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Band structure, magnetic, and transport properties of two dimensional compounds $\text{Sr}_{2-x}\text{Gd}_x\text{CoO}_4$

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Band structure, magnetic, and transport properties of two dimensional compounds Sr_{2-x}Gd_xCoO₄

Abstract

The layered perovskite compound Sr_{2-x}Gd_xCoO₄ has not yet been subjected to detailed study so far. In this report, structures, transport, magnetic properties, and first principle calculations will be reported for the two dimensional compounds Sr_{2-x}Gd_xCoO₄ (x 0.5, 0.75, 1, 1.25). Rietveld refinement revealed that these compounds are crystallized in K₂NiF₄-type structures with space group I4/mmm. It was found that the lattice parameter c decreases as x increases. Through the Curies Weiss fitting of the temperature dependent magnetization, it was found that the Sr_{1.25}Gd_{0.75}CoO₄ sample exhibits a weak ferromagnetic to paramagnetic transition at about 62 K, with a Curie constant of 0.113 emu K/mol. Band structure calculations indicated that electrons of these compounds are spin polarized at the Fermi level. The 2-D Variable Range Hopping model fitting indicated that the two dimensional variable range hopping mechanism could be used to account for the conducting mechanism for these samples. 2013 American Institute of Physics.

Keywords

compounds, dimensional, two, properties, transport, sr2, magnetic, xgdxcOO4, structure, band

Disciplines

Engineering | Physical Sciences and Mathematics

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Band structure, magnetic, and transport properties of two dimensional compounds $\text{Sr}_{2-x}\text{Gd}_x\text{CoO}_4$

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Band structure, magnetic, and transport properties of two dimensional compounds $\text{Sr}_{2-x}\text{Gd}_x\text{CoO}_4$

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The layered perovskite compound $\text{Sr}_{2-x}\text{Gd}_x\text{CoO}_4$ has not yet been subjected to detailed study so far. In this report, structures, transport, magnetic properties, and first principle calculations will be reported for the two dimensional compounds $\text{Sr}_{2-x}\text{Gd}_x\text{CoO}_4$ ($x = 0.5, 0.75, 1, 1.25$). Rietveld refinement revealed that these compounds are crystallized in K_2NiF_4 -type structures with space group $I4/mmm$. It was found that the lattice parameter c decreases as x increases. Through the Curies Weiss fitting of the temperature dependent magnetization, it was found that the $\text{Sr}_{1.25}\text{Gd}_{0.75}\text{CoO}_4$ sample exhibits a weak ferromagnetic to paramagnetic transition at about 62 K, with a Curie constant of 0.113 emu K/mol. Band structure calculations indicated that electrons of these compounds are spin polarized at the Fermi level. The 2-D Variable Range Hopping model fitting indicated that the two dimensional variable range hopping mechanism could be used to account for the conducting mechanism for these samples. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4799780>]

I. INTRODUCTION

Very recently, metallic ferromagnetism with a Curie temperature T_c of 250 K has been discovered in the K_2NiF_4 -type two-dimensional layered perovskite Sr_2CoO_4 ceramic produced by a high pressure and high temperature technique,¹ with large magnetic anisotropy, and quasi-two-dimensional electrical transport properties. In fact two dimensional compounds with the K_2NiF_4 -type structure has been a great interest for materials researchers in recent years,²⁻¹⁰ due to their interesting properties such as superconductivity, ionic and electronic conductivity, magnetoresistance, dielectric properties, catalysis, spin/charge stripes in nickelates, manganites, etc. The non-magnetic yttrium doping of Sr_2CoO_4 polycrystalline samples fabricated under high pressure was found to change the system from ferromagnetic metal to antiferromagnetic semiconductor.¹ It would be interesting to see the changes in physical properties such as the transport properties, Curie temperatures, and the electronic structures of the Sr_2CoO_4 by doping it with the Gd which has large magnetic moments.

II. EXPERIMENT AND CALCULATIONS

Polycrystalline samples $\text{Sr}_{2-x}\text{Gd}_x\text{CoO}_4$ ($x = 0.5, 0.75, 1, 1.25$) were synthesized by conventional solid-state reaction method. Fine and pure (99.9%) powders of Gd_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 by the powder x-ray diffraction (XRD). Structure refinements were carried out by the Rietveld method using the RIETICA program.¹¹ Magnetic and electrical transport properties were investigated using a commercial Quantum Design magnetic property measurement system (MPMS) and physical property measurement system (PPMS) system in magnetic fields up to 8 T. First principles calculations were performed to the compounds using the WIEN2K package.¹²

III. RESULTS AND DISCUSSIONS

The XRD measurements of the $\text{Sr}_{2-x}\text{Gd}_x\text{CoO}_4$ samples showed that the diffraction peaks of all the four samples fit well with the XRD profile of the Sr_2CoO_4 single phase. A small unknown phase diffraction peak was found in the range of 32.5° to 33° in the XRD patterns for the samples where $x \geq 0.75$. Fig. 1 shows the Rietveld refinement result of the $\text{Sr}_{1.25}\text{Gd}_{0.75}\text{CoO}_4$ sample. The lattice parameters a and c were obtained through the refinement results. As shown in the inset of Fig. 1, the lattice parameter a was found to be not sensitive to the doping level of Gd and remains around 3.75 Å for all samples, while the lattice parameter c decreases as the Gd doping level x increases. This is in agreement with the fact that the Pauling ionic radius of Gd^{3+} (radius 1.08 Å) is smaller than the ionic radius of Sr^{2+} (radius 1.32 Å).¹³

The temperature dependence of the electrical resistivity in a temperature range of 25 K to 350 K for the samples with $x = 0.75, 1, \text{ and } 1.25$ is shown in Fig. 2(a). The resistivity of all these samples in temperatures below 25 K became too large that they were beyond the measurable range of the PPMS. All three samples exhibited semiconductor-like

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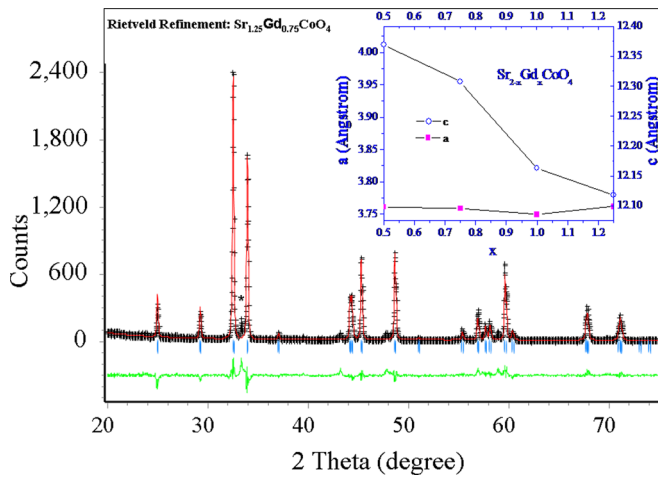


FIG. 1. Rietveld refinement for $\text{Sr}_{1.25}\text{Gd}_{0.75}\text{CoO}_4$ showing the observed (crosses), calculated (solid line), and difference (bottom line) profiles at 300 K (refinement factors $R_p = 14.3\%$, $R_b = 6.2\%$). The star marks the small unknown phase peak in the range of 32.5° and 33° . Inset shows the Lattice parameters a and c vs x for $\text{Sr}_{2-x}\text{Gd}_x\text{CoO}_4$.

behavior over the measurable range. It can also be seen that the Gd doping increases the resistivity of the compound. It should be noted that, through our conventional method of doping by Gd, the ceramic compound Sr_2CoO_4 changes from a metal to semiconductors, while Wang has reported that smaller amount of doping by Gd to this ceramic compound (e.g., $\text{Sr}_{1.7}\text{Gd}_{0.3}\text{CoO}_4$) by high pressure method did not change much of the compound's transport property.¹⁴ The log of the resistivity (ρ) vs $\exp(1/T)^{1/3}$ for these samples is shown in Fig. 2(b). It can be seen that the data for these samples basically fit well with the variable range hopping (VRH) model in their measurable ranges. This suggests that the 2D VRH mechanism could be used to account for the conducting mechanism for these samples.

Fig. 3 shows the temperature dependence for field-cooled and zero-field-cooled measurements from 5 K to 300 K of the magnetization of the $\text{Sr}_{2-x}\text{Gd}_x\text{CoO}_4$ samples with $x = 0.75$ and 1, measured in a magnetic field of 0.2 T. Inset shows the Curie Weiss fitting for both measurements. Both samples appear to be in the paramagnetic state over the whole measured temperature range from the magnetization (MT) curves. The SrGdCoO_4 sample shows typical features

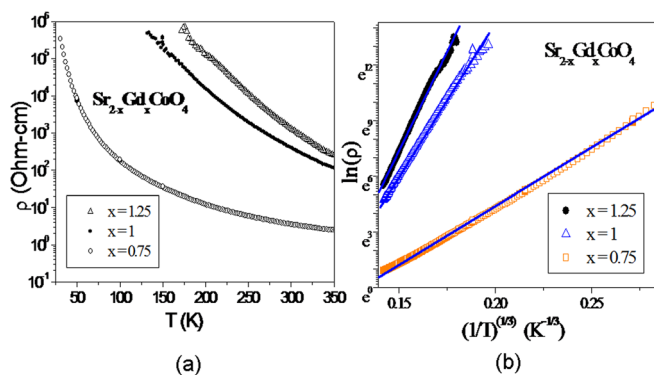


FIG. 2. (a) Resistance vs temperature for $\text{Sr}_{2-x}\text{Gd}_x\text{CoO}_4$ ($x = 0.75, 1, 1.25$). (b) $\ln(\rho)$ vs $\exp(1/T)^{1/3}$ for $\text{Sr}_{2-x}\text{Gd}_x\text{CoO}_4$ ($x = 0.75, 1, 1.25$). Straight lines are linear fittings to the 2D VRH model.

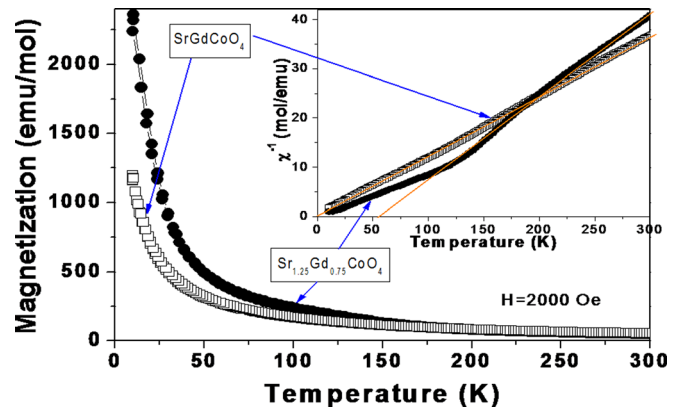


FIG. 3. Temperature dependence of the magnetization of the $\text{Sr}_{2-x}\text{Gd}_x\text{CoO}_4$ samples with $x = 0.75, 1$. Inset shows the Curie Weiss fitting of the samples.

of a paramagnet. Furthermore, as can be seen in the inset in Fig. 3, a slight concavity in the temperature dependence of the inverse susceptibility is observed at around 120 K for the $\text{Sr}_{1.25}\text{Gd}_{0.75}\text{CoO}_4$ sample, indicating a short range ferromagnetic or antiferromagnetic state change at this point for this compound. Magnetization hysteresis measurements for both samples measured at 10 K (not shown here) confirm a weak ferromagnetic interaction in the low field range for this sample. From the Curies Weiss fitting, it was found that the $\text{Sr}_{1.25}\text{Gd}_{0.75}\text{CoO}_4$ sample exhibited a weak ferromagnetic to paramagnetic transition at about 62 K, with a Curie Constant of 0.113 emu K/mol.

It should be noted that the resistivity monotonically increases with decreasing temperature from 350 to 5 K (Fig. 2(a)), and no anomaly occurs at magnetic transition temperature observed. All samples 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

The first-principal calculations performed for the SrGdCoO_4 compound in ground state indicated that the spin polarization is high in this compound. Lattice parameters and atomic positions obtained from the Rietveld refinements for this sample were used as the starting unit cell parameters for the calculations. Geometry optimization was employed to find the optimal parameters for the final calculation. An eight atom supercell was used for the calculation; a $10 \times 10 \times 3$ k mesh was used for the Brillouin sampling. It should be noted that the supercell choice of the calculation does not affect the resulting DOS in this case (as it was a $1 \times 1 \times 1$ supercell), and all DOS units are given as per formula unit. Fig. 4(a) shows the total DOS of SrGdCoO_4 (with the Fermi energy set at zero). The spin down DOS is approximately three times the spin up DOS value at the Fermi level. Our result is in good agreement with the results of the electronic structure from Wang *et al.* which was obtained by a different calculation package.¹⁴ Fig. 4(b) shows the total DOS (thick yellow curves) vs the Gd's DOS (thin blue curve) of the compound. It can be seen that the Gd atom does not contribute to any electronic density at the Fermi level. Fig. 4(c) shows the total DOS (thick yellow curves) vs the $\text{Co}2$'s DOS (thin blue curve). It can be seen that the main DOS at the Fermi level

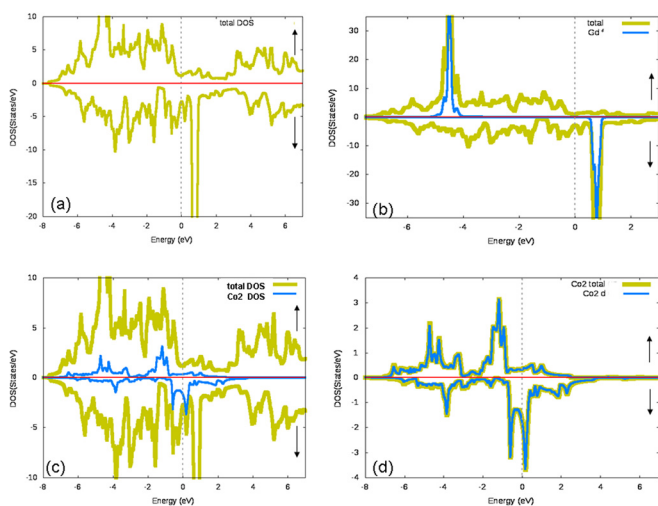


FIG. 4. Calculated DOS of SrGdCoO₄. (a) The total DOS of SrGdCoO₄. (b) The total DOS of SrGdCoO₄ (yellow and thick curves) and the Gd's DOS (blue and thin curves). (c) The total DOS of SrGdCoO₄ (yellow and thick curves) and the Co's DOS (blue and thin curves). (d) Co's total DOS (yellow and thick curves) and the contribution from Co's 3d electrons (blue and thin curves).

mainly comes from the contribution of the Co atoms. It should be noted that the spin polarization of the compound comes from the Co atoms, since basically both of the two O atoms and the Gd atom in the unit cell do not contribute to the DOS of the compound at the Fermi level. Fig. 4(d) shows the Co's total DOS (thick yellow curves) vs the DOS of the Co's 3d electrons (thin blue curve). It can be seen that the two curves are overlapping over the calculated range, indicating that the Cobalt's 3d electrons are the only contributors to Cobalt atom's DOS.

In conclusion, Gd doping by the conventional solid state reaction method changes the Sr₂CoO₄ ceramic compound from a ferromagnetic metal to paramagnets, the lattice parameter *c* decreases as the Gd doping level increases. The

Sr_{1.25}Gd_{0.75}CoO₄ sample exhibited a weak ferromagnetic to paramagnetic transition at about 62. First principle calculations indicated that these compounds show high spin polarization (which contributed mainly by the Cobalt's 3d orbital electrons) at the Fermi level.

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