Exploring lattice effects on transport properties in La$_{0.7}$Sr$_{0.3}$MnO$_3$/Al$_2$O$_3$ superlattices

Yuansu Luo and Konrad Samwer
I. Physikalisches Institut, Universität Göttingen, Friedrich-Hund-Platz 1, D-37077 Göttingen, Germany
E-mail: yluo@gwdg.de

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Abstract. Superlattice modulation and interfacial dilatation in manganite/alumina multilayers were used to explore lattice effects on transport behaviour. Epitaxial growth and high quality of stacking as well as structural coherency were confirmed by x-ray measurements. As the measure of lattice distortion, the average lattice spacing, structural coherency length, Curie temperature, magnetization, coercive field \( H_c \) as well as resistance are found to be functions of the interface fraction. Accordingly, we divided each manganite layer into two parts, i.e., weakly distorted ‘innermost’ atomic layers and strongly dilated interfacial atomic layers, as is well clarified by observation of two component magnetization loops and huge variation in resistance measured with current in and perpendicular to plane (i.e. CIP and CPP). The low-resistive innermost part with a ‘bulk’-like soft magnetic behaviour functions as a conductance channel for the CIP case, whereas the high-resistive interfacial part rules the CPP data, leading to a low-magnetotunnelling effect at 4.2 K and an enhanced colossal magnetoresistance at the relevant transition temperature.
1. Introduction

Colossal magnetoresistance (CMR) [1, 2] manganites La_{1-x}(Ca, Ba or Sr)xMnO3 present additionally a rich variety of intriguing physical phenomena deriving from a delicate balance of interactions among strongly coupled charge, spin and lattice degrees of freedom. A metal-isolator transition caused by eg electron hopping between Mn^{4+} and Mn^{3+} ions is directly connected to ferromagnetism via the double-exchange mechanism [3, 4] and may be accompanied commonly by intrinsic electronic phase separation [5]–[7]. Several experiments have clarified that the Curie temperature $T_C$ and CMR effect are optimized when $\sim 30\%$ of Mn$^{3+}$ at the B site is converted to Mn$^{4+}$ by substituting divalent ions for the trivalent La at the A site in compounds. A pioneering work on bulk lattice effects was carried out earlier by Hwang et al [8]. They observed a drop in $T_C$ and an increase in CMR with a decrease in the Mn–O–Mn bond angle affected by substituting different rare earth ions for La.

Moreover, because of a highly spin-polarized electronic structure [9, 10] these compounds become candidates for magnetotunnelling electrodes. Designed junction structures consisting of two manganite layers separated by an isolator as electrical barrier showed indeed a large tunnelling magnetoresistance (TMR) [11, 12] though mostly at low temperatures. The potential application motivates an intense interest in investigations on thin films and manganite/isolator multilayers. Some sensitive experiments [13, 14] showed that the surface or interface magnetism significantly differs from that of bulk samples. Also some manganite superlattices with SrTiO$_3$ as space layers were reported recently [15, 16], showing higher CMR over a large temperature region in comparison to a peak-like structure for a single layer (SL). Commonly, lattice distortion, chemical disorder as well as Mn–O–Mn bond breakup at interfaces are responsible for decrease in $T_C$, loss in magnet moment and increase in the resistivity. In some cases, the lack of Mn$^{4+}$ at the interface leads to a local antiferromagnetic coupling according to the super-exchange mechanism [17] and in other cases, the exposure of Mn ions gives rise to a partial filling of the d$_{xz}$ orbital which drives a double-exchange-like spin ordering of surface and subsurface Mn [18]. The mentioned effect is recapitulated as interface-induced electronic phase separation. It has been shown however by all-manganite superlattice systems [19, 20] that the phase separation at interfaces could be suppressed by preserving the Mn–O chain network [19], thus favouring the double-exchange in under doped manganite layers [20].

This paper deals with another superlattice system of manganite/isolator with a bilayer number $m$ and a period length $\Lambda$ to take advantage of a large signal originating from $2m$ interfaces for exploring an underlying lattice effect on transport properties due to uniaxial distortion of MnO$_6$ octahedra which is expected to occur in the superlattice system because of its
Table 1. Structural parameters and transport properties of LSMO/Al₂O₃ super lattices ML1 and ML2 including the reference layer SL.

|                            | ML1 | ML2 | SL |
|-----------------------------|-----|-----|----|
| LSMO layer thickness (nm)   | 8.5 | 6.5 | 115|
| Al₂O₃ layer thickness (nm)  | 2.2 | 2.2 | –  |
| Bilayer number m            | 6   | 10  | –  |
| Designed bilayer period Λ (nm) | 10.7| 8.7 | –  |
| Measured average d₀ (Å)     | 1.954| 1.963| 1.940|
| Measured coherency length ξ (nm) | 16.5| 10.5| 20.5|
| Fitted average d₀ (Å)       | 1.95(0)| 1.95(3)| |
| Fitted atomic plane number na | 44 | 33 | 593|
| Fitted atomic plane number nb | 11 | 11 | –  |
| Curie temperature (K)       | 300 | 250 | 330|
| Ms at 4.2 K (emu/cm³)       | 360 | 160 | 400|

peculiar nature, i.e. out-of-plane lattice spacing modulation and interfacial dilatation, and should be proportional to interfacial fraction 1/Λ [21]. The manganite used here is La₀.7Sr₀.3MnO₃ (LSMO) and the isolator is Al₂O₃ which is the mostly used barrier for TMR junction structures. In thermodynamic non-equilibrium deposition conditions, an epitaxial growth for this system is likely due to metastable polymorphs of the alumina which, except the equilibrium phase (hexagonal), shows several cubic structures with a lattice constant from 3.95 to 3.974 Å [22] (depending on the oxygen stoichiometry) slightly larger than that of 3.88 Å of the LSMO manganite with regard to a quasi-cubic perovskite lattice. Due to the moderate lattice mismatch of ~2% for this system a lattice spacing expansion or a systematical change in elastic strains in manganite layers is expected.

2. Experimental details

Samples with a layer stack of [a/b]ₘ+a were prepared onto MgO(100) substrates by reactive sputtering alternately from compound LSMO and pure Al targets, where a is denoted as the manganite layers LSMO and b as isolator space layers Al₂O₃, with thicknesses of few nanometres (table 1). The reactive sputtering was carried out in a gas mixture (1:1) of argon and oxygen at substrate temperature Tₛ = 750 °C. In between for each bilayer, an additional oxidation (1 bar oxygen/10 min) was performed at the same Tₛ, to optimize the oxygen stoichiometry. Two samples denoted as ML1 and ML2 were intensively studied and their detailed structural parameters are listed in table 1. As a reference, a 115 nm thick SL of LSMO was also studied. Superlattice structures were analysed by x-ray scattering experiments, using CuKα radiation and symmetric reflectivity geometry, i.e. with a scattering vector q parallel to the growth direction. The magnitude of q is equal to (4π/λ) sin θ with θ denoted as the scattering angle and λ as the x-ray wavelength. Symmetric reflectivity measurements yield out-of-plane structural information in the superlattice system.

In-plane magnetization loops M(H) were measured by a vibrating sample magnetometer at different temperatures T = 4.2, 100, 200 and 300 K with a magnetic field (H) up to 10 kOe.
Temperature scans $M(T)$ were carried out in applied field of 1000 Oe to determine $T_c$. The measured magnetization is normalized in emu cm$^{-3}$, where only the volume of manganite layers was taken into account. Resistive measurements were carried out with current in plane (CIP) and current perpendicular to plane (CPP) geometries, as schematically shown in inset of figure 4. For the CIP case, the electric current is restricted in separated manganite layers, which corresponds to parallel connection of resistors. Accordingly, the CPP is analogous to connecting resistors in series and is dominant by high-resistive interface layers as well as by Al$_2$O$_3$ layers. Magnetoresistance $\Delta R/R_{\text{max}}$ was determined with in-plane magnetic field up to 70 kOe.

3. Results and discussion

Figure 1(a) illustrates small-angle x-ray scattering patterns measured for ML1 and ML2 samples, including the reference LSMO layer. One can identify a superlattice structure with sharp and regular satellites marked by the order number of 1, 2 and 3, whereas the SL reveals merely a monotonic oscillation, from which the thickness of the film was measured. As is known, the small-angle superlattice structure originates from a well-defined and contrastive chemical modulation along the growth direction. The distance $\Delta q$ of adjacent satellites gives the period length $\Lambda = 2\pi/\Delta q$ which coincides with the designed bilayer thickness. Note that the satellite peaks of ML2 seem to be sharper than those of ML1. Actually, it derives from a larger $m$ (see table 1). The data indicate a high quality of stacking with limited layer roughness and
thickness fluctuation which are estimated to be within ±1 monolayer [23] and seem to be independent of 1/Λ. The result can be attributed to the ceramic nature of LSMO and Al₂O₃, i.e. to their extremely high-thermal stability. An interdiffusion of the elements may hardly take place in the concerned temperature range and the alumina holds the metastable cubic phase without a polymorph transition, as experimentally observed below.

The wide-angle x-ray diffraction patterns measured for ML1 and SL are depicted in figure 1(b). Both exhibit several diffraction peaks, which are identified by (00l) (l = 1, 2 and 3) in regard to a quasi-cubic perovskite, with an intensity comparable to each other. This indicates epitaxial growth of Al₂O₃/LSMO layers on MgO(001) substrates, i.e. thin alumina layers preferentially form a metastable phase (cubic) to match the lattice of the manganite layers. As a result, this carries a definite magnitude of structural coherence length ξ (ξ > Λ, see table 1) along the growth direction and thus gains more diffraction intensity compared with structurally incoherent (ξ < Λ) manganite/Al₂O₃ superlattices with non-crystalline space layers prepared at low Tₛ = 150 °C [23].

The corresponding wide-angle superlattice patterns are shown in figure 1(c). The satellite peaks denoted by 0, ±1 and ±2 occur just in the vicinity of the (002) reflection, from the position of which the Mn–O bond length of MnO₆ octahedra along the c-axis can be determined. The distance between the adjacent satellites gives again the same period length Λ and the full width at half-maximum corresponds approximately to the correlation length ξ. For larger 1/Λ the superlattice peaks of ML2 become broader compared to those of the ML1, even though a larger m should lead to the sharpening of the satellite peaks as measured for the small-angle superlattice (figure 1(a)). This indicates that ξ is disproportional to 1/Λ, but is independent of m. According to the Scherrer formula [24], ξ was estimated to be ~1.5Λ for ML1 and ~1.2Λ for ML2, respectively. These values are smaller than those reported for several cubic metal–metal superlattice structures [25, 26], in which ξ = (2 ~ 3)Λ, despite of a large lattice mismatch, for instance ~8% for the Ir/Co system [26]. From this comparison we conclude that a peculiar superlattice disorder exists in the present system, presumably due to rotations and tilting of MnO₆ octahedra, caused by uniaxial lattice expansion, similar to the cooperative JT-effect. The structural disorder is found to be proportional to the interface fraction 1/Λ, since the interface lattice is maximally dilated. In any case, the occurrence of the wide-angle superlattice demonstrates an out-of-plane lattice spacing modulation, i.e. a c-axis lattice spacing expansion in manganite layers.

Moreover, the central satellite peak yields the average d₀ and obviously it is d₀ = Λ/(nₐ + nₜ) with nₐ and nₜ referred to the numbers of atomic planes per manganite and alumina layer, respectively. Commonly, the average d₀ contains interface dilatation δ and out-of-plane lattice expansion η in layers caused by systematic changes in elastic strains, though the symmetric diffraction measurements cannot distinguish both contributions. Here, δ is defined as δ = dₐₜ – (dₐ + dₜ)/2, i.e., a deviation of interfacial lattice spacing dₐₜ from the mean bulk d-value of the constituents and it increases linearly with 1/Λ. The evaluated d₀ is listed in table 1 and plotted versus 1/Λ in figure 2(a) as well, showing indeed a strong 1/Λ dependence, where the ‘bulk’ value (1.940 Å) obtained from the reference layer was used approximately for the case of 1/Λ = 0. Since nₜ used is constant and much smaller than nₐ (see table 1), the change in d₀ (figure 2(a)) reflects mostly the change in δ and η in the manganite layers. Actually, the mean lattice spacing for manganite layers can be estimated to be about 1.950 Å for ML1 and 1.953 for ML2 by fitting the x-ray data with one-dimensional model [24]. Compared with the ‘bulk’ value, the lattice spacing expansion η is ~0.01 Å on average, i.e. 0.5%.
The interfacial dilatation $\delta$ could be roughly estimated to be in the range from 0.01 to 0.02 Å, i.e. larger than $\eta$ but not exceeding the half of the lattice mismatch, if we assumed the bulk value $d_b \sim 1.98$ Å [22].

The out-of-plane lattice expansion in manganite layers corresponds to an increase in the Mn–O–Mn bond length of MnO$_6$ octahedra along the c-axis, which is expected to affect transport properties. Figures 3(a) and (b) present temperature-dependent magnetization $M(T)$ and in-plane magnetization hysteresis $M(H)$ (4.2 K) measured for the relevant samples. As can be seen, both $T_c$ and $M$ for superlattice samples are lower than those for the SL and show again a $1/\Lambda$-dependence because of the increase of $d_0$ (see figure 2 and table 1). More interestingly, the $M(H)$ loops measured at 4.2 K for the superlattice structures show a hysteresis originating from two components (i.e., two steps) with inflection points as marked by triangles in figure 3(b). Obviously, one is soft magnetic with a $H_c$ independent of $1/\Lambda$ and comparable with that for the SL. The other one is hard magnetic and becomes then more pronounced, as $1/\Lambda$ increases. Above 100 K, the second magnetic component vanishes. We suppose that the first magnetic component originates from weakly distorted ‘innermost’ atomic layers, because it behaves as the ‘bulk’-like in spite of low $T_c$ and $M$. The second component might originate from strongly dilated interfacial atomic layers because it strongly depends on the interface fraction $1/\Lambda$ and shows even lower transition temperature. The magnetic ordering in interfacial atomic layers can be monitored by measuring the coercivity $H_c$ for different temperatures. As shown in figure 3(c), $H_c$ for ML1 increases with decreasing $T$: first linearly down to $\sim 100$ K; and then abruptly deviating from the linear dependence found for the SL. Actually, this transition can be
Figure 3. Vibrating sample magnetometer measurements; (a) temperature scan $M(T)$ with $H = 1000$ Oe, where an abrupt increase below 28 K is due to the diamagnetic–paramagnetic transition in MgO substrate, (b) magnetization loops $M(H)$ at 4.2 K and (c) coercive field $H_c$. One sees an additional transition marked by the arrow in (a), two component hysteresis with inflection points marked by triangles in (b) as well as a nonlinear increase in $H_c$ below $\sim 110$ K in (c), suggesting a magnetic ordering of the interfacial atomic layers which differs from that of the innermost atomic layers.

seen already in the $M(T)$ curve measured for the ML2 because of a larger $1/\Lambda$ (see the arrow in figure 3(a)). Two-step hysteresis observed here suggests a weakly magnetic coupling between the two parts, though they are interconnected. A non-collinear alignment of spins at interfaces is likely because of a competition between double-exchange and super-exchange mechanisms accompanied by electronic phase separation in this strongly distorted layer part, as discussed below along with resistive measurements.

Figure 4(a) presents temperature-dependent resistance $R(T)$ measured for the superlattice ML1 with the CIP geometry and magnetic field $H = 0$ and 50 kOe. Due to parallel connection effect, the CIP resistance is low and dominated by the low-resistive layer part, i.e. weakly distorted innermost regions. A peak resistance of about 2.5 k$\Omega$ can be shown at about 290 K, indicating a metal-isolator transition correlated to Curie temperature $T_c = 300$ K for the innermost part. Below the peak temperature $T_p$, $R$ decreases abruptly with decreasing $T$, followed by saturation (0.2 k$\Omega$) below $\sim 50$ K. A magnetic field suppresses $R$ particularly near $T_p$, as is usually observed in CMR manganites. A maximal CMR effect measured at $T_p$ is $\sim 55\%$ (70 kOe) and at 4.2 K the effect becomes insignificant (inset of figure 4(a)). A similar behaviour was measured for the SL, though its $T_p$ ($\sim 320$ K) is slightly higher.

The corresponding CPP data are depicted in figure 4(b). Because of series connection effect, the CPP resistance (of the order of M$\Omega$) is dominated by the high-resistive layer part, including the barrier of Al$_2$O$_3$ layers. The contribution from the innermost layer part is insignificant and only
shows a trace near 290 K. However, a broad peak can be seen at about 110 K. Not surprisingly, it can be explained by a magnetic transition in the interfacial layers, as is observed by magnetic measurements (figure 3(c)). Below 50 K, \( R \) increases again due to isolator layers of \( \text{Al}_2\text{O}_3 \). The resistance decreases in applied magnetic field and the effect is more significant near \( T_p \). The inset of figure 4 gives the CPP-magnetoresistance measured near \( T_p \) and 4.2 K, respectively. The CMR effect about 60% obtained near \( T_p \) derives mostly from the part at the LSMO interfaces. However, the effect of about 40% observed at 4.2 K is the sum of CMR and TMR. The latter of about 20% occurs in low-magnetic field (\( H < 5\text{kOe} \)) with a hysteresis comported with the soft component in the corresponding \( M(H) \) loop (figure 3(b)). The magnitude of TMR is lower than that of trilayer junction structures [11, 12, 23], but comparable to grain boundary tunnelling effect measured for polycrystalline manganite films [23]. The limited TMR ratio observed in our superlattice structures is partly due to accumulated interfacial roughness and large total resistance.
which increase with m, and partly due to effective barrier width enhanced by the high-resistive interfacial layer part.

4. Conclusion

In conclusion, we studied superlattice structures of manganite/alumina by x-ray scattering and transport measurements. The nature of out-of-plane lattice spacing modulation and interfacial dilatation established by ~2% lattice mismatch was analysed in detail to explore lattice distortion effects in manganite layers. The small-angle superlattice with sharp and regular satellite peaks demonstrates a high quality of stacking and well-defined chemical modulation along the growth direction. Conversely, the property of the wide-angle superlattice, which verifies the out-of-plane lattice spacing modulation as looked for, is sensitive to the interface fraction 1/Λ, showing simultaneously an increase in interfacial dilatation and loss in structural coherency. The limited coherency length (~1.5Λ) implies a peculiar kind of structural disorder in superlattices containing manganite layers, which may be associated with the rotation and tilting of MnO₆ octahedra. The average d₀, which contains additionally the lattice spacing expansion of the layers, is found to be proportional to 1/Λ. Two-step magnetization loops and an additional magnetic transition measured at low temperature conclude that each manganite layer can be divided into two parts, i.e. weakly distorted innermost atomic layers and strongly dilated interfacial atomic layers. The former provides the conductance channel for CIP transport measurements and shows a bulk-like soft magnetic behaviour, even despite a ~0.5% mean expansion in out-of-plane lattice spacing, which causes a decrease in magnetic moment and lowers Tc by 30–70 K. The interfacial layer part rules the CPP resistive data along with isolator layers of alumina and displays a much lower transition temperature (~110 K), accompanied by a relatively large CMR effect. The non-bulk-like nature is signified by a strong dependence upon 1/Λ. The results strongly point out the significance of the interfacial coherency for high TMR values.

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