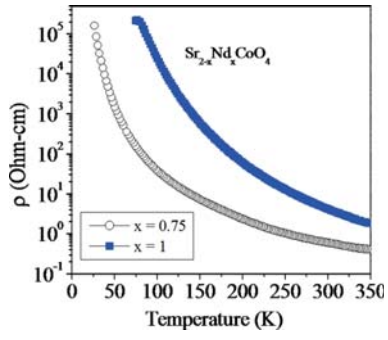

FIG. 2. (Color online) Resistivity (ρ) vs temperature for $Sr_{2-x}Nd_xCoO_4$ ($x = 0.75, 1$).

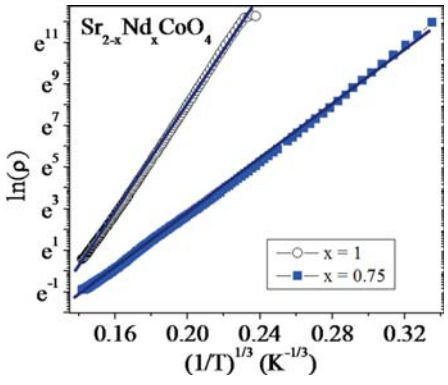

FIG. 3. (Color online) $\ln(\rho)$ vs $\exp(1/T)^{1/3}$ for $Sr_{2-x}Nd_xCoO_4$ ($x = 0.75, 1$). Straight lines are linear fittings to the 2D VRH model.

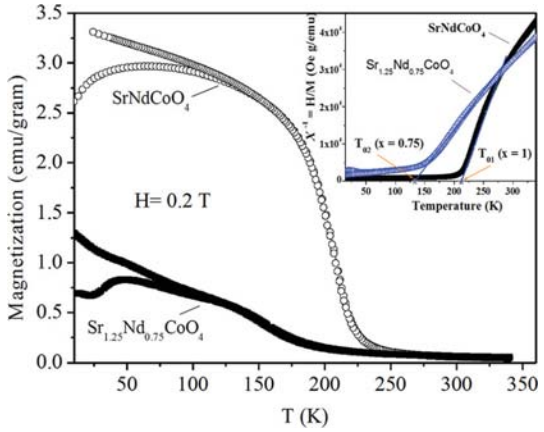

FIG. 4. (Color online) Temperature (T) dependence from 10 to 340 K of the magnetization of the $Sr_{2-x}Nd_xCoO_4$ samples with $x = 0.75, 1$. Inset shows the Curie Weiss fittings.

amount (about 0.5 states/eV/f.u.) of spin down polarized states to the Sr_2CoO_4 compound at the Fermi level, while the spin up states from Os is near 0 at the Fermi level.

In conclusion, Nd doping changes the Sr_2CoO_4 compound from ferromagnetic metal to ferromagnetic semiconductor, the lattice parameter c decreases as the Nd doping level increases. First principles calculations indicated that

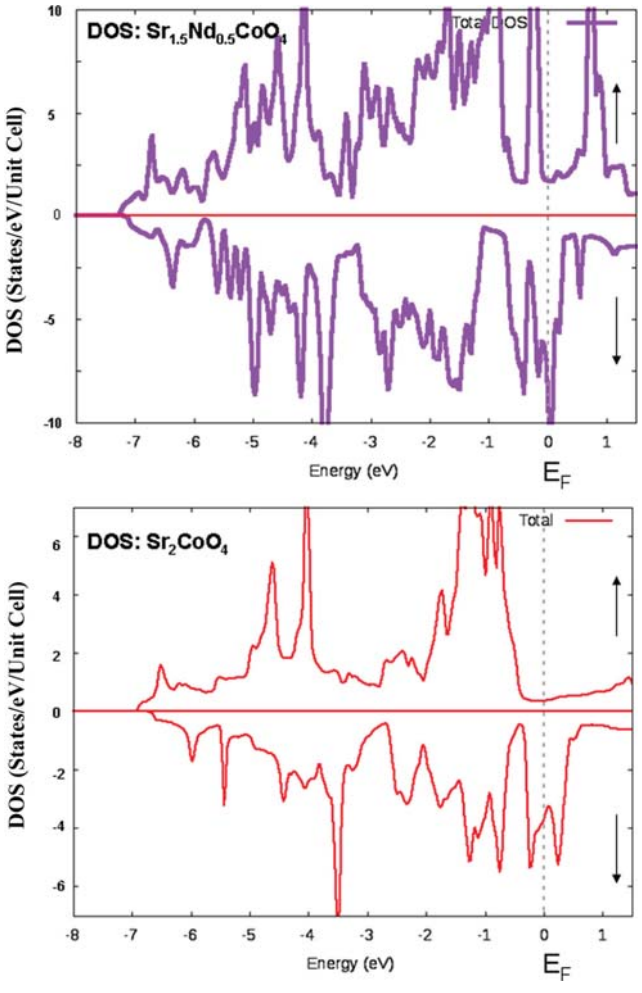

FIG. 5. (Color online) Calculated total density of states of $Sr_{1.5}Nd_{0.5}CoO_4$ (upper panel) and Sr_2CoO_4 (lower panel).

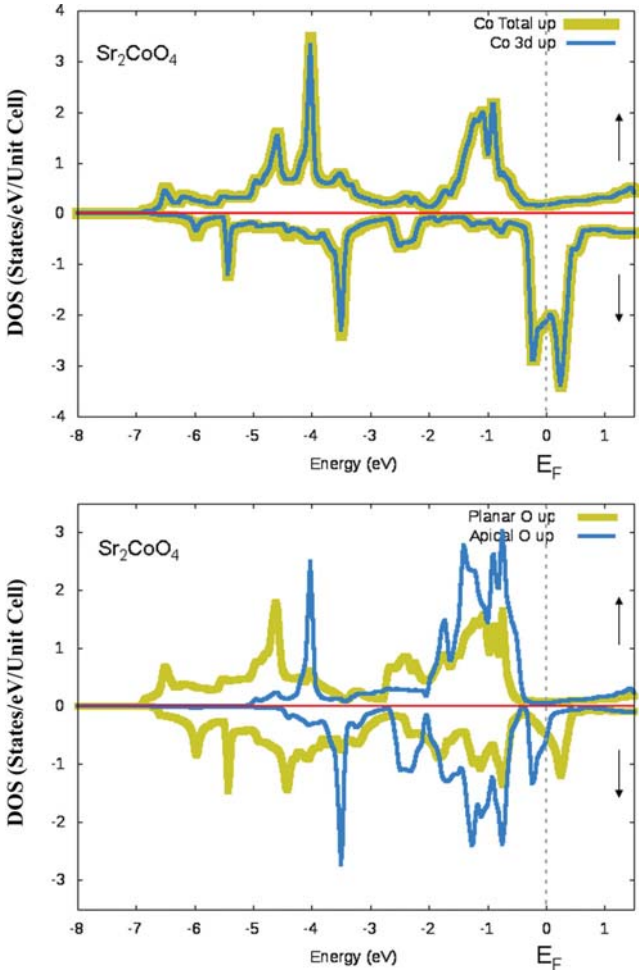

FIG. 6. (Color online) Calculated partial density of states of Co and Os for Sr_2CoO_4.

the compounds showed high spin polarization. The 2D variable-range hopping mechanism could be used to account for the conducting mechanism for the samples.

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