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Abstract

The authors present their studies on the band structures and on the magnetic and magnetotransport properties of the high pressure phase of $Sr_{2-x}RE_xCoO_4$ [rare earth (RE)=Gd and Y, x=0.1-0.5] compounds which were synthesized by a high pressure and high temperature technique. The authors found that as x increases, the magnetoresistance $\{(\rho_H-\rho_0)/\rho_0\}$ increases up to -17% at 5 K and 7 T, which is 2.5 times higher than that for undoped Sr_2CoO_4, although the ferromagnetic transition drops from 255 to 200 K for the Gd doping with x=0.3. The saturation moments at low temperature are significantly enhanced for the Gd doped Sr_2CoO_4. Observation of a close correlation between resistance and field revealed a strong spin-dependent tunneling magnetoresistance. First-principles band structure calculations indicate that high spin polarization is present for both undoped and doped compounds.

Keywords

Band, structures, magnetic, properties, enhanced, magnetoresistance, high, pressure, phase, doped, two, dimensional, perovskite, Sr2CoO4, compounds

Disciplines

Engineering | Physical Sciences and Mathematics

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Band structures, magnetic properties, and enhanced magnetoresistance in the high pressure phase of Gd and Y doped two-dimensional perovskite Sr_2CoO_4 compounds

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The authors present their studies on the band structures and on the magnetic and magnetotransport properties of the high pressure phase of $Sr_{2-x}RE_xCoO_4$ [rare earth (RE)=Gd and Y, $x=0.1-0.5$] compounds which were synthesized by a high pressure and high temperature technique. The authors found that as x increases, the magnetoresistance $\{(\rho_H-\rho_0)/\rho_0\}$ increases up to −17% at 5 K and 7 T, which is 2.5 times higher than that for undoped Sr_2CoO_4, although the ferromagnetic transition drops from 255 to 200 K for the Gd doping with $x=0.3$. The saturation moments at low temperature are significantly enhanced for the Gd doped Sr_2CoO_4. Observation of a close correlation between resistance and field revealed a strong spin-dependent tunneling magnetoresistance. First-principles band structure calculations indicate that high spin polarization is present for both undoped and doped compounds. © *2007 American Institute of Physics*.
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Finding novel ferromagnetic materials showing negative magnetoresistance and studies of polarized spin-dependent tunneling magnetoresistance are hot topics within spintronics.[1,2] So far, several magnetoresistance (MR) oxide systems have been found and extensively investigated. (1) The perovskite ferromagnetic manganites in the form of $RE_{1-x}A_xMnO_3$, with RE standing for a rare earth and A for a divalent ion such as Ca, Sr, or Ba, exhibit the well known type of colossal magnetroresistance in fields of several tesla.[3] (2) Pyrochlore-type $Tl_2Mn_2O_7$ shows large MR near the Curie temperature of 140 K.[4] The double-perovskite ferromagnets, Sr_2FeMoO_6 and Sr_2FeReO_6, exhibit large low-field MR below high Curie temperatures T_C of about 400 K.[5] MR is also present in simple oxides, such as CrO_2 and Fe_3O_4. CrO_2 crystallizes in the rutile structure and exhibits giant tunneling MR at low temperatures.[6] Fe_3O_4 is a good candidate for room temperature device applications[7] because it has a very high T_C of 858 K. Analogous to the perovskite manganites, giant magnetoresistance is also observed in the cobalt based perovskite compounds $RE_{1-x}A_xCoO_3$,[8,9] as well as in oxygen deficient $LnBaCo_2O_5$ (Ln=Eu and Gd) compounds.[10] When the dimensionality is reduced from three to two dimensions, the MnO_2 or CoO_2 network is confined to the ab plane. Spin-related property changes are also expected. Layered perovskite manganites, defined as the Ruddlesden-Popper family of compounds $(RE,A)_{n+1}Mn_nO_{3n+1}$, consist of n layers of MnO_6 octohedra separated by n layers of REO_2.[11] Very recently, metallic ferromagnetism with a Curie temperature T_C of 250–255 K has been discovered in the K_2NiF_4-type two-dimensional layered perovskite Sr_2CoO_4 in the form of both single crystalline films fabricated by pulsed laser deposition[12] (PLD) and bulks produced by a high pressure and high temperature technique.[13] A metal insulator transition with large negative MR values was observed in the vicinity of T_C. The MR increases at low temperatures and reaches a maximum at the coercive field H_c.[12,13] Y^{3+} doping into Sr^{2+} made the Sr_2CoO_4 gradually change from a ferromagnetic metal to an antiferromagnetic semiconductor.[13] Band structure calculations by Lee and Pickett[14] revealed that the Sr_2CoO_4 can be either a ferromagnetic metal for the thin film samples or a half metal for the high pressure phase samples. They pointed out that the newly discovered Sr_2CoO_4 in the form of bulks fabricated by the high pressure technique and thin films made by PLD introduces new transition metal oxide physics and may be useful in spin electronics devices.[14] In addition, it should be mentioned that the MR is only about −7.5% at 7 T and 5 K for the high pressure phase Sr_2CoO_4 (Ref. 13) polycrystalline samples made using the high pressure method. It would be interesting to see how the physical properties such as the MR values and Curie temperatures as well as the electronic structures of the Sr_2CoO_4 can be changed or improved by doping with other rare earth elements, in particular, with those having large magnetic moments or no magnetic moments. In this letter, we present our observations on the magnetic properties and the improvement of the negative magnetoresistance, as well as the electron band structures of the Gd or Y doped Sr_2CoO_4.

Polycrystalline samples of $Sr_{2-x}RE_xCoO_4$ (RE=Y or Gd, $x=0,0.1,0.3,0.5$) were prepared by a high pressure and high temperature technique. Fine and pure powders of SrO_2, Co, and Y_2O_3 or Gd_2O_3 were well mixed in the ratio of Sr:RE:Co=2-x:x:1. The samples were compressed at

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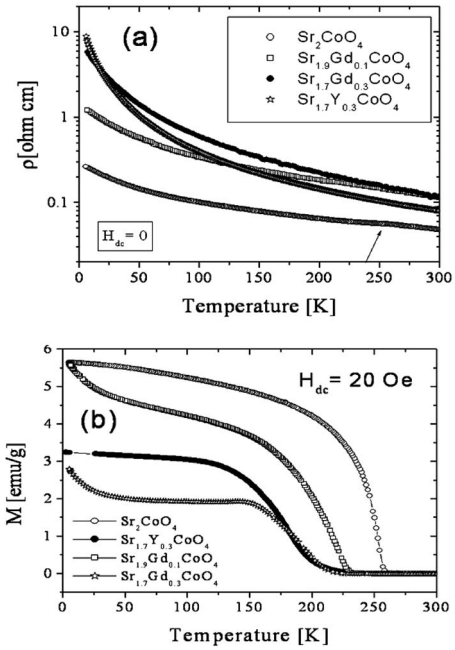

FIG. 1. Temperature dependence of the resistivity (a) and field-cooled magnetization (b) for both Gd and Y doped Sr_2CoO_4.

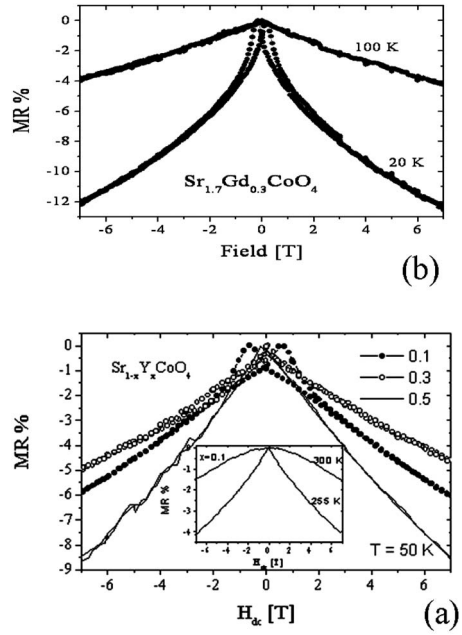

FIG. 2. Magnetoresistance vs magnetic field for Y (a) and Gd (b) doped Sr_2CoO_4 at different temperatures.

6 GPa in a high pressure apparatus and then heated at 1000–1350 °C for 1–3 h and quenched to room temperature, with the quenching followed by a release of pressure.[13] Structure refinements were carried out by the Rietveld method. Magnetic and magnetotransport properties were investigated using commercial Quantum Design magnetic and physical properties measurement sytems between 2 and 330 K in fields up to 7 T.

The temperature dependence of the magnetization reveals that the ferromagnetic transition of Sr_2CoO_4 decreases from 255 to 230 K for Gd doping with $x=0.1$ and to 200 K for both Gd and Y with $x=0.3$, as shown in Fig. 1(b). An upturn at low temperatures in the Gd doped sample is believed to come from the contribution of paramagnetic Gd^{3+} ions. The temperature dependence of the resistivity of those samples is shown in Fig. 1(a). Among these samples, the Sr_2CoO_4 has the lowest resistivity (0.04 Ω cm) over the wide range of temperatures measured. The resistivity for samples with $x=0.1$ and 0.3 for both Gd and Y doping showed a very gradual increase in resistivity with decreasing temperature and does not increase at low temperatures. This indicates that the resistance is dominated by the carrier scattering at grain boundaries, as is widely seen for polycrystalline samples.

The doping effect on the MR is clearly revealed in Fig. 2. The MR values at 50 K increase from −5% up to −8.5%, as the Y doping level is raised from 0.1 to 0.5. The MR values increase to −13% and −14% for the $x=0.1$ and 0.3 samples at 5 K and 7 T. The Gd doping has a similar effect on the MR to that of the Y doping. For $Sr_{1.7}Gd_{0.3}CoO_4$, the MR is −4% at 100 K and 7 T and increases to −12% at 20 K and 7 T, as shown in Fig. 3. It should be mentioned that the MR is only about 7.5% at 7 T and 5 K for undoped Sr_2CoO_4.[13] The MR is much enhanced by both Y and Gd dopings at 5 K. As shown in Fig. 3, the MR values increased to −14% and −17% for the $Sr_{1.7}Y_{0.3}CoO_4$ and $Sr_{1.7}Gd_{0.3}CoO_4$ samples, respectively. With decreasing temperatures, a field-hysteretic MR corresponding to the magnetic hysteresis loop gradually appeared and became much more pronounced at 5 K, as shown in Fig. 3 (lower panel). It can be seen that the maximum field-hysteretic MR occurred at fields of about 2.5, 0.5, and 0.3 T for pure Sr_2CoO_4, $Sr_{1.7}Y_{0.3}CoO_4$, and $Sr_{1.7}Gd_{0.3}CoO_4$, respectively, coinciding with the magnetization process with domain rotation at coercive fields of 2.5, 0.5, and 0.3 T, respectively.

Such a close correlation between the MR and magnetic domain rotation can be well explained in terms of spin-dependent tunneling MR at grain boundaries, which has been well established for granular manganites and other MR oxides. Under the application of magnetic field, the hopping of spin-polarized electrons between grains (domains) is pre-

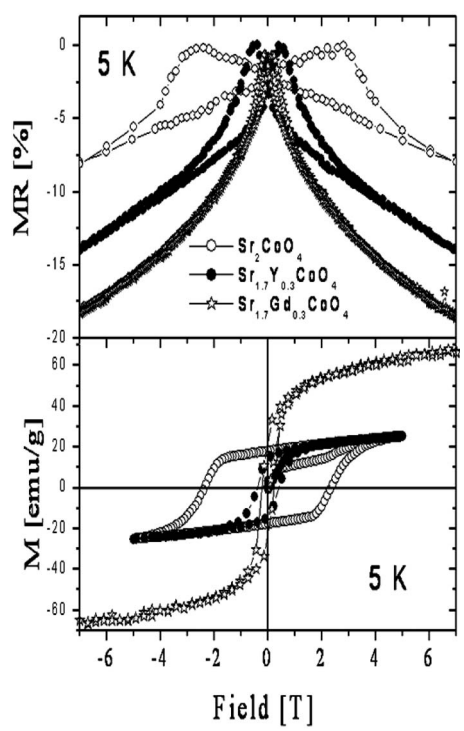

FIG. 3. Magnetoresistance (upper panel) and magnetization M (lower panel) for pure and Y or Gd doped Sr_2CoO_4.

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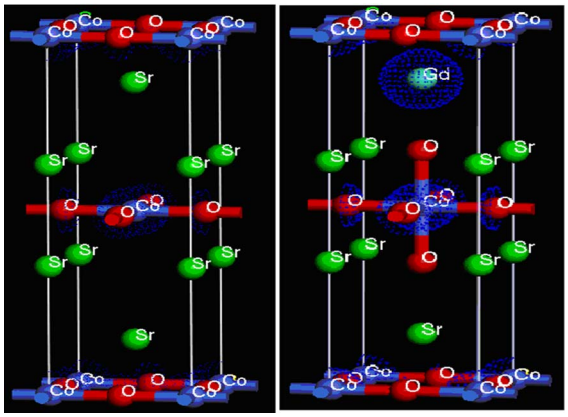

FIG. 4. (Color online) Crystal structure and distribution of spin densities (blue dots) of the pure (left) and Gd (right) doped Sr_2CoO_4.

dominantly affected by the relative angle of the magnetization direction and controlled by the external field through the domain-rotation process. Therefore, the observed field-hysteretic MR is ascribed to the field suppression of the spin-dependent scattering at grain (domain) boundaries. It should be pointed out that the enhanced MR value of −17% in $Sr_{1.7}Gd_{0.3}CoO_4$ is almost two times smaller than that for pure *a*-axis oriented Sr_2CoO_4 single crystal thin films, but it is two times greater than that in Sr_2CoO_4 polycrystalline bulks.[12,13] It is obvious that the grain boundary tunneling between oriented grains is much greater than that between the randomly oriented grains. Therefore, it is expected that the MR values will be further enhanced in textured thin films of either $Sr_{1.7}Gd_{0.3}CoO_4$ or $Sr_{1.7}Gd_{0.3}CoO_4$, with much reduced grain boundary scattering.

First-principles band structure calculations were performed using a density functional theory.[15] We adopted the standard generalized gradient approximation, with the Perdew-Burke-Ernzerhof functional. Lattice parameters and atomic positions obtained from the Rietveld refinement for pure and doped samples prepared under 6 GPa were used as the structural parameters for the band structure calculations. A 14 atom supercell of one Sr_2CoO_4 unit cell containing one Y or Gd atom substituted at the Sr site was used for the calculation. The Y or Gd concentration is thus 25 at. %. A schematic of the crystal structure of the Sr_2CoO_4 is shown in Fig. 4. A $7\times7\times2$ *k* mesh was used for Brillouin sampling with a cutoff energy of 340 eV. A calculation for pure Sr_2CoO_4 was also performed as a comparison. Figure 5 shows the total density of states with majority "up" and minority "down" spins. For the undoped and doped Sr_2CoO_4, both the spin up and spin down states are partially occupied around the Fermi level, with a high spin polarization of the conduction electrons, in good agreement with the results of the electronic structure for Sr_2CoO_4 calculated by Matsuno *et al.*[12] and Lee and Pickett.[14] Note that the densities of states of the minority spins are about 5, 6, and 7 states/eV for pure, Y, and Gd dopings, respectively, indicating that the enhanced density of states could also play a role in the enhanced MR observed for both Y and Gd doped Sr_2CoO_4. The spin density distribution for the pure, Y, and Gd doped Sr_2CoO_4 is also shown in Fig. 4. It can be seen that the polarized spins are contributed by the *p* electrons of the oxygen atoms and the *d* electrons from the Co atoms for both pure and Y doped Sr_2CoO_4, while both *p* and *d* electrons from the Gd atoms also contribute significantly to the polarized spin in the Gd doped Sr_2CoO_4. It can be seen that the significantly enhanced magnetization at 5 K in the Gd doped Sr_2CoO_4, as shown in Fig. 3, mainly comes from Gd^{3+} as well as from the oxygen and cobalt ions. The observation of enhanced magnetoresistance in the Y and Gd doped two-dimensional layer structured Sr_2CoO_4 suggests their potential applications in spintronics and in exploring novel magnetoresistance/spintronic materials in lower dimensional structured systems. Further enhancements in MR values and the Curie temperature are most likely present in other rare earth doped Sr_2CoO_4.

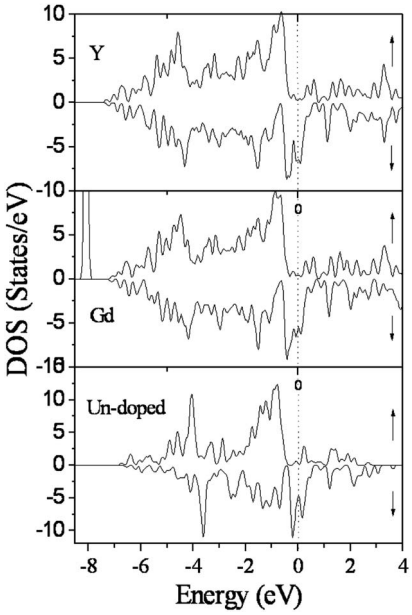

FIG. 5. Total density of states of pure, Gd, and Y doped Sr_2CoO_4, with the Fermi energy set at zero.

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[1]For instance, MRS Bull. **28**, 729 (2003); *Spin Electronics*, edited by M. Ziese and M. J. Thornton (Springer, Heidelberg, 2001).
[2]M. Ziese, Rep. Prog. Phys. **65**, 143 (2002).
[3]R. von Helmont, J. Wecker, B. Holzapfel, L. Schultz, and K. Samwer, Phys. Rev. Lett. **71**, 2331 (1993).
[4]Y. Shimakawa, Y. Kubo, and T. Manako, Nature (London) **379**, 53 (1996).
[5]K.-I. Kobayashi, T. Kimura, H. Sawada, K. Terakura, and Y. Tokura, Nature (London) **395**, 677 (1998).
[6]H. Y. Hwang and S.-W. Cheong, Science **278**, 1607 (1997).
[7]R. A. de Groot, F. M. Muller, P. G. Van Engen, and K. H. J. Buschow, Phys. Rev. Lett. **50**, 2024 (1983).
[8]G. Briceno, H. Chang, X. D. Sun, P. G. Schultz, and X.-D. Xiang, Science **270**, 273 (1995).
[9]I. O. Troyanchuk, N. V. Kasper, D. D. Khalyavin, H. Szymczak, R. Szymczak, and M. Baran, Phys. Rev. Lett. **80**, 3380 (1998).
[10]C. Martin, A. Maignan, D. Pelloquin, N. Nguyen, and B. Raveau, Appl. Phys. Lett. **71**, 1421 (1997).
[11]Y. Moritomo, A. Asamitsu, H. Kuwahara, and Y. Tokura, Nature (London) **380**, 141 (1996).
[12]J. Matsuno, Y. Okimoto, Z. Fang, X. Z. Yu, Y. Matsui, N. Nagaosa, M. Kawasaki, and Y. Tokura, Phys. Rev. Lett. **93**, 167202 (2004).
[13]X. L. Wang and E. Takayama-Muromauchi, Phys. Rev. B **72**, 064401 (2005).
[14]K. W. Lee and W. E. Pickett, Phys. Rev. B **73**, 174428 (2006).
[15]M. D. Segallm, P. J. D. Lindan, M. J. Probert, C. J. Pickard, P. J. Hasnip, S. J. Clark, and M. C. Payne, J. Phys.: Condens. Matter **14**, 2717 (2002).

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