

Large magnetoresistance in spin- and carrier-doped SrTiO₃

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We studied SrTiO₃ into which spins and carriers are doped by Cr substitution for Ti and La substitution for Sr, respectively. It was found that Weiss temperatures vary from negative to positive values with carrier doping, indicating the appearance of a ferromagnetic interaction between Cr spins via the conduction carriers. We also found negative magnetoresistance in these compounds, whose magnitude amounts to 70% at low temperatures. These results demonstrate that magnetic semiconductors with large magnetoresistance can be obtained based on conventional oxides, like SrTiO₃, with independent doping of spins and carriers.

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Coupling between spin and charge degrees of freedom and resultant magnetoresistance are the issues seen in various magnetic conducting materials, for example, perovskite manganites, intermetallic compounds involving rare earth, and diluted magnetic semiconductors. In the case of perovskite manganites,¹ for example, the conduction carriers on the Mn site (in the $3d e_g$ orbital) are coupled to the localized spins existing also on the Mn site (in the t_{2g} orbital), and this coupling produces a ferromagnetic interaction between two spins, which is called “double exchange” coupling. The RKKY interaction,² often observed in rare-earth metals and intermetallic compounds, occurs in a similar way: There appears a magnetic interaction between $4f$ spins on the rare-earth atoms via the itinerant electrons in the conduction band. Diluted magnetic semiconductors are the ones to which both carriers and spins are introduced by doping.³ Compared with the former two systems, it is easier to control the number of carriers and spins in magnetic semiconductors, and thereby they are suitable for the application utilizing both spin and charge degrees of freedom. In these three systems, the magnetic interaction is dominated by conduction carriers, and oppositely the transport properties of conduction carriers are dominated by the magnetic state, and thus by magnetic field. In many cases, coherent motion of conduction carriers is enhanced with ferromagnetically aligned spins, and electrical resistivity is suppressed with magnetic field, i.e., negative magnetoresistance occurs.

As theoretically shown in the RKKY interaction, in which the sign of the magnetic interaction changes depending on the relation between the Fermi wave number of conduction carriers and the distance between neighboring magnetic moments, the numbers of spins and carriers are the most important parameters for the coupling between spin and charge degrees of freedom. In none of the systems above, however, these two numbers can be controlled independently. Even in diluted magnetic semiconductors, spins and carriers are often introduced by a single dopant, for example, by Mn for (Ga,Mn)As. In this paper, we experimentally demonstrate that various parameters, including the magnitude of magnetoresistance, can be optimized by controlling the number of spins and carriers independently.

The parent compound studied here is perovskite SrTiO₃, a simple band insulator whose conduction band is composed

of the Ti $3d$ state and the oxygen $2p$ state. There are several advantages to use this compound as a parent compound for spin and carrier doping: First, it forms a simple cubic crystal structure, and thus is free from any structural complexity. Second, this compound has two cations, which can be used for independent spin and carrier doping. It is known that the substitution of La³⁺ for Sr²⁺ introduces electrons into the conduction band (electron doping).⁴ On the other hand, spins can be introduced by the substitution of other transition metal ions for Ti. Here, we choose Cr as a dopant, which is stable as a trivalent ion (Cr³⁺) in the $3d^3$ high-spin configuration ($S=3/2$). Finally, since SrTiO₃ is one of the most common oxides, which can be used even as a substrate of thin-film growth, the magnetoresistance on the derivatives of SrTiO₃ is suitable for possible future applications.

We made polycrystalline samples of Sr_{1-x-y}La_{x+y}Ti_{1-x}Cr_xO₃ by a solid state reaction method, starting from SrTiO₃, LaTiO₃, and LaCrO₃. These compounds were mixed and sintered in the flow of forming gas (H₂ 7%/Ar) at 1350 °C. SrTiO₃ was made from SrCO₃ and TiO₂, LaTiO₃ from La₂O₃, TiO₂, and Ti (sintered also in the forming gas), and LaCrO₃ from La₂O₃ and Cr₂O₃. In the notation of Sr_{1-x-y}La_{x+y}Ti_{1-x}Cr_xO₃, x represents the number of Cr³⁺ ions, i.e., the number of spins, and y represents the number of Ti³⁺ ions, i.e., the number of conduction electrons. X-ray diffraction measurement indicates that all the samples have a cubic perovskite structure. As an example, the x-ray diffraction patterns of the sample with $x=0.2$ and $y=0.1$ is shown in the upper panel of Fig. 1. Electrical resistivity was measured by a conventional four probe technique with sputtered gold as electrodes. Magnetoresistance was measured by using 5 T and 14 T superconducting magnets. Magnetization was measured by a SQUID magnetometer.

The middle panels of Fig. 1 shows the inverse magnetic susceptibility ($1/\chi$) as a function of temperature (T) for (a) fixing carrier concentration $y=0.2$ and changing spin concentration x (b) fixing spin concentration $x=0.1$ and changing carrier concentration y (c) fixing spin concentration $x=0.2$ and changing carrier concentration y . As shown in Fig. 1(a), the slope of $1/\chi$ vs T decreases with increasing x , consistent with the increase of the number of spins. However, the number of spins estimated from their Curie constants below 50 K

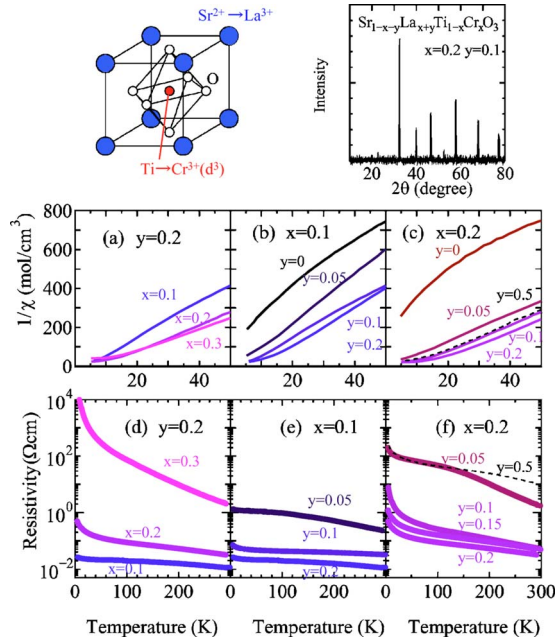


FIG. 1. (Color online) Upper panels: Schematic picture of the crystal structure of $\text{Sr}_{1-x-y}\text{La}_{x+y}\text{Ti}_{1-x}\text{Cr}_x\text{O}_3$ (left) and the x-ray diffraction pattern of the sample with $x=0.2$ and $y=0.1$ measured with $\text{Cu } K_\alpha$ radiation (right). Middle panels: Temperature dependence of inverse magnetic susceptibility for (a) fixing carrier concentration $y=0.2$ and changing spin concentration x , (b) fixing spin concentration $x=0.1$ and changing carrier concentration y , and (c) fixing spin concentration $x=0.2$ and changing carrier concentration. Lower panels: Temperature dependence of resistivity [(d)–(f)]. Spin and carrier concentrations are the same as those at the middle panels.

are approximately 1/3 of the theoretical values. In fact, the T dependence of $1/\chi$ is not completely linear, but is saturated at high T . This nonlinear behavior of $1/\chi(T)$ occurs because the Cr ions are randomly positioned in the crystal and thus, there are various sizes of magnetic interactions between two Cr spins. Figures 1(b) and 1(c) show how $1/\chi(T)$ changes with increasing carrier concentration. In both cases, $1/\chi(T)$ shows approximately a parallel shift to higher temperatures with increasing carrier concentration y . The Weiss temperature estimated from $1/\chi(T)$ between 20 K and 50 K is negative at $y=0$, indicating the antiferromagnetic interaction between two Cr spins with no itinerant carriers. Note that the 100% Cr-substituted compound, LaCrO_3 , is an antiferromagnetic insulator below 290 K,⁵ and this antiferromagnetic interaction observed for $y=0$ can be attributed to a simple superexchange coupling between Cr spins. However, the Weiss temperatures become positive at finite values of y (carrier concentration), as shown in Figs. 1(b) and 1(c). These results indicate that doped electrons into the conduction band induce a ferromagnetic interaction between the localized spins on the Cr site. We have searched for a long-range ferromagnetic state in these compounds, but so far such a state has not been observed.

The T dependence of electrical resistivity [$\rho(T)$] is shown in Figs. 1(d)–1(f) in the same manner. Unlike the result of single crystals, $d\rho/dT$ is negative even without Cr doping ($x=0$, not shown). This comes from a grain-boundary effect

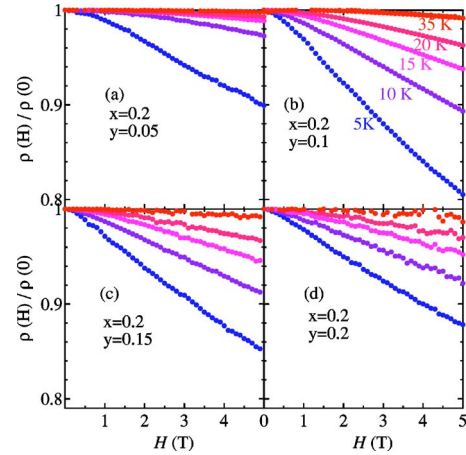


FIG. 2. (Color online) Magnetic-field dependence of resistivity normalized to the value at zero field for fixing spin concentration $x=0.2$ and changing carrier concentration (a) $y=0.05$, (b) $y=0.1$, (c) $y=0.15$, and (d) $y=0.2$. Data taken at 5 K, 10 K, 15 K, 20 K, and 35 K are shown in each panel.

of polycrystalline samples, which is known to be substantial in the transport properties of La-doped SrTiO_3 .⁶ With increasing Cr concentration x , $\rho(T)$ increases, particularly at low T , as shown in Fig. 1(d). There are two sources of the scattering of conduction electrons by Cr: one is the spin-independent scattering by the impurity potential of Cr, and the other the spin-dependent scattering by Cr spins. As demonstrated by the negative magnetoresistance discussed below, a part of the increase of $\rho(T)$, particularly at low temperatures, is caused by the spin-dependent scattering of carriers. Figures 1(e) and 1(f) show how $\rho(T)$ varies with increasing carrier concentration y . As is the same with La doped SrTiO_3 previously reported,⁴ $\rho(T)$ decreases with increasing carrier concentration y below $y \leq 0.2$.

With further increasing carrier concentration y , however, ρ increases again, as exemplified by $x=0.2$ and $y=0.5$ [the dashed line in Fig. 1(f)]. The inverse magnetic susceptibility also shifts left [Fig. 1(c)], indicating the suppression of the ferromagnetic interaction. Though we do not fully understand the origin of this increase of resistivity and the suppression of the ferromagnetic interaction, we speculate that they are related to the electron-correlation effect between itinerant carriers and/or the orthorhombic distortion of the crystal, both of which becomes substantial at large La concentration. Since the behavior of large y is the unwanted direction in terms of a large ferromagnetic coupling, we focus on the low-carrier-concentration regime ($y \leq 0.2$) in the present paper, but further investigations in the high-carrier-concentration as well as the high-spin-concentration regimes are necessary in the future.

A dominant role of magnetism on $\rho(T)$ can be seen when magnetic field is applied to the samples. Figure 2 shows the magnetic-field (H) dependence of ρ , which is normalized to the value at zero field, at various values of x and y and temperatures. Here, the magnetic field is applied perpendicular to the electrical current. As can be seen, ρ of all the samples decreases with increasing H , i.e., negative magnetoresistance occurs, and the magnitude of magnetoresistance,

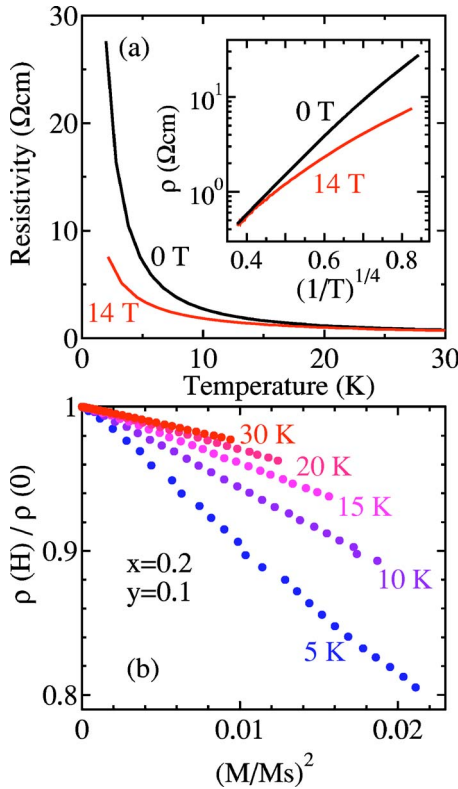


FIG. 3. (Color online) (a) Temperature dependence of resistivity at 0 T and 14 T for $x=0.2$ and $y=0.1$ ($\text{Sr}_{0.7}\text{La}_{0.3}\text{Ti}_{0.8}\text{Cr}_{0.2}\text{O}_3$). The inset shows the plot of ρ vs $(1/T)^{1/4}$ (b) Magnetization (M) dependence of resistivity. M_s is the theoretical value of saturation moment of this compound, assuming $S=3/2$ spins existing at each Cr site.

$\Delta\rho/\rho$ is enhanced with decreasing T for all samples. This indicates that transport properties are substantially dominated by its magnetic state in $\text{Sr}_{1-x-y}\text{La}_{x+y}\text{Ti}_{1-x}\text{Cr}_x\text{O}_3$. We measured the magnetoresistance up to 14 T for $x=0.2$ and $y=0.1$ ($\text{Sr}_{0.7}\text{La}_{0.3}\text{Ti}_{0.8}\text{Cr}_{0.2}\text{O}_3$) at 2 K, and found that $\Delta\rho/\rho$ amounts to 70%, i.e., resistivity becomes less than 1/3 with applying magnetic field, as shown in Fig. 3(a). Note that large magnetoresistance is observed in several transition metal oxides having e_g electrons (e.g., perovskite manganites), but such a large magnitude of magnetoresistance is rare in the transition-metal oxides having only t_{2g} electrons.

In the perovskite manganites with a modest size of magnetoresistance ($\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$, for example), magnetoresistance shows a universal M^2 scaling at different temperatures.⁷ This scaling was explained based on the Hamiltonian with Hund's rule coupling between itinerant electrons and localized spins.⁸ Note that, if the transfer energy of electrons is dominated by the spin-spin correlation function, $\langle S_i \cdot S_j \rangle$, the M^2 scaling is derived with mean-field approximation. This means that the M^2 scaling of magnetoresistance is not limited to perovskite manganites but could be applied to other magnetic conductors with localized spins and itinerant carriers. Therefore, we first check if this M^2 scaling holds in the present compound. We measured the magnetization of $\text{Sr}_{1-x-y}\text{La}_{x+y}\text{Ti}_{1-x}\text{Cr}_x\text{O}_3$ with $x=0.2$ and $y=0.1$ as a function of magnetic field, and plot the relation between resistivity and magnetization in Fig. 3(b). As can be

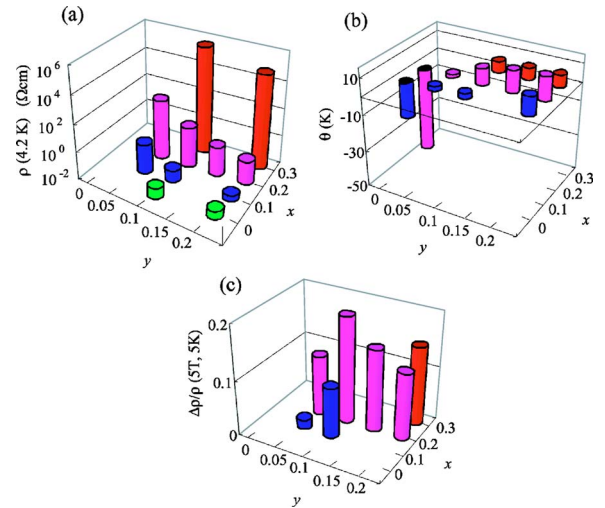


FIG. 4. (Color online) Summary of various parameters, (a) magnitude of resistivity at 4.2 K, (b) Weiss temperature, and (c) the magnitude of magnetoresistance at 5 T and 5 K, as a function of x (spin concentration) and y (carrier concentration).

seen, the variation of resistivity shows approximately M^2 dependencies, but the lines at different temperatures do not merge to a universal one. In addition, the coefficient of the M^2 dependence, i.e., the C value in $\Delta\rho/\rho=C(M/M_s)^2$, where M_s is the saturation moment, is ~ 40 at 5 K, which is much larger than that of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($C\sim 4$). Such absence of the M^2 scaling in the present compounds indicates that the coupling between localized spins and itinerant carriers alone does not explain the observed behavior of magnetoresistance.

One possible mechanism of large magnetoresistance in the present compounds is the delocalization of localized carriers (either by a polaronic effect or a disorder effect) by magnetic field, which is also responsible for the ‘‘colossal’’ magnetoresistance in perovskite manganites. In the inset of Fig. 3(a), $\log \rho$ is plotted against $(1/T)^{1/4}$. The linear behavior for $H=0$ indicates that the T dependence of resistivity at low T in this sample is dominated by the three-dimensional variable-range-hopping of localized carriers.² However, $\rho(T)$ with $H=14$ T obviously deviates from the linear relation, particularly at low T . This indicates that the wave function of the carriers becomes more extended with the evolution of magnetic moment under magnetic field, and this can be regarded as the origin of large magnetoresistance in the present compounds.

Figure 4 is a summary of various parameters, (a) the magnitude of electrical resistivity (ρ) at the lowest temperatures, (b) Weiss temperatures (θ), and (c) the magnitude of magnetoresistance of 5 T at 5 K ($\Delta\rho/\rho$), as a function of spin concentration x and carrier concentration y . Here, ρ in Fig. 4(a) shows a monotonic change with x and y , i.e., increases with x (spin concentration) and decreases with y (carrier concentration). However, the dependence of Weiss temperature θ on x or y is not monotonic [Fig. 4(b)]. With increasing y (carrier concentration) from 0 to 0.05, θ sharply increases from negative to positive values. However, with further increasing y , the variation of θ is saturated. This sharp increase and a

successive saturation of θ with increasing carrier concentration y is reminiscent of the carrier-doping dependence of Curie temperatures in $\text{Eu}_{1-x}\text{Gd}_x\text{S}$, which was attributed to the RKKY oscillation.⁹ Theoretically, the RKKY interaction is proportional to

$$J \propto \frac{k_F^2}{r^2} \left\{ \frac{\cos k_F r}{2k_F r} - \frac{\sin k_F r}{(2k_F r)^2} \right\}, \quad (1)$$

where k_F is the Fermi wave number and r the distance between two magnetic moments. The interaction oscillatorily changes its sign with $k_F r$: It is zero when $k_F=0$, and positive when $k_F \ll 1/r$, increases with increasing k_F , and then is saturated and becomes negative when $k_F \sim 1/r$. In the present compounds, k_F and r given by y (carrier concentration) and x (spin concentration), respectively. In addition to this RKKY interaction, there is a superexchange antiferromagnetic interaction between Cr spins in these compounds, which exists independent of itinerant carriers. The experimental result of the present compounds is qualitatively consistent with the sum of the carrier-independent superexchange antiferromagnetic interaction and the carrier-dependent RKKY interaction.

The x (spin concentration) dependence of θ is not monotonic either: It first increases from $x=0.1$ to 0.2, but decreases from 0.2 to 0.3. One possible origin of this nonmonotonic behavior against spin concentration is the competition between the RKKY ferromagnetic interaction mediated by doped carriers and the superexchange antiferromagnetic interaction. With increasing the distance between magnetic moments, the magnitude of the RKKY interaction falls off much more slowly than the superexchange interaction. In other words, the RKKY interaction is a more longer-range interaction. Thus, the RKKY ferromagnetic interaction is effective in the low-spin-concentration regime, whereas the superexchange antiferromagnetic interaction becomes effective in the high-spin-concentration regime, and this competition can explain the nonmonotonic spin-concentration dependence of Weiss temperatures $|\theta|$.

Another possible origin of the decrease of θ with increasing Cr concentration x is the increase of electrical resistivity (decrease of conductivity), as seen in Fig. 4(a), which suppresses the magnetic interaction mediated by itinerant carriers.

The magnitude of magnetoresistance at 5 K and 5 T as a function of x and y is also nonmonotonic. For example, with fixing the spin concentration $x=0.2$ and changing the carrier concentration y , $\Delta\rho/\rho$ increases with increasing carrier concentration y at small y , but becomes maximum around $y=0.1$, and then decreases with further increasing y . With increasing carrier concentration y , the ferromagnetic interaction increases and that can enhance magnetoresistance. Simultaneously, however, the absolute value of resistivity decreases with increasing y and that can suppress magnetoresistance. Therefore, the nonmonotonic behavior of magnetoresistance against the carrier concentration can be explained by the competition of the increasing ferromagnetic interaction and the decreasing absolute value of resistivity. These results indicate the importance of independent control of spin and carrier concentrations for enhancing the magnitude of magnetoresistance in magnetic conductors.

In summary, we made independent spin and carrier doping into SrTiO_3 , and found that ferromagnetic coupling between Cr spins appears with increasing carrier concentration. We also found large negative magnetoresistance, indicative of strong spin-charge coupling in this series of compounds. From systematic studies, we demonstrated that the magnitude of magnetoresistance can be maximized by controlling carrier and spin concentrations independently in SrTiO_3 .

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¹A. J. Millis, *Nature (London)* **392**, 147 (1998), and references therein.

²N. F. Mott, *Metal-Insulator Transitions* (Taylor and Francis, New York, 1990), and references therein.

³T. Dietl, H. Ohno, F. Matsukura, J. Cibert, and D. Ferrand, *Science* **287**, 1019 (2000), and references therein.

⁴Y. Tokura, Y. Taguchi, Y. Okada, Y. Fujishima, T. Arima, K.

Kumagai, and Y. Iye, *Phys. Rev. Lett.* **70**, 2126 (1993).

⁵J. J. Neumeier and H. Terashita, *Phys. Rev. B* **70**, 214435 (2004).

⁶Y. Maeno, S. Awaji, H. Matsumoto, and T. Fujita, *Physica B* **165**, 1185 (1990).

⁷A. Urushibara, Y. Moritomo, T. Arima, A. Asamitsu, G. Kido, and Y. Tokura, *Phys. Rev. B* **51**, 14103 (1995).

⁸N. Furukawa, *J. Phys. Soc. Jpn.* **64**, 3164 (1995).

⁹A. Mauger and C. Godart, *Phys. Lett., C* **2**, 51 (1986).