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Progress in Physics (59)

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Investigating oxide heterostructures: Towards new materials with tailored electronic properties

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In this short paper, we review some of the efforts carried out in Geneva in the group of Prof. Jean-Marc Triscone on the realization and studies of oxide films and heterostructures. This research area is rapidly progressing on a worldwide scale with strong activities in Switzerland – for instance at ETH, EPFL, the Universities of Fribourg and Zürich and at PSI. It is not the goal here to give a comprehensive view of the efforts pursued in Switzerland or throughout the world, but rather to spark the reader's interest in this fascinating field of research.

Oxide materials

Oxides belong to a large family of chemical compounds sharing the common feature of having at least one oxygen atom. They can have different structures, from simple individual molecules to more complex polymeric and crystalline structures (bixbyite, corundum, fluorite, garnet, perovskite, pyrochlore, scheelite, spinel, wolframite, wurtzite, zircon and many others). We will focus here on perovskites.

One of the fascinations for oxide materials is that they display a wide range of electronic properties providing a plethora of possible functionalities that can be useful for applications. Ferroelectricity, high-temperature superconductivity, multiferroicity, piezoelectricity, thermoelectricity are exciting properties that can be used in many areas, including spintronics, transparent electronics, and photonics or energy harvesting, to name but a few. Oxide materials already display a broad spectrum of properties in bulk. Once in the nanoscale form and combined with other materials, further

new intriguing phenomena appear. Devices incorporating oxides are already widely found in our standard electronic equipment.

Among oxide materials, perovskites (see inset of Figure 1), with their simple ABO_3 formula, are a unique class of compounds due to their simple crystal structure and to their flexibility: changing the A and B cations modifies the properties of the system without substantially changing the crystal structure. This allows such perovskites to be combined in perfect epitaxial heterostructures, as schematically represented in Figure 1 – just like children building with Lego® blocks – creating new functional materials with tailored electronic properties. The properties of such heterostructures can be further tuned by modulating strain, doping, stoichiometry or oxygen octahedral rotations.

Nowadays, these exciting materials are in the spotlight of many theoretical and experimental research groups worldwide. With the recent advances in deposition techniques, artificial materials can be produced with atomic-scale control

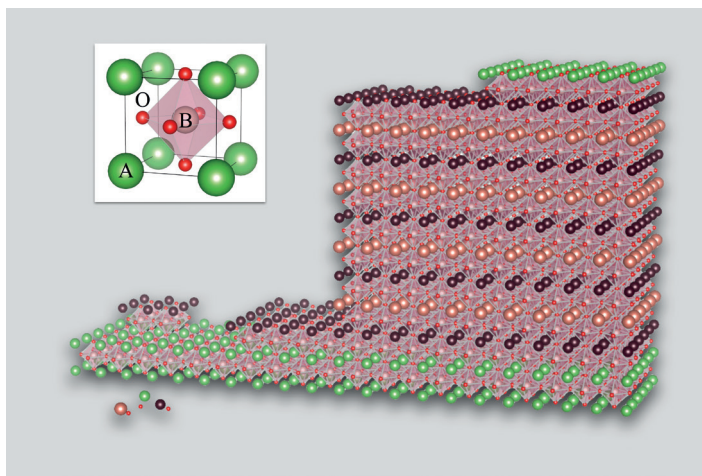


Figure 1. Schematic representation¹ of a heterostructure combining different perovskite materials with a perfect crystallographic alignment, a precision attained today with different growth techniques. The inset shows the simple perovskite structure ABO_3 , with the B-cation at the center, surrounded by an oxygen-octahedron, and with the A-cation at the corners of the unit-cell.

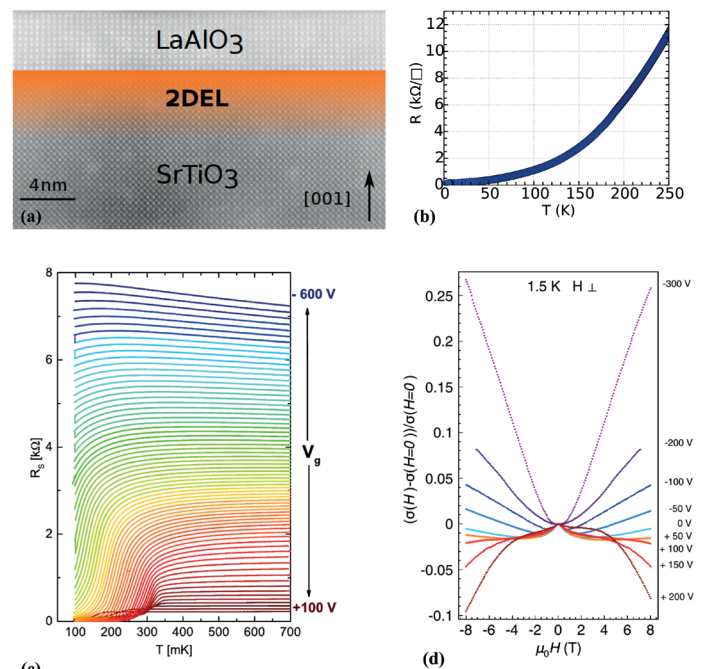


Figure 2. In this figure are summarized the main properties of the electron system confined at the interface between $LaAlO_3$ and $SrTiO_3$. (a) TEM image of the heterostructure, with the region where the electrons are confined highlighted in orange. (b) Sheet resistance of a standard interface as a function of temperature. (c) Sheet resistance between 100 and 700 mK for different gate voltages: by moving from a positive to a negative gate voltage, the system evolves from a superconducting to an insulating state [S. Gariglio, M. Gabay and J.-M. Triscone, *APL Materials* 4, 060701 (2016)]. (d) Effect of the gating on the magnetoresistance of the 2DEL at 1.5 K. A transition from a weak-localization to a weak-antilocalization regime is observed as a function of doping [A. D. Caviglia et al., *Phys. Rev. Lett.* 104, 126803 (2010)].

¹ Drawn using VESTA [K. Momma and F. Izumi, *J. Appl. Crystallogr.*, 44, 1272-1276 (2011).]

- as demonstrated with the transmission electron microscopy (TEM) image shown in Figure 2 (a) - using various epitaxial growth techniques, such as molecular beam epitaxy, pulsed laser deposition and sputtering. Here we focus on heterostructures based on perovskite materials grown and investigated in Geneva: $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces and vanadates grown by pulsed laser deposition, and ferroelectrics and nickelates grown by sputtering.

Conducting oxide interfaces

At the frontier between two complex oxide materials, new physics can emerge. A remarkable example is the interface between the two insulating oxides LaAlO_3 and SrTiO_3 (Figure 2). Between these two good insulators, a two-dimensional electron liquid (2DEL) forms when a thin layer of LaAlO_3 is epitaxially grown on a SrTiO_3 substrate. The metallic conduction at the interface between these two excellent band insulators was discovered by Ohtomo and Hwang [A. Ohtomo and H. Y. Hwang, *Nature* 427, 423 (2004)] and triggered intensive research activities around the globe. In collaboration with the group of Prof. Mannhart (MPI Stuttgart), it was found in Geneva, in 2007, that this interface is not only conducting but also superconducting [N. Reyren *et al.*, *Science* 317, 1196 (2007)]. Among its spectacular electronic properties, the 2DEL displays a large Rashba type spin-orbit coupling. The superconducting T_c and the spin-orbit coupling strength can be tuned by an electric field in a unique way allowing, for instance, superconductivity to be switched on and off [A. D. Caviglia *et al.*, *Nature* 456, 624 (2008)]. High magnetic field studies of high mobility samples reveal complex Shubnikov-de Haas quantum oscillations of the resistance.

Currently, the superconducting state is attracting considerable interest with open questions on the pairing mechanism itself, the possible role of spin-orbit coupling and its impact on the symmetry of the superconducting order parameter.

Related publications can be found directly on our website at: <http://dqmp.unige.ch/triscone/research.php?topic=conductingoxides>

Nanoscale ferroelectrics

Perovskites also display exciting properties while remaining entirely insulating. Here we very briefly discuss some of the properties of ferroelectric films and structures.

Ferroelectrics are insulating materials characterized by a spontaneous polarization that can be reversed by the application of an electric field (Figure 3 (a,b)). Regions of different polarization orientations are called domains. These domains and their domain walls – the boundaries between different domains – deeply affect the sample properties. Domain walls by themselves are also the focus of current intensive research, boosted by the discovery of their room temperature electrical conductivity in BiFeO_3 [J. Seidel *et al.*, *Nat. Mater.* 8, 229 (2009)], making them interesting for nanoscale applications.

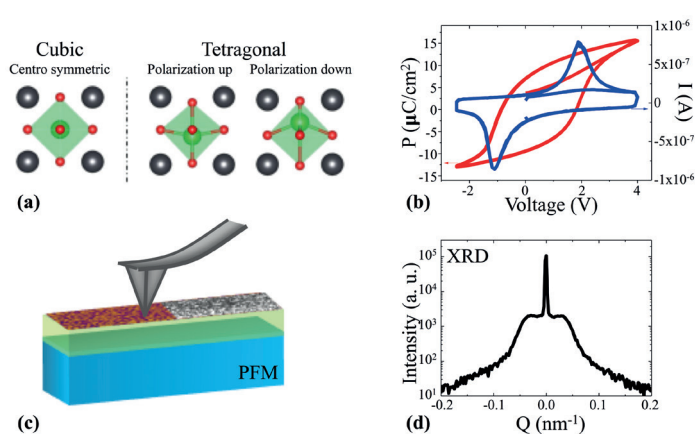


Figure 3. Ferroelectrics are insulating materials characterized by a spontaneous polarization that can be reversed by the application of an electric field. (a) In the perovskite structure, the polarization is related to a displacement of the O-octahedron and the B-cation with respect to the A-atom cage. (b) The application of a voltage results in the well-known P-V loop (in red), obtained by measuring the switching current (in blue). Domains of opposite polarizations can be observed by PFM (c) or XRD (d), but can be observed simultaneously using both techniques only in very specific cases, as discussed in the text (here: PST thin film with $x = 0.8$ and thickness = 42 nm).

In ferroelectric ultrathin films, the properties are to a large degree affected by the electrical boundary conditions [C. Lichtensteiger *et al.*, Ch. 12 in *Oxide Ultrathin Films, Science and Technology*, Wiley (2011)]. In collaboration with the group of Prof. Paruch (University of Geneva), we found that the polarization orientation, stability and domain formation in PbTiO_3 ultrathin epitaxial films can be controlled by choosing the correct electrodes and by tuning their effectiveness via the insertion of spacer layers of varying thicknesses [C. Lichtensteiger *et al.*, *NanoLetters* 14, 42025 (2014), C. Lichtensteiger *et al.*, *New Journal of Physics* 18 043030 (2016)].

By combining PbTiO_3 and SrTiO_3 , we revealed an interesting type of ferroelectricity for very short wavelength superlattices (i.e. with a few unit cells of PbTiO_3 and SrTiO_3). With theoretical support of Prof. Ghosez and his group (University of Liège), it has been shown that this phenomenon is linked to a very particular coupling of different structural instabilities at the interface between the two materials [M. Dawber *et al.*, *Phys. Rev. Lett.* 95, 177601 (2005), E. Bousquet *et al.*, *Nature* 452, 732 (2008)]. This new behavior leads to unusual properties including a very high, temperature-independent dielectric constant, which may be of interest for applications. The coupling of instabilities is one of the paths that is explored today to develop new multiferroic materials – materials that are both ferroelectric and ferromagnetic.

In another series of superlattices composed of PbTiO_3 and SrTiO_3 layers, 180° ferroelectric domains were observed using X-Ray Diffraction (XRD) [P. Zubko *et al.*, *Phys. Rev. Lett.* 104, 187601 (2010); P. Zubko *et al.*, *NanoLetters* 12, 2846 (2012)]. But the small domain size made it challenging to image them by piezo-force microscopy (PFM): it is only within a narrow range of domain sizes that both techniques can be suitable. By incorporating PbTiO_3 and SrTiO_3 into a solid solution of chemical formula $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$ (PST) in thin film form, we found a regime in which the 180° domains had the ideal size allowing their investigation both with x-ray diffrac-

tion (XRD) and PFM to be performed, as shown in Figure 3 (c,d) [S. Fernandez-Pena *et al.*, APL Materials 4, 086105 (2016)]. These PST samples allowed us also to shed light on the effect of domain walls on the sample properties. A clear increase in the dielectric susceptibility for samples with larger domain wall concentrations was observed, which may prove important for possible future applications involving high domain wall density ferroelectric thin films.

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Nickelates

The rare earth nickelates are another fascinating family of oxides with formula $RNiO_3$, R = rare earth. These materials have attracted interest in the oxide community for many years because of their sharp metal to insulator transition (MIT). Indeed, as the temperature is decreased, $RNiO_3$ materials display a bandwidth-controlled MIT and a unique ground state, characterized by a breathing distortion of the NiO_6 units and an uncommon antiferromagnetic order (Figure 4 (a)).

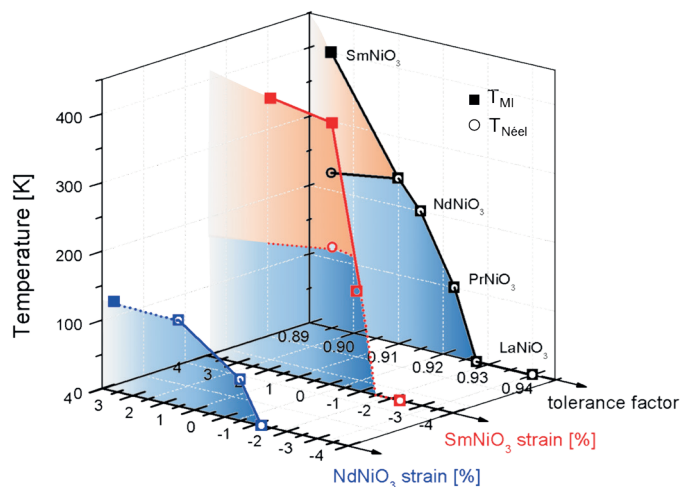
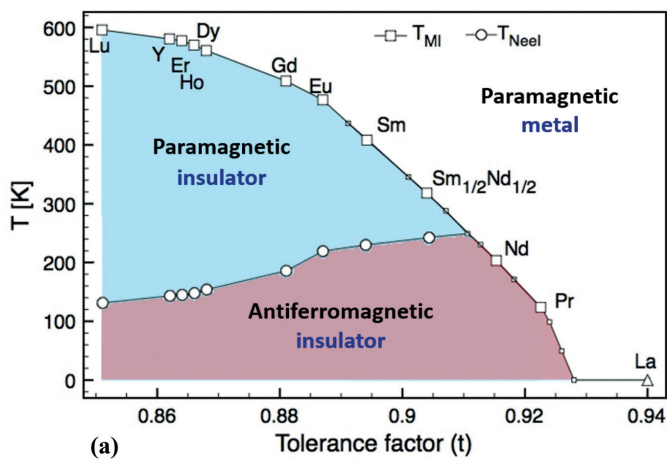


Figure 4. (a) Phase diagram of the nickelate family showing the different MIT and Néel transition temperatures for different rare earth ions. (b) Studying $NdNiO_3$ and $SmNiO_3$ thin films grown on different substrates, we were able to demonstrate that epitaxial strain is as efficient as steric effects to control the MIT and Néel transition temperatures in nickelates

Due to the lack of reasonably sized single crystals, high quality thin films are a unique playground for the study of the nickelates. In Geneva, high quality nickelate thin films and superlattices are grown by radio frequency off-axis magnetron sputtering.

In the past years, we achieved control of the MIT and magnetic properties of $SmNiO_3$ and $NdNiO_3$ through a variety of approaches, using strain, confinement, light excitation, electric field effect or heterostructuring (Figure 4(b)) [see for instance R. Scherwitzl *et al.*, Advanced Materials 22, 5517 (2010), S. Catalano *et al.*, APL Materials 2, 116110 (2014).] Currently, we are studying the role of the growth direction and substrate symmetry on the $NdNiO_3$ properties, focusing on the special clamping conditions provided by $(111)_{pc}$ oriented interfaces [S. Catalano *et al.*, APL Materials 3, 062506 (2015)].

$LaNiO_3$ is the only nickelate that has no MIT and remains paramagnetic at all temperatures in bulk. However, we showed that a transition to an insulating state occurs in $LaNiO_3$ thin films as its thickness is reduced to few unit cells. [R. Scherwitzl *et al.*, Appl. Phys. Lett. 95, 222114 (2009); Phys. Rev. Lett. 106, 246403 (2011)]. Interestingly, for films of 6-11 u.c. thick there is an enhancement of conductivity resulting from the existence of three local structures within the thin films, as revealed by TEM analysis and density functional theory calculations [J. Fowlie *et al.*, Adv. Mater. 29, 1605197 (2017)]. Antiferromagnetism is also stabilized in the ultrathin insulating $LaNiO_3$ layers when grown along the $[111]$ -direction in $LaNiO_3/LaMnO_3$ superlattices [M. Gibert *et al.*, Nat. Mater. 11, 195 (2012); Nat. Commun. 7, 11227 (2016)].

Related publications can be found directly on our website at: <http://dqmp.unige.ch/triscone/research.php?topic=nickelates>

Vanadate superlattices

Finally, let us mention the vanadates AVO_3 , a family of compounds that are metallic or insulating depending on the valence of the A-cation chosen. For example, $SrVO_3$ is a d^1 correlated metal (Sr is 2^+), while $LaVO_3$ is a d^2 Mott insulator (La is 3^+), both of which are being studied in this group.

In $SrVO_3$, studies of electronic transport versus strain and thickness are pursued.

For heterostructures of 3^+ insulating vanadates, ab-initio calculations predict a novel improper ferroelectric ground state coupled to a magnetic structure that should be generated in well-defined superlattices. This effect, linked to an interaction between rotational and anti-polar instabilities, could lead to the observation of a new class of multiferroic compounds with large magnetoelectric coupling.

Related publications can be found directly on our website at: <http://dqmp.unige.ch/triscone/research.php?topic=vanadates>

Frontiers in Quantum Materials Control

Last but not least, October 2013 marked the start of the ERC Synergy Grant research project “Frontiers in Quantum Materials’ Control” (Q-MAC).

This project is a collaboration between the groups of Andrea Cavalleri (Max Planck Institute in Hamburg), Dieter Jaksch (University of Oxford), Antoine Georges (École Polytechnique near Paris/University of Geneva) and this group.

The project combines sophisticated ab-initio approaches, advanced oxide growth techniques allowing artificial materials to be grown layer-by-layer, and state of the art ultrafast laser experiments to explore different ideas to design new superconductors and to tune or improve the properties of superconducting materials on short lengthscales.

As examples, we are investigating methods to both induce and stabilize superconductivity by modifying the atomic structure of a system in particular ways through shining highly controlled laser light on the sample.

More information can be found at:

<http://dqmp.unige.ch/triscone/research.php?topic=q-mac>

Conclusion

Oxides are very promising compounds to design new materials with tailored electronic properties. They display exciting behavior on their own, and when combined in heterostructures their physics is even richer. The very new and exciting field of “interface engineering” brings the scientists to the frontier between fundamental science and possible novel applications. The few examples described in this short article, together with recent developments worldwide, suggest that novel electronic properties can be found at oxide interfaces. In addition to the desire to understand the intriguing fundamental physics of these systems, the technological potential is large and is a strong motivation for further research that will undoubtedly continue to be actively pursued in the next years with many opportunities for young researchers. The possibilities offered by combining two or more oxide materials seem endless – the main limitation currently being our imagination!

Acknowledgements

The author would like to thank everyone in the group, and especially Margherita Boselli, Sara Catalano, Stéphanie



Fernandez, Elias Ferreiro, Jennifer Fowlie, Stefano Gariglio, Marta Gibert, Hugo Meley and Jean-Marc Triscone for their valuable contribution in the preparation of this article and for their nice illustrations.

Collaborations

A few collaborations were cited directly in the text. Below is a more complete list of the present on-going collaborations throughout Switzerland and worldwide.

IN SWITZERLAND: Felix Baumberger, Antoine Georges (also from Collège de France/École Polytechnique), Thierry Giamarchi, Alberto Morpurgo, Patrycja Paruch, Christoph Renner and Dirk van der Marel from the University of Geneva; Cinthia Piamonteze, Thorsten Schmitt, and Phil Willmott from the Paul Scherrer Institut; Philipp Aebi and Christian Bernhard from the University of Fribourg; Hans-Josef Hug from EMPA; Ulrich Aschauer from the University of Bern.

IN FRANCE: Marc Gabay and Odile Stéphan from the University Paris Sud; Michel Viret from Iramis-Saclay; Nicolas Jaouen from SOLEIL.

IN ITALY: Marco Saluzzo and Daniela Stornaiuolo from the Università degli Studi di Napoli Federico II; Daniele Marré from the University of Genoa.

IN BELGIUM: Philippe Ghosez from the University of Liège.

IN LUXEMBOURG: Jorge Iniguez and Jens Kreisel from the Luxembourg Institute of Science and Technology.

IN GERMANY: Andrea Cavalleri from the Max Planck Institute in Hamburg; Jochen Mannhart and Bernhard Keimer from MPI Stuttgart.

IN THE NETHERLANDS: Andrea Caviglia from the Delft University of Technology.

IN THE UK: Dieter Jaksch at the University of Oxford; Pavlo Zubko from the University College London.

IN AUSTRALIA: Nagarajan Valanoor from the University of New South Wales.

IN CANADA: George Sawatzky from the University of British Columbia.

Reviews

The interested reader might find more information on oxide heterostructures and interfaces in the following reviews:

M. Lorenz et al., The 2016 Oxide Electronic Materials and Oxide Interfaces Roadmap, *J. Phys. D: Appl. Phys.* **49**, 433001 (2016)

J. Mannhart, and D. G. Schlom, Oxide Interfaces – An Opportunity for Electronics, *Science* **327**, 1607 (2010)

P. Zubko, S. Gariglio, M. Gabay, P. Ghosez, and J.-M. Triscone, Interface Physics in Complex Oxide Heterostructures, *Annu. Rev. Condens. Matter Phys.* **2**, 141 (2011)

H. Y. Hwang, Y. Iwasa, M. Kawasaki, B. Keimer, N. Nagao, and Y. Tokura, Emergent Phenomena at Oxide Interfaces, *Nature Materials* **11**, 103 (2012)