

Large Increase of the Curie Temperature by Orbital Ordering Control

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Using first principle calculations we showed that the Curie temperature of manganites thin films can be increased by far more than an order of magnitude by applying appropriate strains. Our main breakthrough is that the control of the orbital ordering responsible for the spectacular T_c increase cannot be imposed by the substrate only. Indeed, the strains, first applied by the substrate, need to be maintained over the growth direction by the alternation of the manganite layers with another appropriate material. Following these theoretical findings, we synthesized such superlattices and verified our theoretical predictions.

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Ferromagnetic superlattices with very high T_c present obvious interest for electronic applications. This is the first step required to design and control magnetism in more elaborate structures. Perovskite manganese oxides of generic formula $A_{1-x}B_x\text{MnO}_3$ (A being a trivalent cation and B a divalent one) are metallic and ferromagnetic in the approximative range of doping values $0.17 < x < 0.5$ [1]. These properties are directly related to the $3d$ shell of the manganese atoms and can be easily explained by the double-exchange mechanism. The Curie temperature is thus directly related to the delocalization within the e_g orbitals of the $\text{Mn}^{3+}/\text{Mn}^{4+}$ ions [2], that is to the manganese ions orbital order. Finding a way to design such materials with the desired $3d$ orbital order would thus open the way to the design of artificial materials with the desired magnetic properties, and thus to novel magneto-electronic applications, including spin-valve devices or nonvolatile magnetic memory working far above room temperature.

The manganese e_g shell is doubly degenerated (in a regular octahedron environment), however only partly occupied. The Mn^{3+} ions are thus Jahn-Teller active, and small distortions of the oxygen octahedra can stabilize one of the e_g orbitals with respect to the other. If one could impose a specific geometry around the Mn ions (for instance using synthesis in thin films), it should thus be possible to choose, between the $d_{3z^2-r^2}$ and the $d_{x^2-y^2}$ orbitals, which one will be occupied and which one will be empty. If the $d_{3z^2-r^2}$ is occupied, the double exchange will take place essentially along the \vec{c} direction (see Fig. 1). On the contrary, if the $d_{x^2-y^2}$ is stabilized, the intralayer double exchange will be very strong and the interlayer one weak. In an essentially two-dimensional (2D) system such as thin films, only the in-plane interactions are important and the control of the orbital ordering should thus allow the control of magnetic exchange and of the associated Curie temperature, T_c . According to the above argument, the Curie temperature of 2D thin films will be maximized if one (i) stabilizes the $d_{x^2-y^2}$ orbital over the $d_{3z^2-r^2}$ and

(ii) maximizes the in-plane effective exchange integral between the $d_{x^2-y^2}$ orbitals, by preventing the tilt of the octahedra observed in the bulk [3]. Indeed, in the double-exchange mechanism, T_c scales as

$$T_c \sim J \sim t_{dp}^2 \sim S_{dp}^2 \quad (1)$$

(J : effective exchange between adjacent Mn ions, t_{dp} : $\text{Mn}d - \text{O}2p$ transfer integral and S_{dp} : overlap), and the octahedra tilt lowers the S_{dp} overlap between the Mn $d_{x^2-y^2}$ and the O $2p_\lambda$ bridging orbitals.

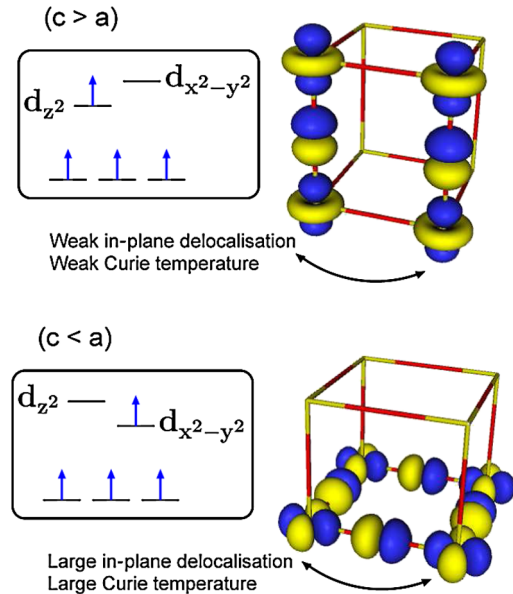


FIG. 1 (color online). Schematic representation of orbital ordering induced by cell distortions in a two-dimensional system. ($c > a$) The elongation in the \vec{c} direction favors the $d_{3z^2-r^2}$ orbital occupation and weak in-plane ferromagnetic coupling, the delocalization being essentially in the \vec{c} direction. ($c < a$) The contraction of the c parameter favors the $d_{x^2-y^2}$ orbital occupation, strong in-plane ferromagnetic coupling, and large Curie temperature.

$A_{1-x}B_x\text{MnO}_3$ thin films deposited on a cubic substrate with $a = b$ parameters slightly larger than the bulk magnetite value should thus ensure an increase of the magnetite in-plane parameters and, in order to approximately conserve the cell volume, a decrease of the c parameter. With $c/a < 1$ the $d_{x^2-y^2}$ orbital occupation and large T_c should be favored, as desired.

Several authors synthesized such systems as, for instance, $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ (LSMO) thin films deposited on the SrTiO_3 cubic substrate [4]. They found that for a small number of LSMO unit cells in the \vec{c} direction, the magnetization as well as the Curie temperature are strongly decreased compared to the 370 K bulk value [5]. From 12 deposited unit cells, however, the bulk behavior is approximately recovered with just a slight T_c reduction. It is clear that the expected behavior and thus orbital ordering is not realized in these films. In fact, the quick recovering of the bulk magnetic behavior tells us that the strains imposed by the substrate are essentially very quickly relaxed as a function of the film thickness. This is most probably the case for the octahedra tilt present in the LSMO bulk. One should thus find a way to maintain the desired strains (in-plane cell parameter elongation and quadratic symmetry) over the whole film. For this purpose one can think to alternate LSMO layers with layers of an adequate cubic material as in $[(\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3)_n(\text{BaTiO}_3)_p]_q$ superlattices. We thus explored this possibility using first principle calculations.

We studied, using periodic density functional theory [6], the $(\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3)_3(\text{BaTiO}_3)_3$ superlattice deposited on a lattice matched SrTiO_3 (001)-oriented substrate (see Fig. 2). Since the epitaxial films normally follow the structure of the perovskite substrate, we imposed to our system the substrate in-plane lattice constants, $a = b = 3.9056 \text{ \AA}$. The c parameter was optimized as well as atomic positions.

The superlattice is built from metallic LSMO layers and insulating BaTiO_3 (BTO) layers. It is thus of crucial im-

portance for the reliability of the results to be able to accurately position the LSMO Fermi level referring to the BTO gap. For this purpose we used hybrid functionals known to correctly reproduce insulating gaps, that is B3LYP [7] and the very recent B1WC [8], specifically designed to obtain the correct properties on ferroelectric materials such as BaTiO_3 . We used the CRYSTAL package [9] with the basis sets and effective core pseudopotentials (ECP) of Ref. [10]. Another important technical point is the treatment of the La/Sr disorder. Indeed, in periodic calculations it is not possible to properly mimic the ionic disorder. We thus made a whole set of calculations associated with the two extreme cases, that is with the Sr ions totally ordered (3 different positions) and with average La/Sr ions. These average ions were modeled either using ordered La/Sr ECPs but with averaged effective nuclear charges (3 possibilities) or by using only La ECPs with average effective charges. All seven different approximations of the ionic disorder were computed with the two functionals. All of them yielded equivalent results and physical properties (geometries with equivalent characteristics, equivalent density of states and atomic magnetic moments), even if one finds slight numerical differences. One set of numerical values (corresponding to B3LYP functional, ordered ECPs with the strontium in the middle layer and averaged charges) are presented as a matter of example.

Considering the fact that the LSMO layers are extended in the (\vec{a}, \vec{b}) directions compared to the bulk ($a = b = c = 3.87 \text{ \AA}$), our results (Fig. 2) are at first quite surprising. Indeed, the two LSMO layers at the interfaces with the BaTiO_3 are extended not only in the \vec{a} and \vec{b} directions, but also in the \vec{c} direction. It results in a strong extension of the associated subcell volume with, respectively, 66.57 \AA^3 —for the interface with a Ba-O layer—and 61.41 \AA^3 —for the interface with a Ti-O layer—to be compared with the bulk pseudocubic unit cell volume of 58.3 \AA^3 [3]. On the contrary, the central LSMO layer is strongly contracted in the \vec{c} direction resulting in a reduction of the associated subcell volume (56.87 \AA^3). One sees immediately that for the interface layers the $c'/a > 1$ anisotropy strongly favors the stabilization of the $d_{3z^2-r^2}$ orbital. This stabilization is indeed associated in our calculations with a larger occupation of the $d_{3z^2-r^2}$ orbital compared to the $d_{x^2-y^2}$ one. The anisotropy is reversed for the central layer ($c'/a < 1$), the $d_{x^2-y^2}$ orbital is stabilized and presents a larger occupation number. The magnetism is essentially two dimensional, supported by the Mn ions (with $3.467\mu_B$ for the atomic spin Mulliken population of the Mn atoms belonging to the interface with a Ba-O layer, $3.541\mu_B$ for the Mn atoms belonging to the interfacial layer, $3.886\mu_B$ for the Mn atoms belonging to the interface with a Ti-O layer). The BaTiO_3 layers remain essentially nonmagnetic. We can thus predict two magnetic behaviors in these superlattices. The first one is related to the inter-

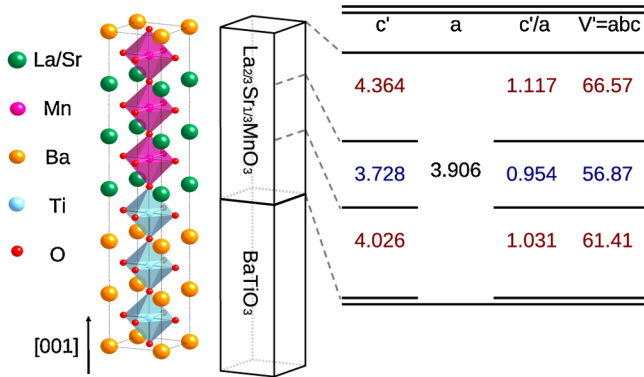


FIG. 2 (color online). Schematic representation of the superlattice and calculated interplanar distances c' and associated subcell volumes V' for the LSMO layer (Å).

facial layers and is associated with a weak in-plane double exchange and thus a weak Curie's temperature (T_{c1}). The second one is related to the central layers and is associated with a strong in-plane double exchange and thus a strong Curie's temperature (T_{c2}). One can thus predict three different phases, the first one at very low temperature with all three LSMO layers participating to the magnetization, the second one at larger temperature with only the central layer participating to the magnetism, and finally, at high temperature, the paramagnetic phase.

In an attempt to estimate the order of magnitude of T_{c1}/T_{c2} , one can estimate the double-exchange magnetic coupling. Whereas in bulk manganites the double exchange is not always sufficient to explain the physics, and polaron formation should be considered [11], in fully strained films such as the present one we do not expect such relaxation mechanism to take place. The double-exchange integral is directly proportional to the delocalization between adjacent magnetic ions and thus to the square of the overlap integral between the magnetic $3d$ orbital and the ligand $2p$ bridging orbital. The $T_{c1}/T_{c2} \approx |\langle \text{Mnd}_{3z^2-r^2} | \text{O}2p_x \rangle \langle \text{Mnd}_{x^2-y^2} | \text{O}2p_x \rangle|^2$ integral ratio can thus be analytically evaluated if the orbitals are assumed to be the product of a Gaussian radial part and the appropriate spherical harmonic. The distances between the atoms are taken from our calculations. The result can be undervalued by $\{\sqrt{3}[1 + \langle r_{2p}^2(\text{O}^{2-}) \rangle / \langle r_{3d}^2(\text{Mn}^{3+}) \rangle]^2\}^2$ which in turn can be undervalued by $1/(2^2\sqrt{3})^2 = 1/48$. Of course, this is a calculation using crude approximations; however, it tells us that there is more than an order of magnitude between T_{c1} and T_{c2} .

Another important result is that the BaTiO_3 triple layer does not preserve its insulating character but exhibit a weak, however non-null, density of states at the Fermi level in the dominant LSMO spin orientation. This electronic delocalization through the BaTiO_3 triple layer ensures the ferromagnetic coupling between the different LSMO layers by what we could call a long-range double-exchange mechanism.

As a conclusion, first principles calculations predict for the superlattice (i) two different ferromagnetic phases, associated with two Curie temperatures differing by nearly 2 orders of magnitude, (ii) an optimized high Curie temperature expected to be larger than the bulk one (no octahedra tilt).

We thus synthesized $(\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3)_3(\text{BaTiO}_3)_3$ superlattices using laser-MBE deposition [12] on a [001]-oriented SrTiO_3 substrate. We also synthesized similar superlattices using the isoelectronic calcium manganite: $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ (LCMO). Indeed, one can expect in the LCMO superlattice similar orbital ordering effects, for similar reasons, as predicted in the strontium one.

The pulsed laser deposition was performed in low pressure (5×10^{-4} mbar) to enable control of the growth using the reflexion high energy electron diffraction (RHEED).

While the growth of the structures was carried out in low ozone content (0.1% volume), to promote a maximum oxidation of the superlattice without favoring a strong diffusion between the different layers, the structures were rapidly cooled in high ozone concentration (7% volume). The deposition of each material, namely, BTO and LSMO or LCMO, was measured and calibrated by growing them independently under the same conditions (620 °C, pressure 5×10^{-4} mbar, ozone concentration 0.1% volume) using an *in situ* RHEED control for a precise control of the growth of each layer. Figure 3 shows two RHEED patterns, taken along the [110] azimuth of the substrate. These two pictures evidence a streaky diffraction pattern in agreement with a 2D growth of the superlattice.

The comparison between the two patterns taken at the end of the deposition (a) and at the end of the cooling (b) evidences two features. First, there is no drastic modification of the pattern after the cooling process. Second, the in-plane structure of the superlattice exhibits the same lattice parameters as the SrTiO_3 substrate and thus can be described in a perovskitelike subcell. The (b) pattern also presents Kikuchi lines indicating the high quality of the deposited film. These lines are not observed in pattern (a), due to the important scattering of the electrons at the deposition pressure.

To achieve a better structural characterization of the superlattices, an x-ray diffraction study was carried out using a four-circle diffractometer. Two different set of reflections were studied: the out-of-plane reflections and the so-called asymmetric reflections. From the first set of reflections, the value of the out-of-plane lattice parameter could be calculated for the $[(\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3)_3 \times (\text{BaTiO}_3)_3]_{25}$ superlattice. We measured an out-of-plane lattice parameter of 24.281 Å, corresponding almost (1%) to the value determined from the theoretical calculations (24.519 Å). This value is larger than the expected value, calculated from the average out-of-plane parameters of films of the two starting materials. A Williamson-Hall analysis carried out on the [001] reflections shows that the coherence length of the diffraction along that direction

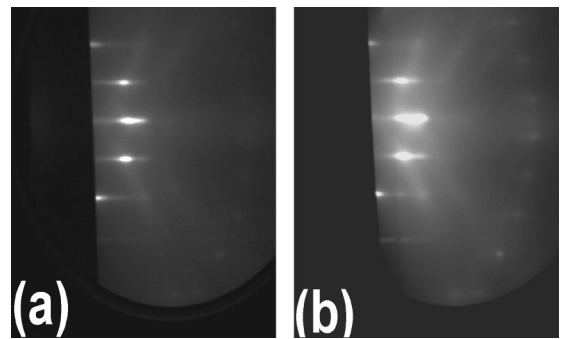


FIG. 3. RHEED patterns for the BTO/LSMO superlattice along the [110] azimuth of the SrTiO_3 substrate. (a) 620 °C, 5×10^{-4} mbar ($\text{O}_2 + \text{O}_3$). (b) 120 °C, 5×10^{-7} mbar.

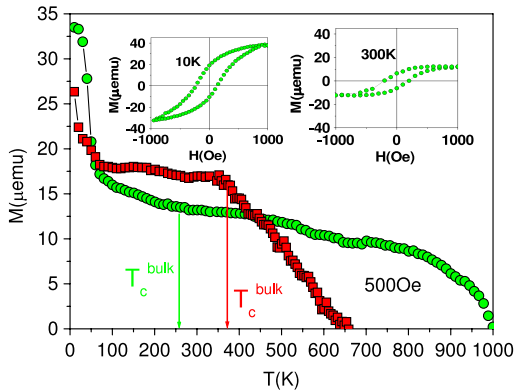


FIG. 4 (color online). Magnetization (500 Oersteds) for the $[(\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3)_3(\text{BaTiO}_3)_3]_{25}$ (red squares) and $[(\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3)_4(\text{BaTiO}_3)_4]_{20}$ (green circles) superlattices. Hysteresis loops of the calcium superlattice, recorded at 10 and 300 K, are presented in the insets. The arrows mark the bulk Curie temperatures. The surface of both samples is 16 mm^2 .

corresponds to 600 \AA , that is the thickness of the deposited film. The same analysis carried out on asymmetrical reflections ($[011]$, $[022]$, ...) indicates that the in-plane lattice parameter is 3.9048 \AA , in agreement with the substrate lattice parameter, and that the coherence length of the diffraction along an in-plane direction is 1000 \AA , in agreement with the size of the terraces observed on the SrTiO_3 substrates.

The magnetic measurements (Fig. 4), carried out in the temperature range 4–1000 K, evidence two ferromagnetic phases, as predicted. The first one at low temperature and the second for $T_{c1} < T < T_{c2}$. The low Curie temperature, expected to correspond to the two interfacial manganite layers, is about $T_{c1} \approx 25 \text{ K}$ for the LSMO superlattice and $T_{c1} \approx 50 \text{ K}$ for the LCMO one. The high Curie temperature, expected to correspond to the central manganite layer, is about 1000 K for the LCMO system and about 650 K for the LSMO one, that is far above both T_{c1} and the bulk Curie temperatures, as predicted by theoretical calculations. Indeed, the Curie temperature of LSMO bulk [5] or thin films [13] is 370 K and in the range 250–260 K for LCMO bulk [1,14] and thin films [15]. The two insets of Fig. 4 show that magnetic loops can be registered both at 10 and 300 K, proving true ferromagnetic phases.

In summary, we showed that it is possible to increase the Curie temperature of a manganite ferromagnetic thin film far above the bulk Curie temperature, by the control of orbital ordering. The key idea to reach this result is that the strains applied by the substrate are not sufficient by themselves and that they must be maintained using the regular intercalation of adequate layers. Our findings open new opportunities for the design and control of magnetism in artificial structures and pave the way to novel magneto-

electronic applications, including nonvolatile magnetic memory working far above room temperature.

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- [1] A. Urushibara, Y. Moritomo, T. Arima, A. Asamitsu, G. Kido, and Y. Tokura, *Phys. Rev. B* **51**, 14 103 (1995); P. Schiffer, A. P. Ramirez, W. Bao, and S.-W. Cheong, *Phys. Rev. Lett.* **75**, 3336 (1995).
- [2] J. B. Goodenough, *Magnetism and Chemical Bond* (Wiley, New York, 1963).
- [3] G. Venkataiah, V. Prasad, and P. Venugopal Reddy, *J. Alloys Compd.* **429**, 1 (2007).
- [4] M. Huijben, L. W. Martin, Y.-H. Chu, M. B. Holcomb, P. Yu, G. Rijnders, D. H. A. Blank, and R. Ramesh, *Phys. Rev. B* **78**, 094413 (2008).
- [5] A. Urushibara, Y. Moritomo, T. Arima, A. Asamitsu, G. Kido, and Y. Tokura, *Phys. Rev. B* **51**, 14 103 (1995).
- [6] P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964); W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965).
- [7] A. D. Becke, *J. Chem. Phys.* **98**, 5648 (1993); J. Muscat, A. Wander, and N. M. Harrison, *Chem. Phys. Lett.* **342**, 397 (2001).
- [8] D. I. Bilc, R. Orlando, R. Shaltaf, G. M. Rignanese, J. Iniguez, and Ph. Ghosez, *Phys. Rev. B* **77**, 165107 (2008).
- [9] R. Dovesi *et al.*, *CRYSTAL06 User's Manual* (University of Torino, Torino, 2006).
- [10] Relativistic ECPs and associated basis sets are from the Stuttgart/Cologne Group (www.theochem.uni-stuttgart.de/pseudopotentials) and references therein). The basis sets have been reduced to 3ζ quality and exponents larger than 0.8 for Ti, O, and La, and larger than 0.11 for Ba and Mn. The precise ECPs are Ti^{4+} and $\text{Mn}^{3+\delta}$: ECP10MDF, Ba^{2+} : ECP46MDF, O^{2-} : ECP2SDF, La^{3+} : ECP46MWB.
- [11] See, for instance: M. Quijada, J. Cerne, J. R. Simpson, H. D. Drew, K. H. Ahn, A. J. Millis, R. Shreekala, R. Ramesh, M. Rajeswari, and T. Venkatesan, *Phys. Rev. B* **58**, 16 093 (1998).
- [12] B. Mercey, P. A. Salvador, W. Prellier, T.-D. Doan, J. Wolfman, J. F. Hamet, M. Hervieu, and B. Raveau, *J. Mater. Chem.* **9**, 233 (1999).
- [13] H. L. Ju, C. Kwon, Qi Li, R. L. Greene, and T. Venkatesana, *Appl. Phys. Lett.* **65**, 2108 (1994).
- [14] E. O. Wollan and W. C. Koehler, *Phys. Rev.* **100**, 545 (1955).
- [15] S. Jin, Th. Tiefel, M. MacCormack, R. A. Fastnacht, R. Ramesh, and Lh. Chen, *Science* **264**, 413 (1994).