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Ferrimagnetic transition in the compound $\text{Sr}_{0.9}\text{La}_{0.1}\text{Ti}_{0.9}\text{Co}_{0.1}\text{O}_3$

J. Yang,^{1,a)} D. F. Shao,¹ X. B. Zhu,¹ Z. R. Yang,¹ Y. P. Sun,^{1,2,b)} and Y. P. Lee³

¹Key Laboratory of Materials Physics, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, People's Republic of China

²High Magnetic Field Laboratory, Chinese Academy of Sciences, Hefei 230031, People's Republic of China

³Quantum Photonic Science Research Center and Department of Physics, Hanyang University, Seoul 133-791, Korea

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We have investigated the structural and magnetic properties of $\text{Sr}_{0.9}\text{La}_{0.1}\text{TiO}_3$ and $\text{Sr}_{0.9}\text{La}_{0.1}\text{Ti}_{0.9}\text{Co}_{0.1}\text{O}_3$. Both samples can be indexed by a cubic lattice with the space group $\text{Pm}\bar{3}\text{m}$ at room temperature. The measurements of x-ray photoelectron spectroscopy and electron paramagnetic resonance confirmed the presence of Ti^{3+} ions in the samples. The sample $\text{Sr}_{0.9}\text{La}_{0.1}\text{TiO}_3$ exhibits a strongly enhanced Pauli-paramagnetism behavior, whereas $\text{Sr}_{0.9}\text{La}_{0.1}\text{Ti}_{0.9}\text{Co}_{0.1}\text{O}_3$ undergoes a ferrimagnetic transition at 127 K confirmed by a small λ anomaly at 128 K in the curve of specific heat. This transition may originate from a local charge transfer that creates some $\text{Co}^{3+}\text{-Ti}^{3+}$ antiferromagnetic pairings. © 2013 American Institute of Physics.

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SrTiO_3 is a wide band-gap and diamagnetic insulator. It is an easily functionalizable material and is a prototype of investigations on a variety of phenomena.¹ The crystal structure of SrTiO_3 at room temperature belongs to a cubic structure with an empty 3d band of Ti^{4+} . Doping SrTiO_3 with La^{3+} will introduce Ti^{3+} with 3d¹ configuration giving rise to a continuous filling of 3d band of Ti ions, and therefore, a metallic phase will occur when the doping level of La exceed 0.1 (Ref. 2). $\text{Sr}_{1-x}\text{La}_x\text{TiO}_3$ might be one of the most desirable systems in which the critical dependence of physical parameters on the band filling can be investigated in the vicinity of the Mott-Hubbard transition.³ $\text{Sr}_{1-x}\text{La}_x\text{TiO}_3$ as a typical filling-control metal-insulator transition system has been reported on the optical-conductivity, thermoelectric, and transport properties.²⁻⁶ Recently, a charge- and spin-controlled system $\text{Sr}_{1-(x+y)}\text{La}_x\text{Ti}_{1-x}\text{Cr}_y\text{O}_3$ was proposed, based on a concept of independent control of the charge and spin degrees of freedom by employing two transition-metal elements (Ti and Cr).⁷ Inaba and Katsufuji observed a giant magnetoresistance in the $\text{Sr}_{1-(x+y)}\text{La}_x\text{Ti}_{1-x}\text{Cr}_y\text{O}_3$ system.^{7,8} Moreover, Parkash *et al.* studied the electrical conductivity and dielectric properties of the valence-compensated solid solution $\text{Sr}_{1-x}\text{La}_x\text{Ti}_{1-x}\text{Co}_x\text{O}_3$ by doping Co^{3+} on Ti site giving rise to eliminate Ti^{3+} ions due to the effect of internal charge compensation in this system.^{9,10} However, the report is not yet available on the magnetic properties of $\text{Sr}_{1-x}\text{La}_x\text{Ti}_{1-x}\text{Co}_x\text{O}_3$. In this paper, we investigated the magnetic properties of $\text{Sr}_{0.9}\text{La}_{0.1}\text{TiO}_3$ (SLTO) and $\text{Sr}_{0.9}\text{La}_{0.1}\text{Ti}_{0.9}\text{Co}_{0.1}\text{O}_3$ (SLTCO). The sample SLTO exhibits a strongly enhanced Pauli-paramagnetism behavior, whereas SLTCO undergoes a ferrimagnetic transition at 127 K.

Polycrystalline samples of SLTO and SLTCO were synthesized by a conventional solid-state reaction in air. The powders mixed in the stoichiometric compositions of high-purity chemical reactants La_2O_3 , SrCO_3 , TiO_2 , and Co_3O_4

were ground, and then calcined at 900 °C for 7 days. The obtained powders were ground, pelletized, and sintered at 1300 °C for 12 h with three intermediate grindings, and finally the furnace was cooled slowly down to room temperature. The crystal structure was determined by powder x-ray diffraction (XRD) using $\text{Cu-K}\alpha$ radiation at room temperature. The measurements of X-ray photoelectron spectroscopy (XPS) were done by ESCALAB 250 using $\text{Al-K}\alpha$. Electron paramagnetic resonance (EPR) spectra were recorded with an X-band Bruker EMXplus 10/12 cw spectrometer operating at 9.4 GHz equipped with an Oxford continuous flow cryostat within the temperature range of 10–300 K. The magnetic measurements were carried out with a Quantum Design superconducting quantum interference device (SQUID) MPMS system ($2 \leq T \leq 400$ K, $0 \leq H \leq 5$ T). The specific heat was measured in a commercial physical property measurement system (PPMS) ($2 \leq T \leq 400$ K, $0 \leq H \leq 7$ T).

Figure 1(a) shows the XRD patterns of SLTO and SLTCO at room temperature. It is found that both samples are single phase with no detectable secondary phases and the samples can be indexed with a cubic lattice with the space group $\text{Pm}\bar{3}\text{m}$. The structural parameters are refined by using the program FULLPROF (Ref. 11) and the fit between the experimental spectra and the calculated values is relatively good based on the consideration of lower R_p value. The lattice parameters of SLTO and SLTCO turn out to be $a = 3.90526(1)$ and $3.90052(16)$ Å, respectively. The lattice parameter slightly decreases upon the doping of Co ions at Ti sites arising from the substitution of ions with a smaller ionic radius of Co^{3+} (0.61 Å) for Ti^{3+} (0.67 Å). The XPS measurement was carried out in order to obtain more electronic structure information of the samples. Fig. 1(b) illustrates the core-level spectra of Ti 2p for SLTO and SLTCO. In both spectra, the spin-orbit split $\text{Ti}^{4+} 2p_{1/2}$ and $\text{Ti}^{4+} 2p_{3/2}$ peaks located at around 463.83 and 458.21 eV, respectively, are obviously visible. Moreover, two small shoulders are present on the low-binding-energy sides of the respective $\text{Ti}^{4+} 2p_{1/2}$ and $\text{Ti}^{4+} 2p_{3/2}$ peaks. The core-level spectra of Ti 2p_{3/2} and the

^{a)}Electronic mail: jyang@issp.ac.cn.

^{b)}Electronic mail: ypsun@issp.ac.cn.

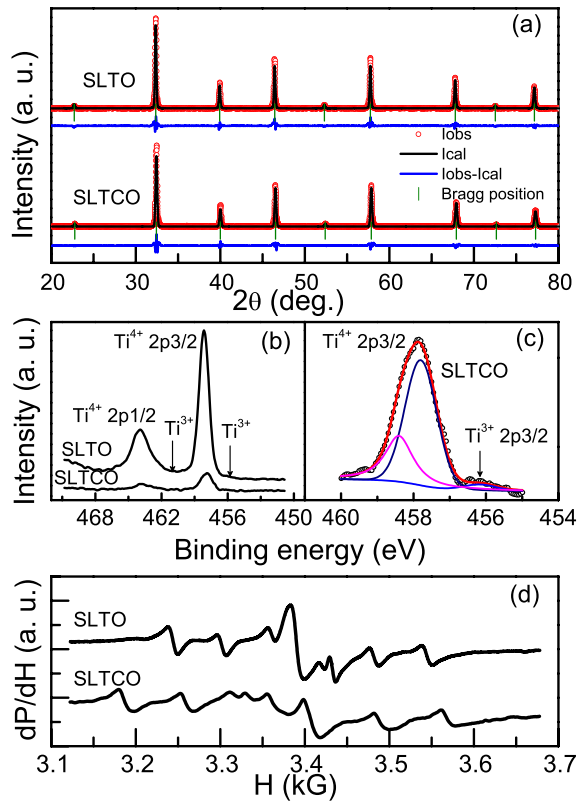


FIG. 1. (a) XRD patterns of $\text{Sr}_{0.9}\text{La}_{0.1}\text{TiO}_3$ and $\text{Sr}_{0.9}\text{La}_{0.1}\text{Ti}_{0.9}\text{Co}_{0.1}\text{O}_3$ at room temperature. Circles indicate the experimental data and the calculated data are the continuous line overlapping them. The lowest curve shows the difference between the experimental and calculated patterns. The vertical bars indicated the expected reflection positions. (b) XPS spectra of Ti 2p. (c) Deconvoluted XPS results of Ti 2p_{3/2}. (d) EPR spectra of $\text{Sr}_{0.9}\text{La}_{0.1}\text{TiO}_3$ and $\text{Sr}_{0.9}\text{La}_{0.1}\text{Ti}_{0.9}\text{Co}_{0.1}\text{O}_3$ at 80 K.

deconvoluted curves in SLTCo are shown in Fig. 1(c). The peaks located at 457.80 and 458.41 eV are normally ascribed to Ti^{3+} ions.¹² Moreover, the core-level spectrum of Co 2p_{3/2} (not shown here) shows that the doped Co ions in SLTCo are 3+ valence state. The EPR spectra were used to further confirm the presence of Ti^{3+} ions in SLTO and SLTCo samples. The EPR spectra consist of a single sextet of hyperfine split lines arising from the hyperfine interactions between one unpaired electron of Ti^{3+} and the neighboring ^{47}Ti nucleus (7.28% natural abundance), which has spin $I = 5/2$. Moreover, the intense lines at around 3400 G corresponding to $g \approx 1.97$ are characteristics of a paramagnetic (PM) Ti^{3+} center.

Figure 2 shows the temperature dependence of magnetization in the zero-field-cooled (ZFC) and the field-cooled (FC) modes at an applied field of 1000 Oe for SLTO. It is found that the FC magnetization (M_{FC}) and the ZFC magnetization (M_{ZFC}) superposed each other and the sample SLTO shows no evidence of a long-range magnetic order. Above 100 K, the magnetization is almost temperature independent, which is reminiscent of the characteristics of Pauli paramagnetism and Van Vleck paramagnetism, but the magnitude of magnetization of SLTO is several orders of magnitude larger than that of the Pauli and Van Vleck PM materials. The linear behavior of the product of χT also indicates the temperature-independent behavior of magnetization, which is more characteristic of a strongly enhanced Pauli paramagnetism instead of

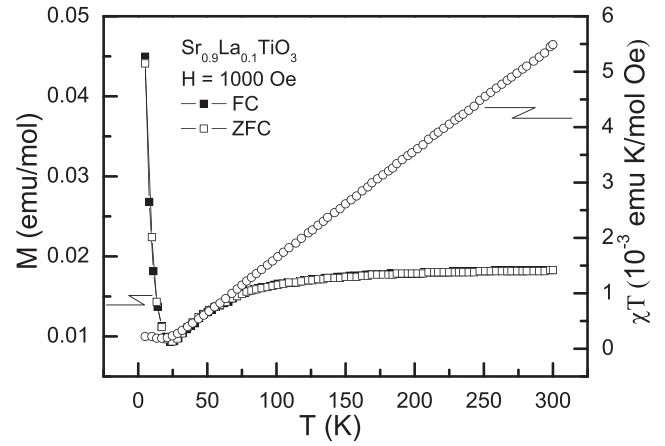


FIG. 2. Temperature dependence of magnetization and the product of χT for $\text{Sr}_{0.9}\text{La}_{0.1}\text{TiO}_3$ in the ZFC and the FC modes measured at $H = 1000$ Oe.

a localized-electron Curie-Weiss paramagnetism. The magnetization increase sharply with decreasing temperature below 25 K and this is typical of the presence of localized electron impurities.¹³

The temperature dependence of magnetization in the ZFC and FC modes for SLTCo at the applied field of 100 Oe is shown in Fig. 3(a). From the plot of M_{FC} , it is found that the sample seems to undergo a PM to ferromagnetic (FM)-

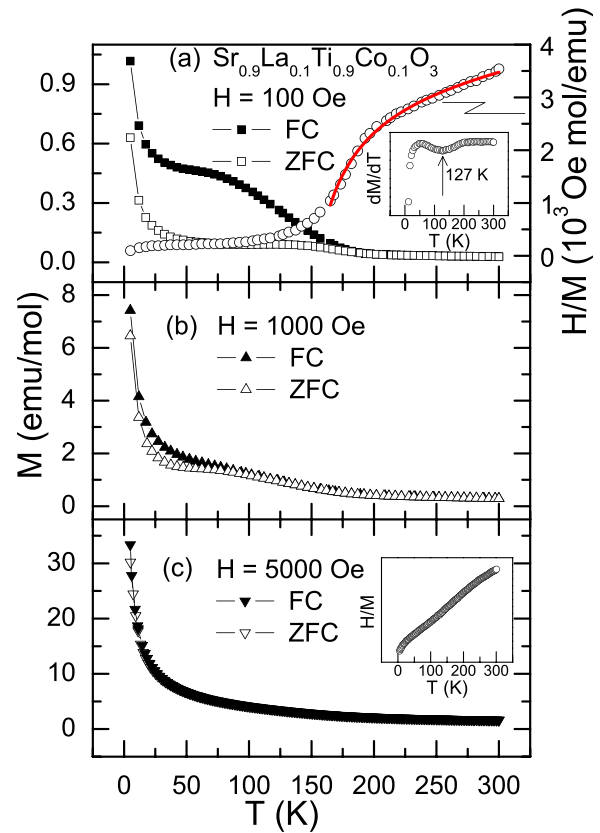


FIG. 3. Magnetization vs. temperature in the ZFC and FC modes for $\text{Sr}_{0.9}\text{La}_{0.1}\text{Ti}_{0.9}\text{Co}_{0.1}\text{O}_3$ at different magnetic fields of (a) 100 Oe, (b) 1000 Oe, and (c) 5000 Oe. The right panel of (a) shows the temperature dependence of the inverse susceptibility of $\text{Sr}_{0.9}\text{La}_{0.1}\text{Ti}_{0.9}\text{Co}_{0.1}\text{O}_3$. The solid line denotes the best fit to the data based on Eq. (1). The inset of (a) shows the plot of dM/dT vs. T based on the data of M_{FC} . The inset of (c) shows the plot of H/M vs. T.

like magnetic transition at around 127 K (defined as the temperature corresponding to the peak of dM/dT), and the magnetization gradually increases with decreasing temperature, then abruptly increases from 20 K with further decreasing temperature. The broad magnetic transition implies the existence of magnetic inhomogeneity in SLTCO. In order to determine the nature of magnetic transition at about 127 K, we plot the temperature dependence of the inverse susceptibility ($1/\chi = H/M$) under the FC modes in the right panel of Fig. 3(a). The hyperbolic behavior of $1/\chi$ -T plot is reminiscent of a ferrimagnet. In the molecular field approximation for temperature above the phase transition, the reciprocal susceptibility of a ferrimagnet can be described by^{14,15}

$$1/\chi = 1/\chi_0 + T/C_m - \sigma/(T - \theta), \quad (1)$$

where χ , C_m , σ , and θ are the fit parameters. The solid line denotes the best fit to the experimental data according to Eq. (1). The obtained θ is 126.6 ± 2.4 K, and this value almost corresponds to the peak value of dM/dT plot, i.e., 127 K as shown in the inset of Fig. 3(a). As a result, the FM-like magnetic transition at 127 K is actually the ferrimagnetic ordering. This ferrimagnetic behavior can be understood by the existence of two magnetic sublattices. The Co-based sublattice aligned with applied field, whereas the Ti-based one antiparallelled. In other words, the Co-based and Ti-based sublattices are in the FM arrangement, but the coupling between two sublattices is antiferromagnetic (AFM). Therefore, the ferrimagnetic transition in SLTCO is likely the result of local charge transfer that creates some $\text{Co}^{3+}\text{-Ti}^{3+}$ AFM pairings due to the differences in the magnetic moment of Ti^{3+} and Co^{3+} ions. Figs. 3(b) and 3(c) show the temperature dependence of magnetization for SLTCO at the applied field of 1000 and 5000 Oe, respectively. It is found that the divergence between M_{FC} and M_{ZFC} curves becomes smaller with increasing magnetic fields, and eventually both are superposed and exhibit a typical PM behavior when the magnetic field is increased to 5000 Oe, as evidenced by the linear behavior of H/M vs. T shown in the inset of Fig. 3(c).

To elucidate the origin of the magnetic behavior of SLTCO, we have also measured the magnetization loops at temperatures between 5 and 300 K (Fig. 4). In Fig. 4(a), the M-H plot exhibits a typical PM behavior at 5 K, which may be dominated by the contribution of the uncoupled $\text{Ti}^{3+}/\text{Co}^{3+}$ PM ions. With increasing temperature to 30 K, the M-H curve begins to exhibit a hysteresis behavior. A further increase in temperature to 80 K makes the hysteresis loop bigger. The hysteresis loop becomes smaller and smaller with further increasing temperature from 80 K to 140 K. At 180 K, the M-H plot shows no hysteresis and becomes linear above 180 K. The magnetic behavior between 30 and 140 K can be understood as the ferrimagnetic ordering in SLTCO, which is consistent with the results in Fig. 3.

The magnetic transition in SLTCO is further confirmed by a small λ anomaly in specific heat. Fig. 5 shows specific heat data of SLTCO. As expected, only one small λ anomaly at around 128 K was observed, which can be clearly seen from the enlarged part of specific heat around the transition temperature shown in the inset. We estimated the lattice specific heat with the Thirring model^{16,17}

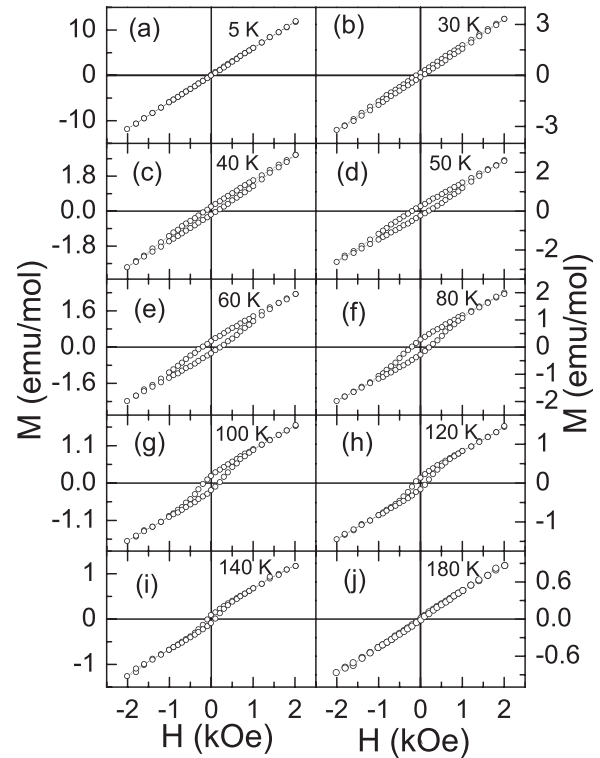


FIG. 4. M-H loops at different temperatures for $\text{Sr}_{0.9}\text{La}_{0.1}\text{Ti}_{0.9}\text{Co}_{0.1}\text{O}_3$: (a) 5, (b) 30, (c) 40, (d) 50, (e) 60, (f) 80, (g) 100, (h) 120, (i) 140, and (j) 180 K.

$$C_{\text{lattice}} = 3NR(1 + \sum_{n=1}^{\infty} b_n \mu^{-n}), \quad (2)$$

where N is the number of atoms in the unit cell, R is the ideal gas constant, $\mu = (2\pi T/\theta_D)^2 + 1$, and θ_D is the Debye temperature. This model can achieve an accuracy of 0.03% with only four terms for a Debye solid at $T = \theta_D/4$. In our fitting, we use n up to 4 and obtained a reasonable accuracy as demonstrated by the solid line in Fig. 5.

In summary, the structural and magnetic properties of SLTO and SLTCO were studied. Both samples show a cubic

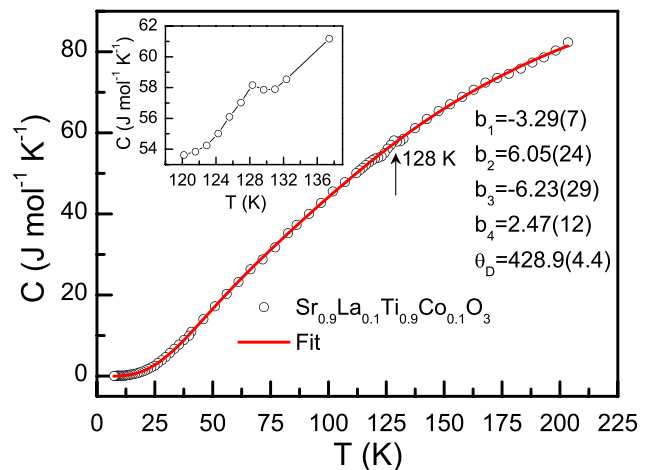


FIG. 5. Temperature dependence of specific heat for $\text{Sr}_{0.9}\text{La}_{0.1}\text{Ti}_{0.9}\text{Co}_{0.1}\text{O}_3$. The solid line is the fit of lattice specific heat with Thirring model. The fitting parameters are also listed. The inset shows the enlarged part of specific heat around the transition temperature.

structure at room temperature, and the valence state of Ti ions is suggested to be the mixed valence state of +3 and +4 based on the XPS and EPR spectra. The sample SLTCO undergoes a ferrimagnetic transition at 127 K arising from Co^{3+} - Ti^{3+} antiferromagnetic pairings due to the differences in the magnetic moment of Ti^{3+} and Co^{3+} ions.

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