Transverse thermoelectric effect in \( \text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3|\text{SrRuO}_3 \) superlattices

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Transverse thermoelectric effects in response to an out-of-plane heat current have been studied in an external magnetic field for ferromagnetic superlattices consisting of \( \text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3 \) and \( \text{SrRuO}_3 \) layers. The superlattices were fabricated on \( \text{SrTiO}_3 \) substrates by pulsed laser deposition. We found that the sign of the transverse thermoelectric voltage for the superlattices is opposite to that for \( \text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3 \) and \( \text{SrRuO}_3 \) single layers at 200 K, implying an important role of spin Seebeck effects inside the superlattices. At 10 K, the magnetothermoelectric curves shift from the zero field due to an antiferromagnetic coupling between layers in the superlattices.

Spin Seebeck effects (SSEs) \(^1\) which enable electricity generation via spin currents as a result of a temperature gradient is a promising candidate for thermoelectric applications \(^2\). Along with the success in the spin caloritronics which focuses on the interaction of spins with heat currents \(^3\)\(^4\) and the discovery of the SSE \(^1\), Nernst-Ettingshausen (Nernst) effects in ferromagnetic conductors have also gained interest in the spintronics field. Nernst effects are the thermoelectric counterparts of Hall effects, viz., generation of a transverse electric field by a longitudinal thermal gradient in the presence of an external magnetic field. In ferromagnetic conductors, anomalous Nernst effects (ANEs), which are caused by the spin-orbit interaction and proportional to the magnetization curve, also appear. ANEs in magnetic conductors have intensively been studied in the field of condensed-matter physics in terms of the topological nature for Bloch electrons \(^5\)\(^6\)\(^7\)\(^8\).

Whereas spintronics or spin-caloritronics experiments have commonly been carried out using conventional alloys and ferrites, perovskite-type oxides have received much attention from the wide science community because of a rich variety of electronic properties \(^9\)\(^10\). Especially, heterostructures of these perovskite oxide materials provide a fertile ground for novel physical phenomena related with interfaces \(^11\). In the Seebeck effect, for example, a positive Seebeck coefficient was observed for superlattices made of \( \text{YBa}_2\text{Cu}_3\text{O}_7-\delta \) and \( \text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3 \), in spite of the negative values for a simple \( \text{YBa}_2\text{Cu}_3\text{O}_7-\delta \) film and a \( \text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3 \) film each \(^12\). The sign change in thermopower by forming superstructures was attributed to an interface effect \(^13\), which suggests that perovskite-based superlattices are an attracting stage for novel spin caloritronic effects.

A ferromagnetic superlattice comprising \( \text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3 \) and \( \text{SrRuO}_3 \) is the target material in the present study. Both \( \text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3 \) and \( \text{SrRuO}_3 \) are known to be ferromagnetic metals; \( \text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3 \) is a soft magnet with high Curie temperature \( T_C \approx 350 \) K, while \( \text{SrRuO}_3 \) is a hard magnet with low \( T_C \approx 150 \) K. A novel magnetic property in this superlattice is an interfacial antiferromagnetic coupling between \( \text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3 \) and \( \text{SrRuO}_3 \) layers, which originates from the hybridization of 2p state of O atoms with 3d states of Mn atoms and 4d states of Ru atoms \(^11\)\(^12\). The interlayer antiferromagnetic coupling induces an exchange bias effect \(^14\); the magnetization loop is shifted so that it is no longer symmetric about the zero magnetic field, as commonly implemented in ferromagnet|antiferromagnet interfaces. Whereas the magnetic properties of \( \text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3|\text{SrRuO}_3 \) superlattices have been investigated well so far \(^11\)\(^12\), there are few studies of cross-plane magnetotransport properties which should strongly reflect the interlayer magnetic coupling.

In the present letter, we study a magnetothermoelectric effect along the Hall direction driven by a heat current transmitting across \( \text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3|\text{SrRuO}_3 \) ferromagnetic superlattices using a so-called longitudinal setup for the measurement of SSEs \(^23\) [see also Fig. 2(c)]. High-quality \( \text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3|\text{SrRuO}_3 \) superstructures which were fabricated by pulsed laser deposition show a strong interlayer antiferromagnetic coupling below 105 K. The measured magnetothermoelectric voltage was found to have an opposite sign to that for a \( \text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3 \) single layer film and a \( \text{SrRuO}_3 \) single layer film at 200 K, which is ascribable to an electronic reconstruction nucleated at the interfaces or generation of spin-current induced voltage in addition to the ANE. At 10 K, clear shifts of hysteresis loops of the transverse thermoelectric voltages were observed. The directions of shifts depend on field-cooling processes, consistent with the exchange bias effect.

Epitaxial films were grown on 0.5-mm-thick \( \text{SrTiO}_3 \) (001) substrates by pulsed laser deposition from polycrystalline targets using a KrF excimer laser. Oxygen partial pressure was 0.3 torr and substrate temperature was kept at 800 °C during the laser ablation. A \( \text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3 \) layer was first grown on a \( \text{SrTiO}_3 \) substrate and then a \( \text{SrRuO}_3 \) layer was deposited. The above bilayer was repeated 10 times. After deposition, samples were annealed at 800 °C in the 400 torr oxygen atmosphere.
and then cooled to room temperature. The samples were characterized by Reflection High Energy Electron Diffraction (RHEED), X-ray diffraction, and transmission electron microscopy (TEM). We have confirmed that the grown samples show metallic resistivity below 300 K; the sheet resistance at room temperature is about 150 Ω and residual-resistance ratio is \( \sim 2 \). Magnetization and magnetothermoelectric-effect measurements were performed in a Physical Property Measurement System (Quantum Design, Inc.), where an external magnetic field was applied parallel to the superlattices.

We show a RHEED pattern taken along [111] at an ambient temperature for a superlattice sample in Fig. 1(a). Clear streaks are observed, which indicate a flat surface of the grown film. Figure 1(b) shows a \( \theta-2\theta \) X-ray diffraction scan for the same sample around the SrTiO\(_3\) (002) reflection peak. Satellite peaks which support the superlattice structure are clearly observed, as numbered in Fig. 1(b). From the peak positions, the superlattice period is calculated using \( \lambda/(2\sin\theta_0 - \sin\theta_{i+1}) \), where \( \lambda = 0.154 \text{ nm} \) for Cu Kα radiation [2]. The obtained value is 5.7 ± 0.2 nm, which corresponds to the thickness of the La\(_{0.67}\)Sr\(_{0.33}\)MnO\(_3\)|SrRuO\(_3\) bilayer.

Figure 1(c) shows a cross-sectional TEM image for a superlattice sample. The clear superlattice structure which has structural integrity of La\(_{0.67}\)Sr\(_{0.33}\)MnO\(_3\) and SrRuO\(_3\) layers was confirmed. Also, all the interfaces between La\(_{0.67}\)Sr\(_{0.33}\)MnO\(_3\) and SrRuO\(_3\) layers are sharp. The thicknesses of La\(_{0.67}\)Sr\(_{0.33}\)MnO\(_3\) and SrRuO\(_3\) layers were determined as \( \sim 2.4 \text{ nm} \) and \( \sim 3.5 \text{ nm} \), respectively, and the total thickness of the superlattice was 57 nm. These values are in agreement with those deduced from the X-ray diffraction measurements.

In Fig. 2(a), we show the temperature (\( T \)) dependence of magnetization (\( M \)), which was measured in the field-cooled condition under \( \mu_0 H = 0.1 \text{ T} \). Here, the diamagnetic contribution of the SrTiO\(_3\) substrate was subtracted from the raw data. As \( T \) decreases, a sharp increase in \( M \) is observed below \( \sim 300 \text{ K} \), which corresponds to the ferromagnetic transition of the La\(_{0.67}\)Sr\(_{0.33}\)MnO\(_3\) layers. The magnitude of \( M \) increases with decreasing \( T \), but below 105 K, where the SrRuO\(_3\) layers undergo a ferromagnetic transition, a clear decrease in \( M \) is observed. This is evidence that the magnetization of the SrRuO\(_3\) layers antiferromagnetically couples to that of the La\(_{0.67}\)Sr\(_{0.33}\)MnO\(_3\) layers. The decrease in \( M \) at 105 K is observed also at 4 T, demonstrating that the interlayer antiferromagnetic coupling is highly strong compared with similar superlattices reported in former studies [21, 22].

Figure 2(b) shows magnetization curves for the superlattice measured at several temperatures. The magnetization increases rapidly in a low-\( H \) region and tends to saturate above \( \sim 0.2 \text{ T} \). Since La\(_{0.67}\)Sr\(_{0.33}\)MnO\(_3\) has a small magnetic anisotropy and a low coercive field, magnetic hysteresis is hardly observed at 300 K or 200 K. On the other hand, SrRuO\(_3\) possesses a strong uniaxial anisotropy and a large coercive field (\( \geq 0.1 \text{ T} \)). In the \( T \) region and...
range below 105 K where the SrRuO$_3$ layers exhibit ferromagnetism, clear magnetic hysteresis of $M$ is observed.

We have measured transverse thermoelectric effects for the La$_{0.67}$Sr$_{0.33}$MnO$_3$/SrRuO$_3$ superlattice, as illustrated in Fig. 2(c). The sample was sandwiched by two AlN blocks; on the top AlN block, a 100-$\Omega$-heater was attached to apply a temperature gradient to the superlattice, while the bottom block was kept at the system temperature. The temperature difference ($\Delta T$) which arises between the two AlN blocks was measured using type-E thermocouples. The magnitude of $\Delta T$ is 0.5-1 K at each temperature. The thermoelectric voltage along the Hall direction induced by charge and spin transports from the hot to cold reservoir across the superlattice was measured between both ends of the film plane, as illustrated in Fig. 2(c). The length between the voltage electrodes and sample width are about 6 mm and 2.5 mm, respectively.

Figure 2(d) presents the $H$ dependence of transverse thermoelectric voltage signal divided by the temperature difference, $V/\Delta T$, at 50, 100, 200, and 300 K. Clear voltage signal which is proportional to the magnetization is observed below 200 K, while it is very small at 300 K. The magnitude of $V/\Delta T$ increases with decreasing $T$ down to 100 K, which is consistent with the $T$ variation of $M$ [Fig. 2(b)]. The sign of $V$ is negative for a positive magnetic field.

We found that the sign of $V/\Delta T$ for the superlattices is opposite to those for La$_{0.67}$Sr$_{0.33}$MnO$_3$ and SrRuO$_3$ single layers at the same temperature (200 K). Figure 3 shows the magnetic-field dependence of Nernst voltage measured in the same experimental setup at 200 K for a 50-nm-thick La$_{0.67}$Sr$_{0.33}$MnO$_3$ film and a 50-nm-thick SrRuO$_3$ film. At 200 K, SrRuO$_3$ is paramagnetic and shows no ANE, while ferromagnetic La$_{0.67}$Sr$_{0.33}$MnO$_3$ shows an ANE. The magnitude of $V/\Delta T$ for the La$_{0.67}$Sr$_{0.33}$MnO$_3$ film, however, much smaller than that for the La$_{0.67}$Sr$_{0.33}$MnO$_3$/SrRuO$_3$ superlattice (Fig. 3) in spite of their similar resistivity values ($\sim 0.5$ m$\Omega$cm). Furthermore, the sign of $V/\Delta T$ for the La$_{0.67}$Sr$_{0.33}$MnO$_3$ film is opposite to that for the La$_{0.67}$Sr$_{0.33}$MnO$_3$/SrRuO$_3$ superlattice. Hence, the transverse thermoelectric effect in the La$_{0.67}$Sr$_{0.33}$MnO$_3$/SrRuO$_3$ superlattices is not explained only by the ANE in La$_{0.67}$Sr$_{0.33}$MnO$_3$ or SrRuO$_3$, unless a drastic change in electronic structure around the Fermi energy, e.g. resonant states, is induced by charge transfer or strain effects at the interfaces. Generation of additional voltages due to spin-current generation effects, e.g. the SSE, may be important in the transverse thermoelectric voltage in the La$_{0.67}$Sr$_{0.33}$MnO$_3$/SrRuO$_3$ superlattices; in fact, very large ANE and SSE signals have been observed in other magnetic superlattices very recently.

Hysteresis loops of magnetization ($M$) and thermoelectric voltage along the Hall direction ($V$) at 10 K are shown in Fig. 4. When the sample was cooled from 150 K in the +4 T magnetic-field before the measurements, the magnetization loop is shifted in the negative direction along the field axis, as shown in Fig. 4(a). The direction of the shift is opposite after cooling from 150 K in −4 T [Fig. 4(a)]. The magnitude of the shifts is about 0.1 T. These results are direct evidence of the exchange bias effect. Because of the strong interfacial antiferromagnetic coupling, the magnetization of the SrRuO$_3$ layers are pinned in the opposite direction to the applied magnetic field in the field-cooling processes, which causes the negative exchange bias effect. Corresponding to the exchange bias observed in the magnetization curves at 10 K, hysteresis loops of transverse thermoelectric voltages are also shifted from the zero field depending on the field-cooled processes, as shown in Fig. 4(b). The direction and magnitude of the shifts are consistent with those in magnetization curves [Fig. 4(a)]. Hence, the negative

![Graph 3](image3.png)

**FIG. 3:** Magnetic field ($H$) dependence of the transverse thermoelectric voltage divided by temperature difference ($V/\Delta T$) at 200 K for a 50-nm-thick La$_{0.67}$Sr$_{0.33}$MnO$_3$ (LSMO) film, a 50-nm-thick SrRuO$_3$ (SRO) film, and a La$_{0.67}$Sr$_{0.33}$MnO$_3$/SrRuO$_3$ [(LSMO/SRO)$_{10}$] superlattice film.

![Graph 4](image4.png)

**FIG. 4:** Hysteresis loops at 10 K for (a) magnetization ($M$) and (b) transverse thermoelectric voltage ($V$). The measurements were performed after the sample was cooled from 150 K in an in-plane magnetic field of +4 T (red online) or after cooling from 150 K in −4 T (blue online). The dotted lines are guides for the eyes.
exchange bias effect is clearly observed also in the transverse thermoelectric effect driven by a cross-plane heat current.

In summary, we have studied the magnetothermoelectric effect for La$_{0.67}$Sr$_{0.33}$MnO$_3$/SrRuO$_3$ superlattices, in which ferromagnetic La$_{0.67}$Sr$_{0.33}$MnO$_3$ and SrRuO$_3$ couple antiferromagnetically below 105 K. Clear voltage signals proportional to magnetization curves were observed below 300 K. The sign of the transverse thermoelectric voltage for the superlattice is opposite to that for La$_{0.67}$Sr$_{0.33}$MnO$_3$ and SrRuO$_3$ films at 200 K. Modulation of the ANE by a dramatic electronic reconstruction nucleated at the interfaces or generation of spin-current driven voltage in addition to the ANE may be important in the magnetothermoelectric voltage in the superlattices. At 10 K, depending on magnetic-field directions in field-cooled processes, the magnetothermoelectric voltage loops are shifted from the zero field due to the exchange bias effect in the superlattices.

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