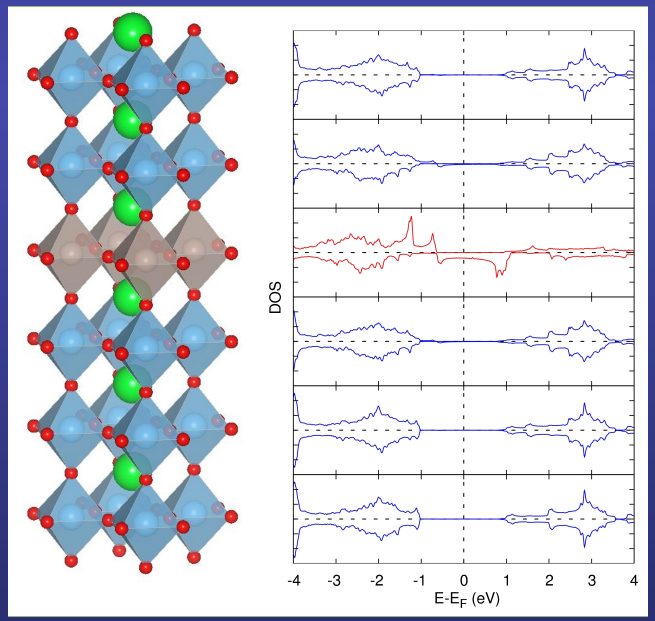
First-principles modeling of titanate/ruthenate superlattices

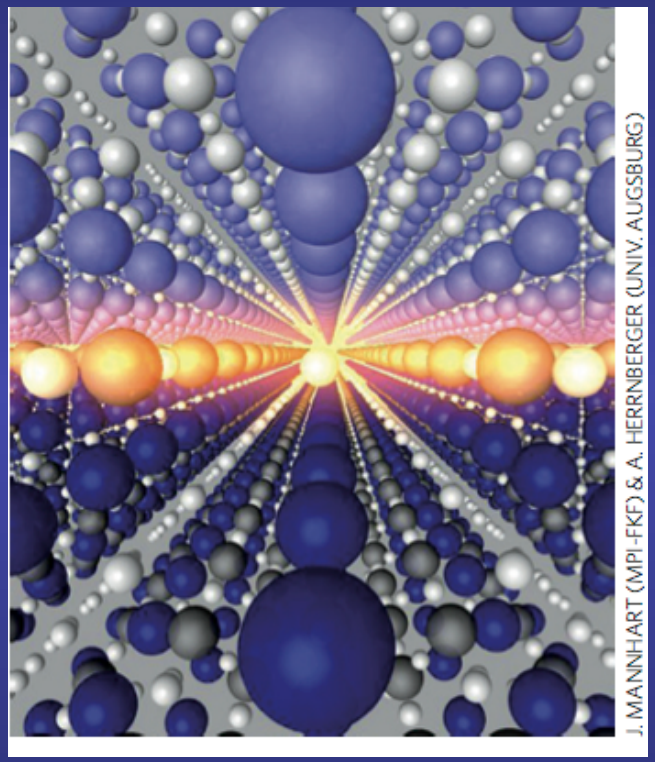
Highly confined spin-polarized two-dimensional electron gas in $SrTiO_3/SrRuO_3$ superlattices



Javier Junquera

UC
UNIVERSIDAD DE CANTABRIA

The interface is still the device

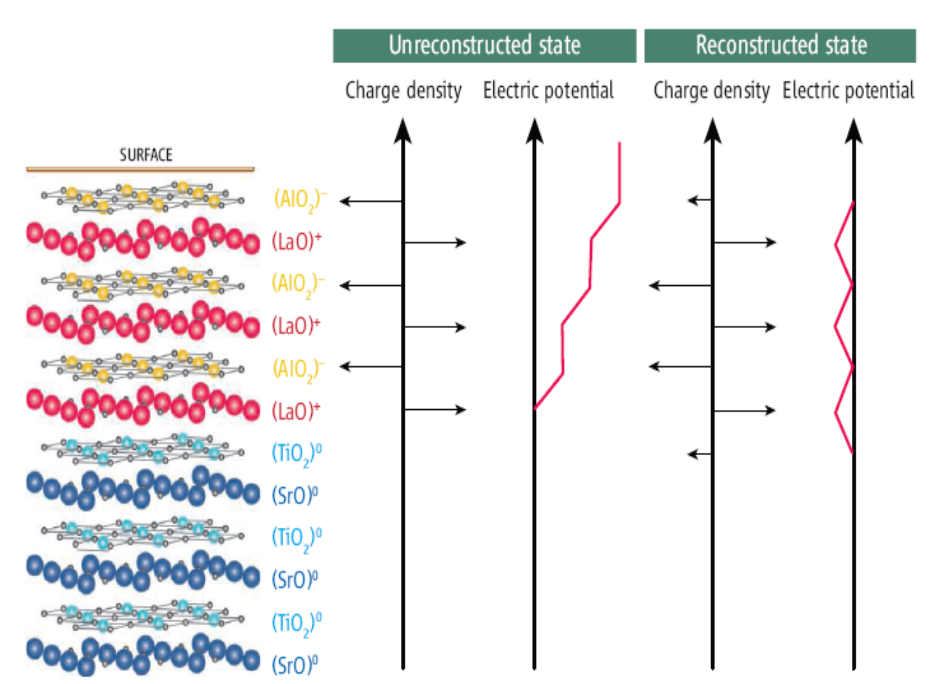


Editorial, Nature Materials 11, 91 (2012)

Some surprises at the interfaces between two oxides

The pristine interface between two good insulators (for instance, $LaAlO_3$ and $SrTiO_3$) is metallic

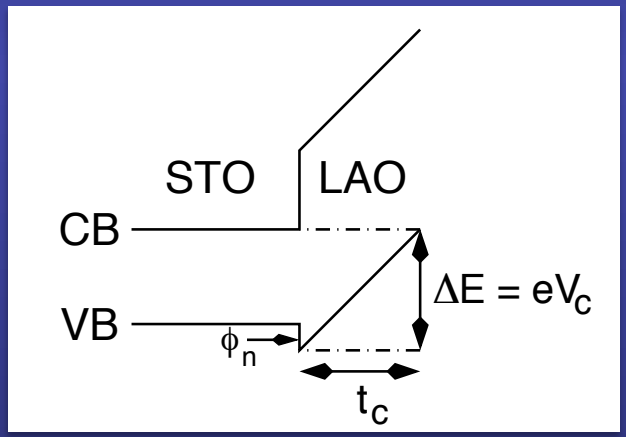
A. Ohtomo and H. Y. Hwang, Nature 427, 423 (2004)



A. Ohtomo and H. Y. Hwang, Nature, 427, 423 (2004)

H. Y. Hwang, Science, 313, 1895 (2006)

Polar catastrophe and Zener breakdown

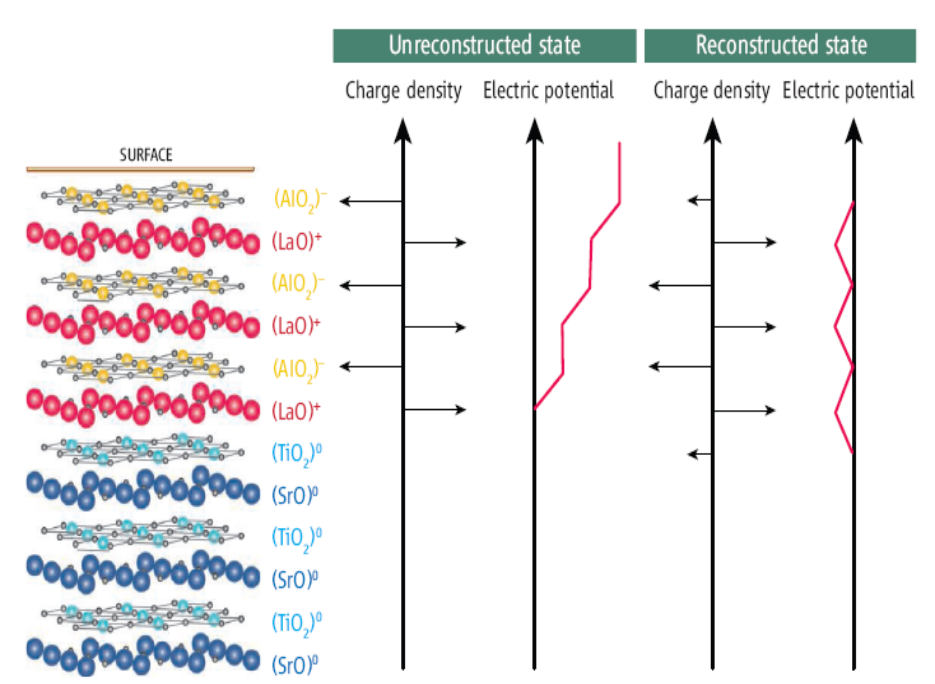


M. L. Reinle-Schmidt *et al.*, Nature Communications 3, 932 (2012)

Some surprises at the interfaces between two oxides

The pristine interface between two good insulators (for instance, $LaAlO_3$ and $SrTiO_3$) is metallic

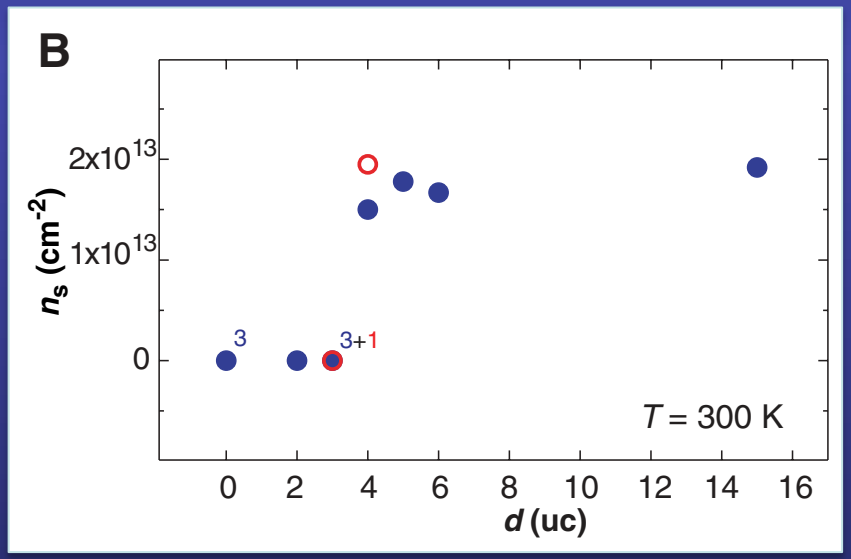
A. Ohtomo and H. Y. Hwang, Nature 427, 423 (2004)



A. Ohtomo and H. Y. Hwang, Nature, 427, 423 (2004)

H. Y. Hwang, Science, 313, 1895 (2006)

Existence of a critical number of layers of $LaAlO_3$ for the formation of the 2-DEG



S. Thiel *et al.*, Science, 313, 1942 (2006)

Two-dimensional electron gases at the interface between oxides opens the door to oxide electronics

REVIEW

Oxide Interfaces—An Opportunity for Electronics

J. Mannhart[1]* and D. G. Schlom[2]*

Science 327, 1607 (2010)

Oxide Nanoelectronics on Demand

Cheng Cen,[1] Stefan Thiel,[2] Jochen Mannhart,[2] Jeremy Levy[1]*

Science 323, 1026 (2009)

- Controversial origin (intrinsic polar catastrophe versus extrinsic origin)
- Localization and extension in the $SrTiO_3$ layer (electron gas localized on Ti)
- Dependence of the properties on the growth conditions
- Coupling with other functional properties (magnetism, superconductivity)

Two questions addressed in this talk

Question: Are there alternative mechanisms to generate two dimensional electron gases with new intrinsic functional properties?

If so, what are they useful for?

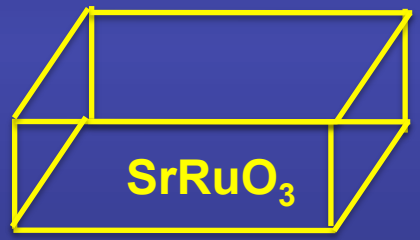
New alternative: take a metal embedded in an insulating matrix and reduce its thickness

1. Take a metallic oxide thin film ($SrRuO_3$)

REVIEWS OF MODERN PHYSICS, VOLUME 84, JANUARY–MARCH 2012

Structure, physical properties, and applications of $SrRuO_3$ thin films

G. Koster *et al.*



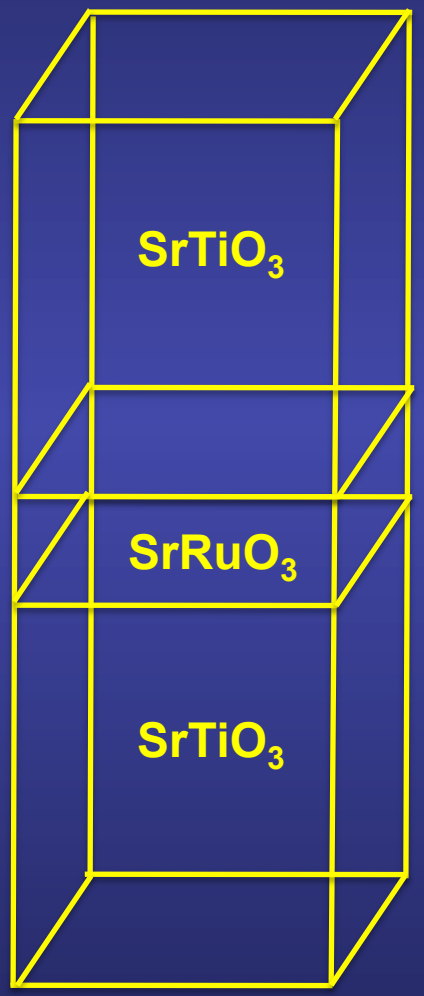
New alternative: take a metal embedded in an insulating matrix and reduce its thickness

1. Take a metallic oxide ($SrRuO_3$)

- In bulk, a correlated metal ferromagnet, T_C = 160 K
- It can be easily epitaxially grown on $SrTiO_3$
- It is frequently used as electrode in capacitors

2. Embeed it in an insulating matrix

3. Reduce the thickness of the metallic layer as much as possible



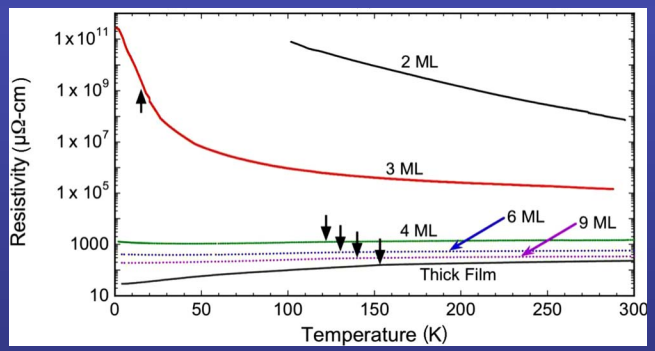
Not trivial question: there might be a critical thickness for metalic and magnetic properties

RAPID COMMUNICATIONS

PHYSICAL REVIEW B **79**, 140407(R) (2009)

Critical thickness for itinerant ferromagnetism in ultrathin films of $SrRuO_3$

Jing Xia,[1,2] W. Siemons,[1,3] G. Koster,[1,3] M. R. Beasley,[1,4] and A. Kapitulnik[1,2,4]



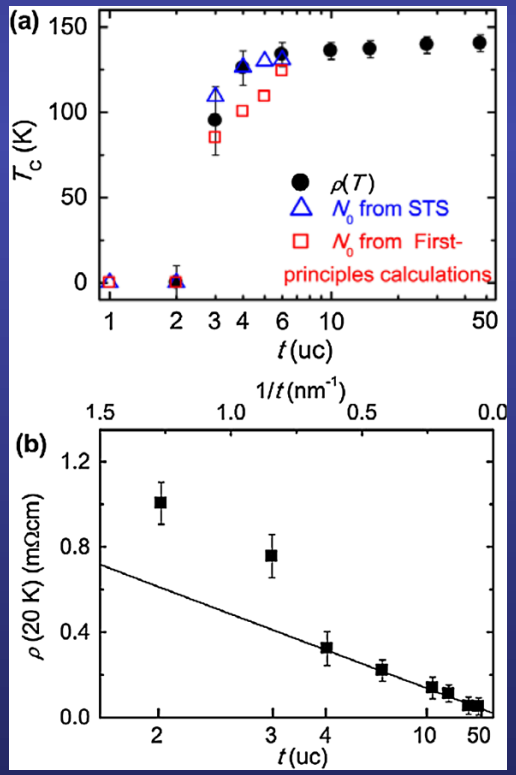
Below 4 uc, $SrRuO_3$ *thin films* on $SrTiO_3$:
- **Insulating**
- **Antiferromagnetic layer with the moments in the plane of the film**

Not trivial question: there might be a critical thickness for magnetic and/or metallic properties

PRL **103,** 057201 (2009) PHYSICAL REVIEW LETTERS week ending 31 JULY 2009

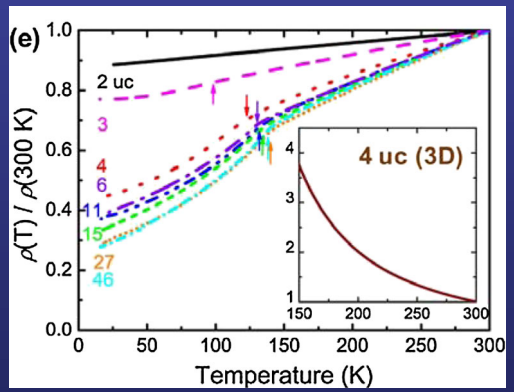
Fundamental Thickness Limit of Itinerant Ferromagnetic $SrRuO_3$ Thin Films

Young Jun Chang,[1] Choong H. Kim,[2] S.-H. Phark,[1] Y. S. Kim,[1] J. Yu,[2] and T. W. Noh[1,*]

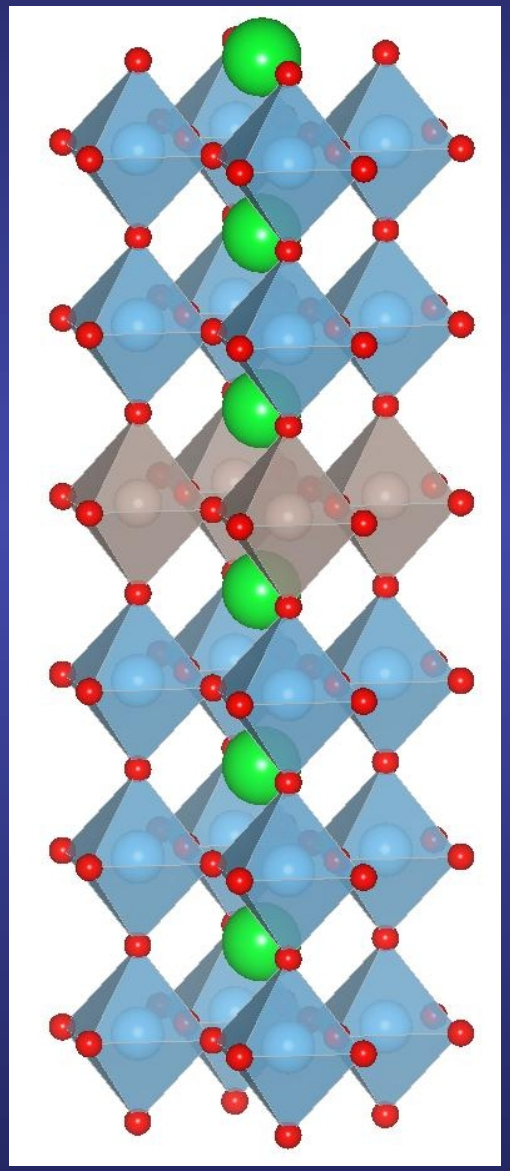


T_c decreases drastically below 4 uc and vanishes for 2 uc

But the metallic state persists down to 2 uc



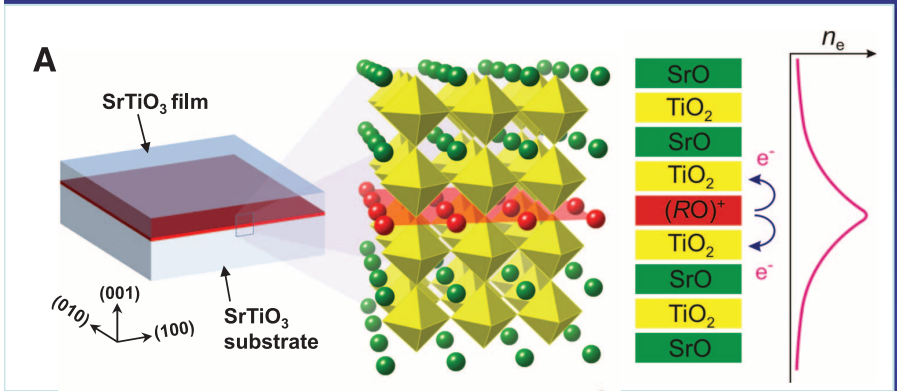
First-principles simulations on $(SrTiO_3)_5/(SrRuO_3)_1$ periodic superlattices



The superlattice can be viewed as a complete doping of the B site (Ti) of a single layer with Ru atoms

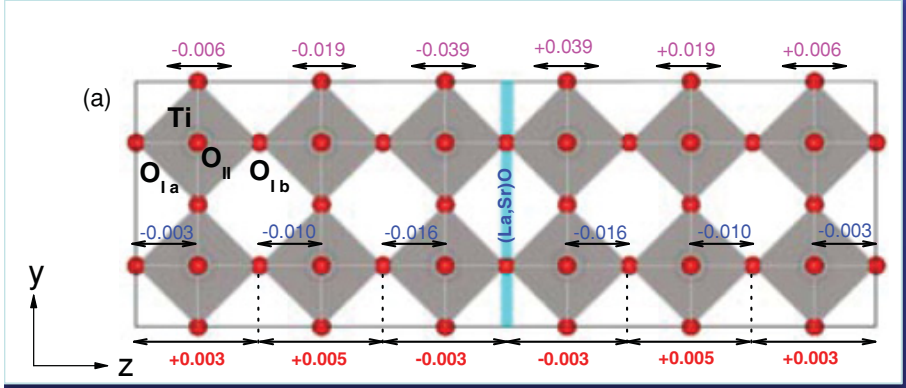
Are there other mechanisms to generate 2DEG at oxide interfaces?

Doping the A-site of a $SrTiO_3$ matrix



Complete replacement of the Sr atom of a single SrO layer **with a rare-earth element**

H. W. Jang *et al.*, Science 331, 886 (2011)

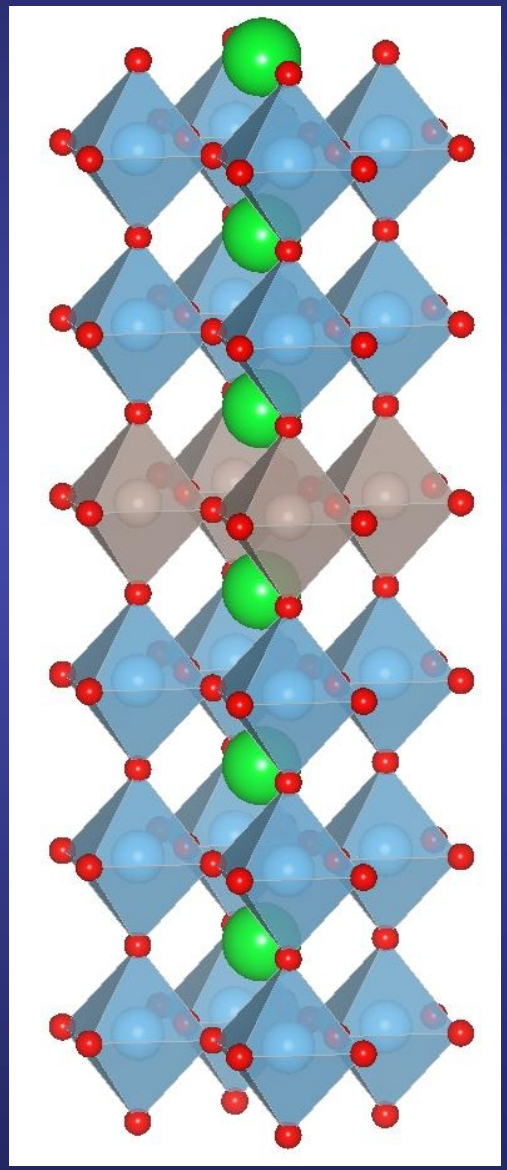


Partial replacement of the Sr atom of a single SrO layer **with La**

P. V. Ong *et al.*, Physical Review B 83, 193106 (2011)

The conduction electrons are transferred to the $SrTiO_3$ matrix but stay near the *R*O layer due to Coulomb attractions

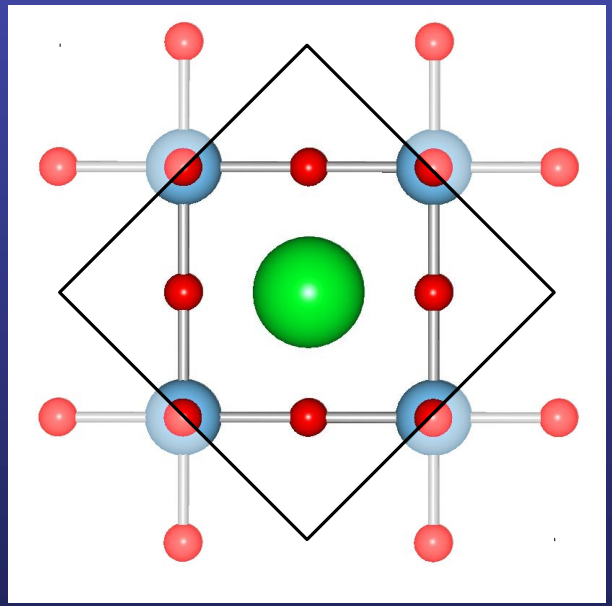
First-principles simulations of $(SrTiO_3)_5/(SrRuO_3)_1$ superlattices



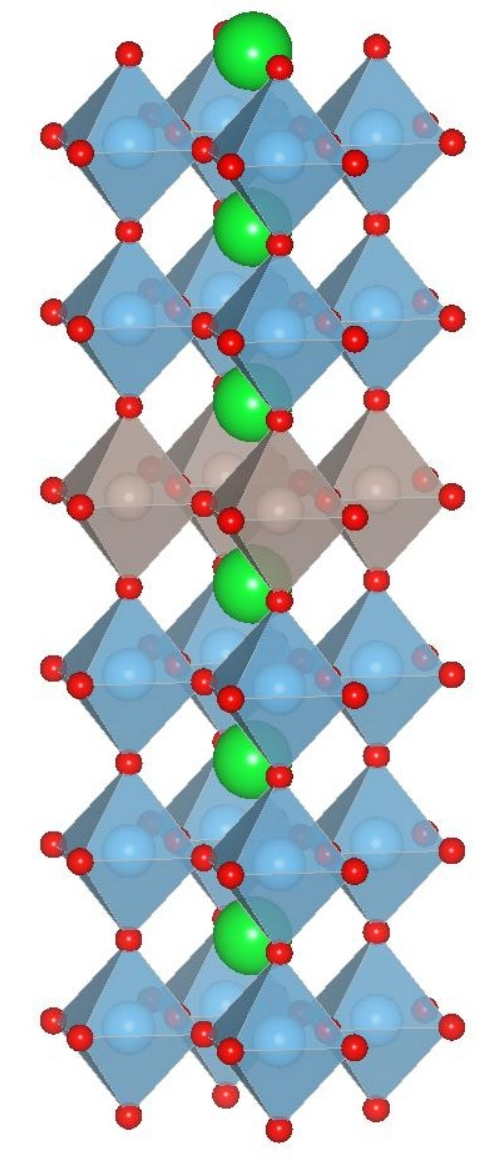
Local Spin Density Approximation + Hubbard U (LSDA+U)

U_{eff} = 4.0 eV, applied only to Ru-d orbitals

$\sqrt{2} \times \sqrt{2}$ in-plane symmetry to allow rotation of oxygen octahedra and different magnetic orders



First-principles simulations of $(SrTiO_3)_5/(SrRuO_3)_1$ superlattices



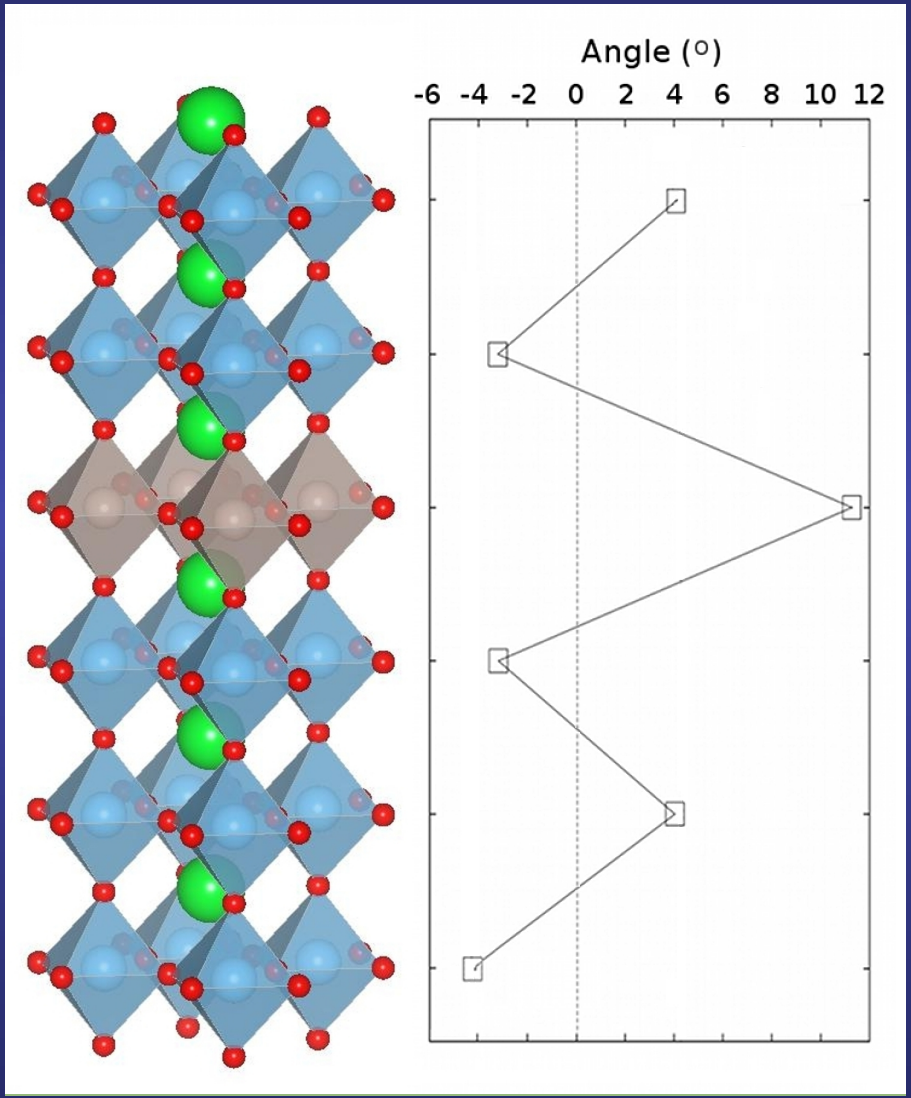
U_{eff} = 4.0 eV, applied only to Ru-d orbitals

$\sqrt{2} \times \sqrt{2}$ in-plane symmetry to allow rotation of oxygen octahedra and different magnetic orders

Full relaxation of atomic coordinates (atomic forces smaller than 0.01 eV/Å)

In-plane lattice constant constrained to the theoretical one of $SrTiO_3$ (3.874 Å)

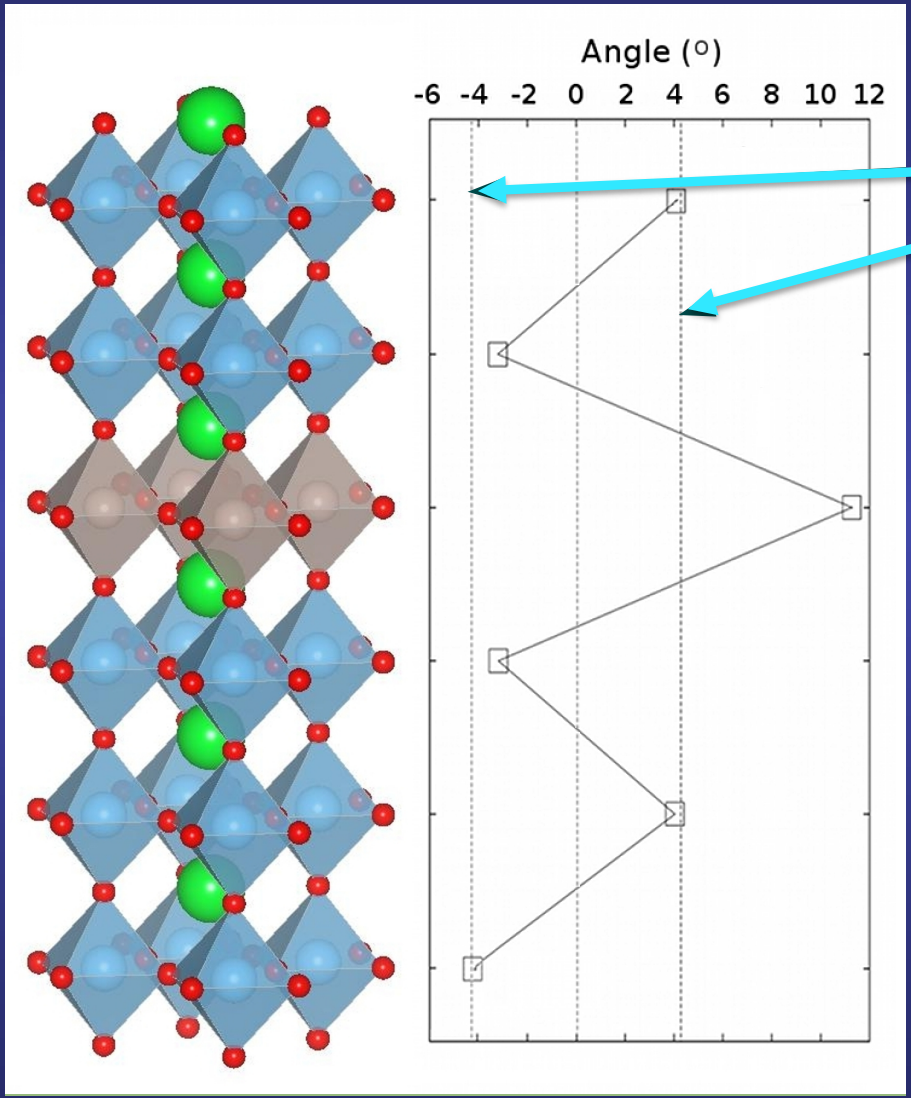
Atomic structure of periodic $(SrTiO_3)_5/(SrRuO_3)_1$ superlattices



RuO_6 oxygen octahedra rotates 11.6°
bulk tetragonal $SrRuO_3$ under the same strain conditions rotates 11.3°

M. Verissimo-Alves *et al.*,
Physical Review Letters 108, 107003 (2012)

Atomic structure of periodic $(SrTiO_3)_5/(SrRuO_3)_1$ superlattices



Theoretical LDA value

$$\theta_{\text{bulk}}^{\text{SrTiO}_3} = 4.2^\circ$$

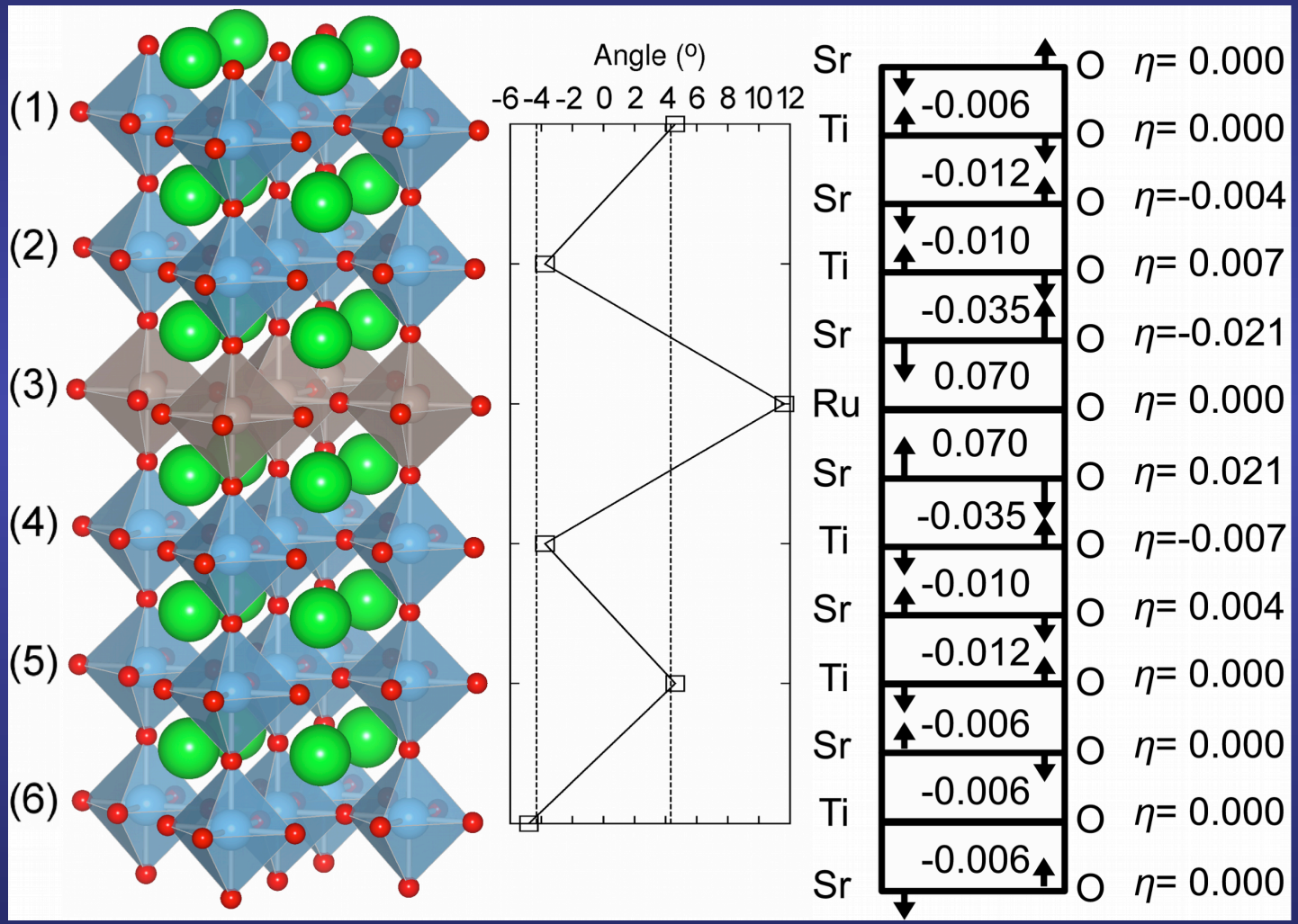
RuO_6 oxygen octahedra rotates 11.6°
bulk tetragonal $SrRuO_3$ under the same strain conditions rotates 11.3°

Interactions between RuO_2 planes well screened already with 5 layers of $SrTiO_3$

M. Verissimo-Alves *et al.*,
Physical Review Letters 108, 107003 (2012)

Atomic structure of periodic $(SrTiO_3)_5/(SrRuO_3)_1$ superlattices

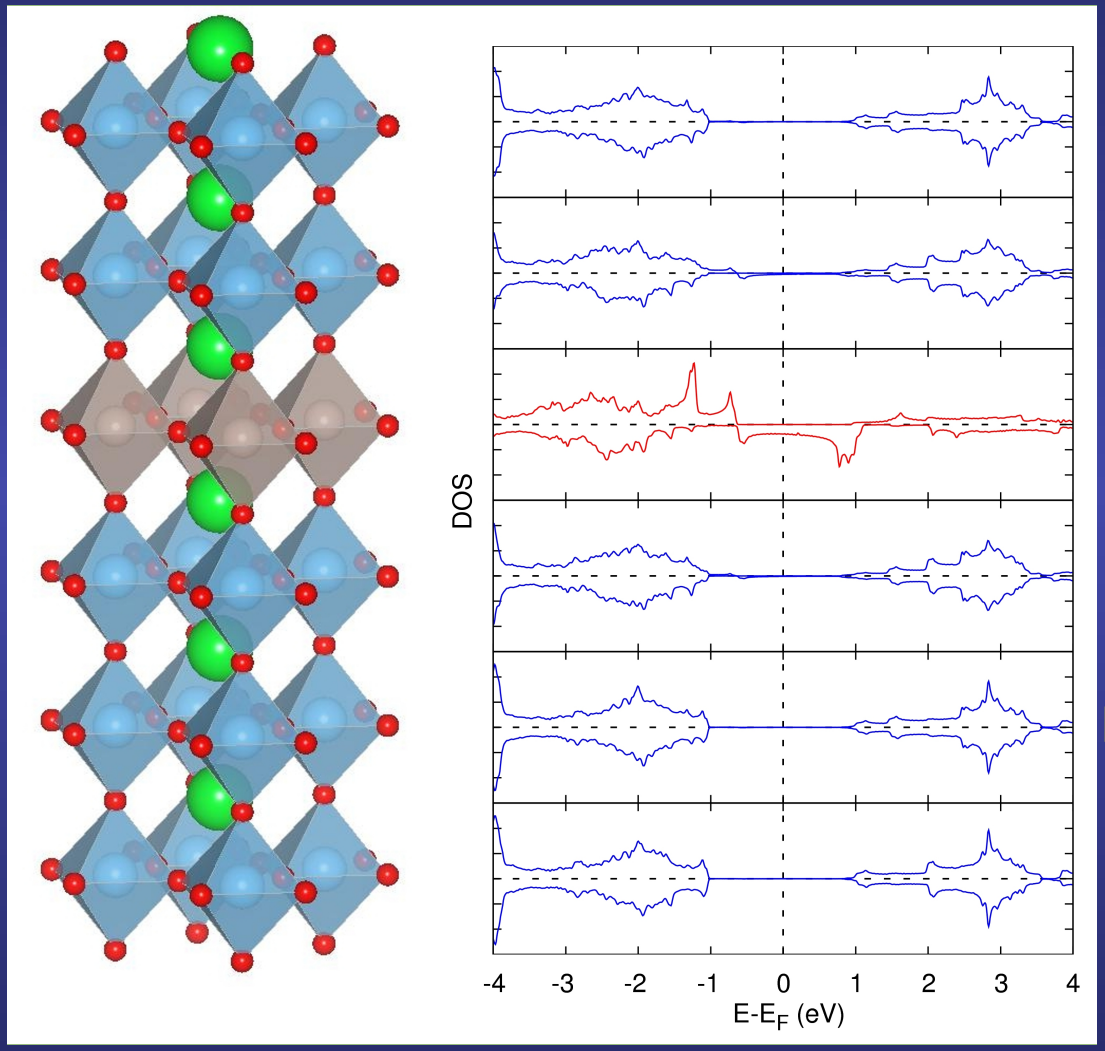
Units in Å



Small atomic rumplings and changes in the interplanar distances

M. Verissimo-Alves *et al.*,
Physical Review Letters 108, 107003 (2012)

Electronic structure of periodic $(SrTiO_3)_5/(SrRuO_3)_1$ superlattices



NO POLAR CATASTROPHE

NO O VACANCIES

Two dimensional electron gas, strictly confined in the $SrRuO_3$ layer

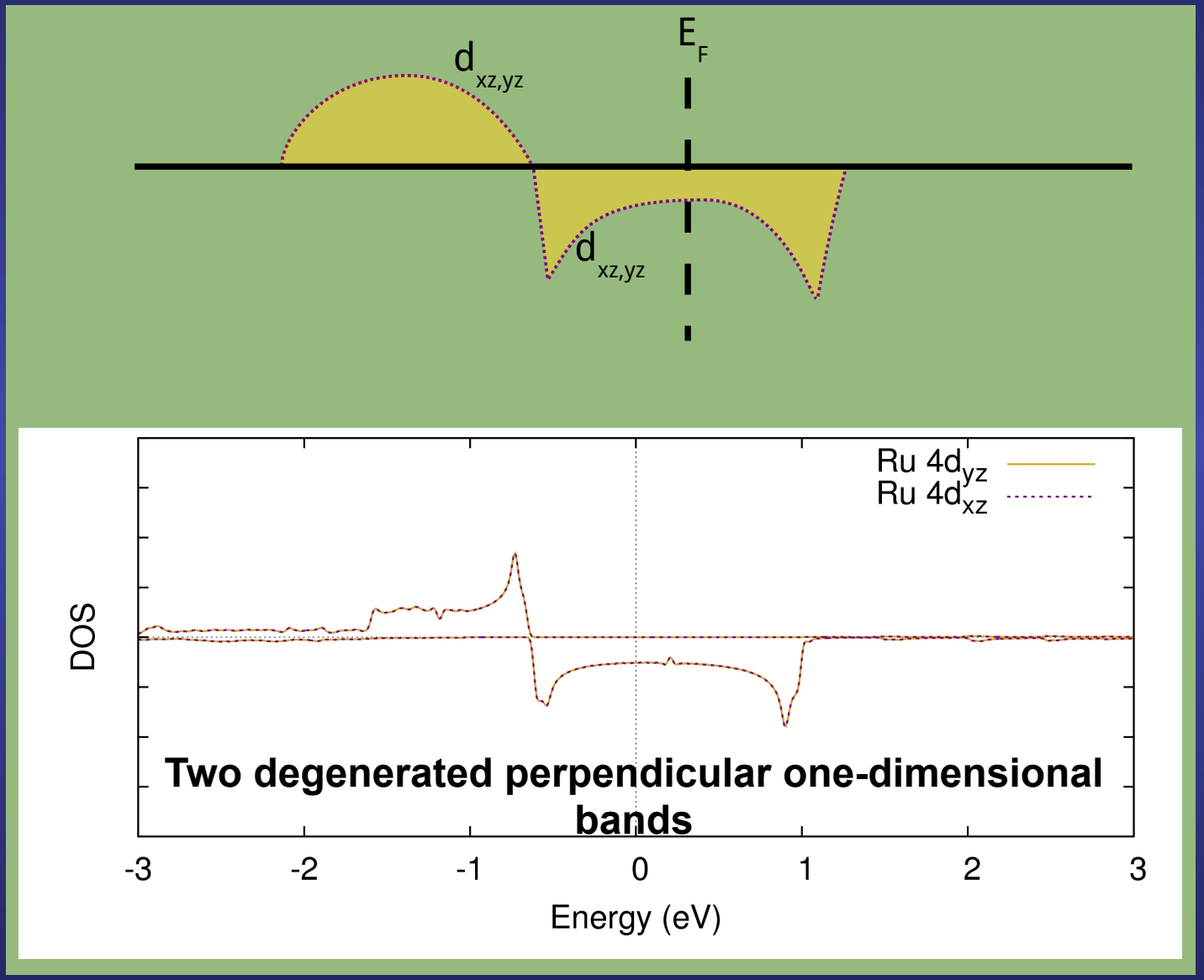
Electronic states around the Fermi level are fully spin polarized, with only the minority spin electrons involved in the charge transport

2DEG exhibit magnetism with magnetic moment $\mu = 2.0\mu_B$ per $SrRuO_3$ unit cell

$$\mu_{Ru} = 1.4\ \mu_B$$

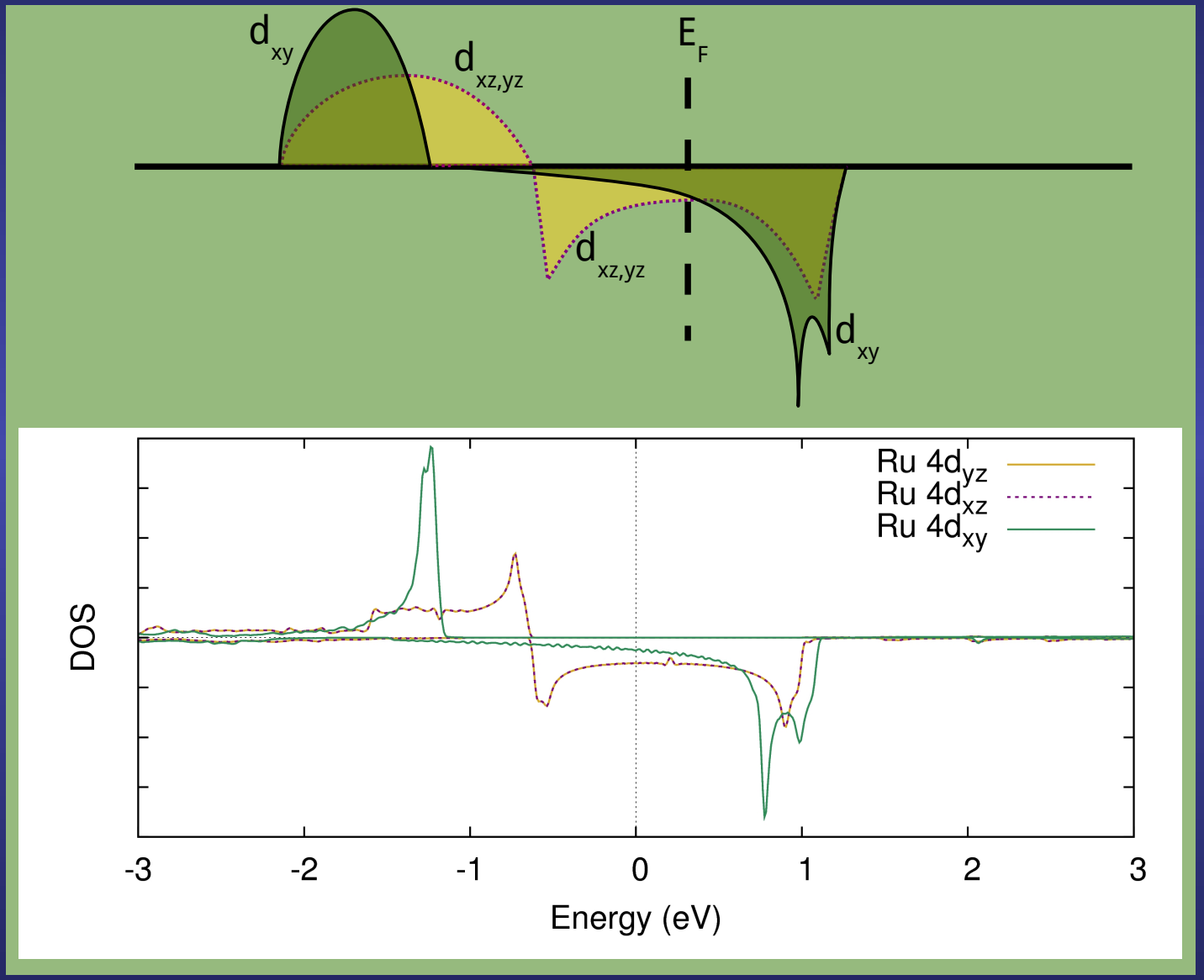
M. Verissimo-Alves *et al.*,
Physical Review Letters 108, 107003 (2012)

Which orbital are responsible for the PDOS in the RuO_2 layer?



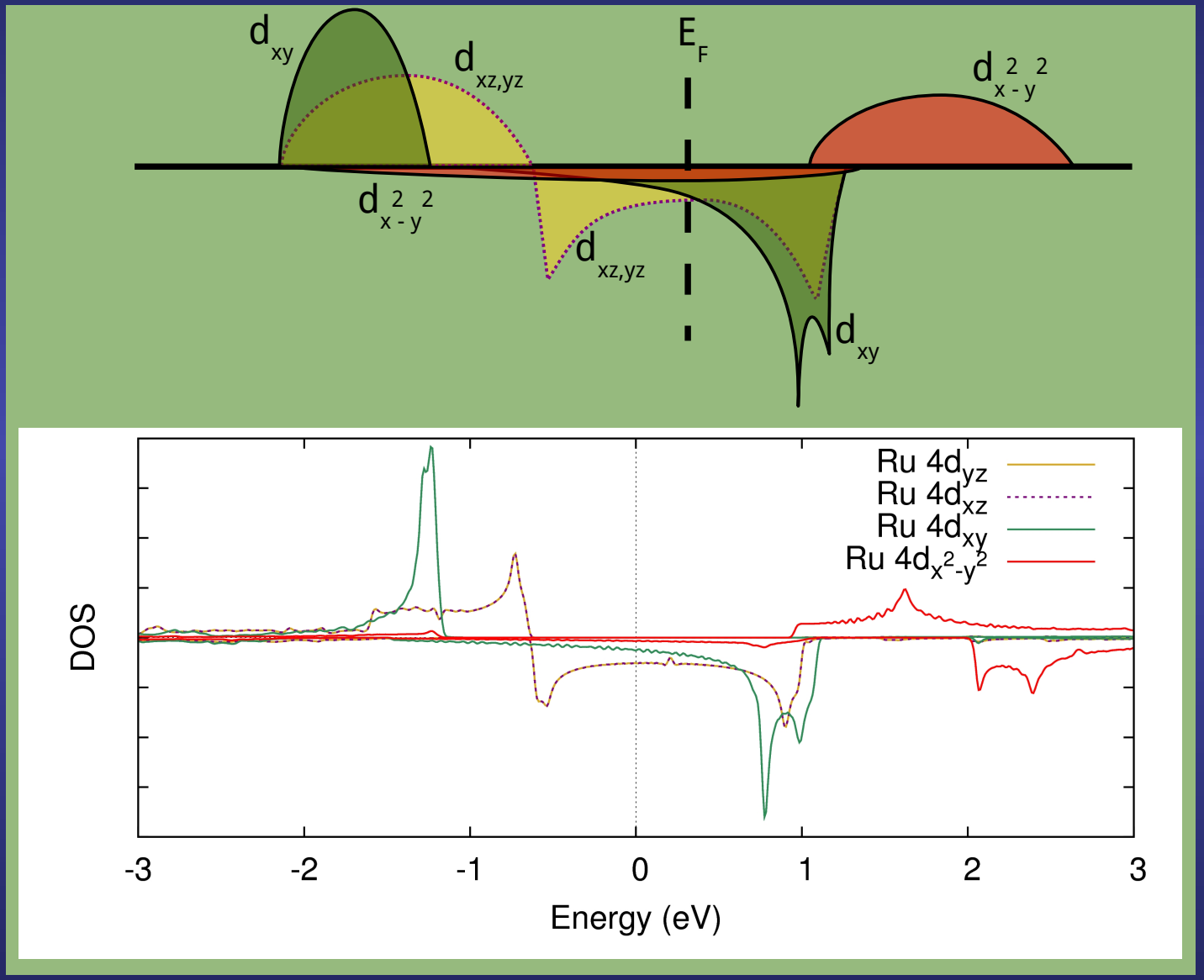
M. Verissimo-Alves *et al.*, Phys. Rev. Lett. 108, 107003 (2012)

Which orbital are responsible for the PDOS in the RuO_2 layer?



M. Verissimo-Alves *et al.*, Phys. Rev. Lett. 108, 107003 (2012)

Which orbital are responsible for the PDOS in the RuO_2 layer?

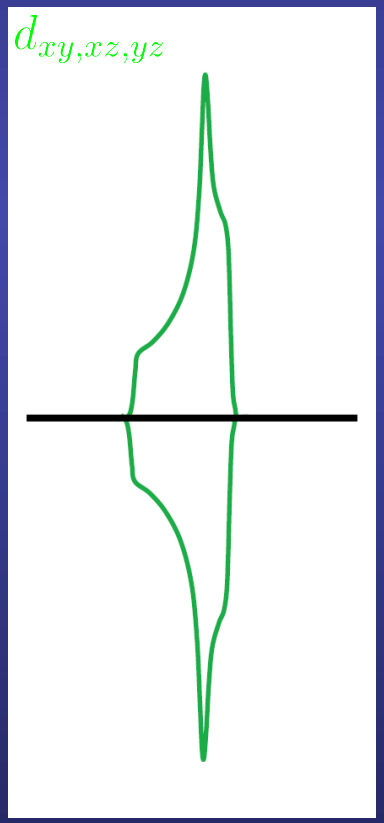


M. Verissimo-Alves *et al.*, Phys. Rev. Lett. 108, 107003 (2012)

The most important feature can be explained within a simple tight-binding model

Only t_{2g} states retained in the basis set

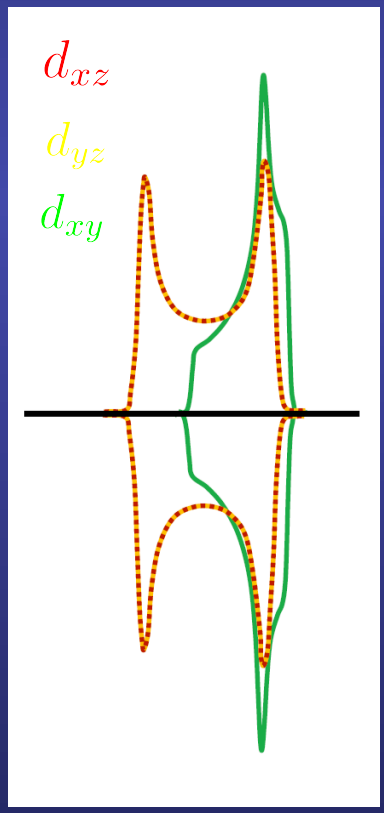
Assuming cubic symmetry, the PDOS of a full three dimensional solid



d_{xy} band unaltered

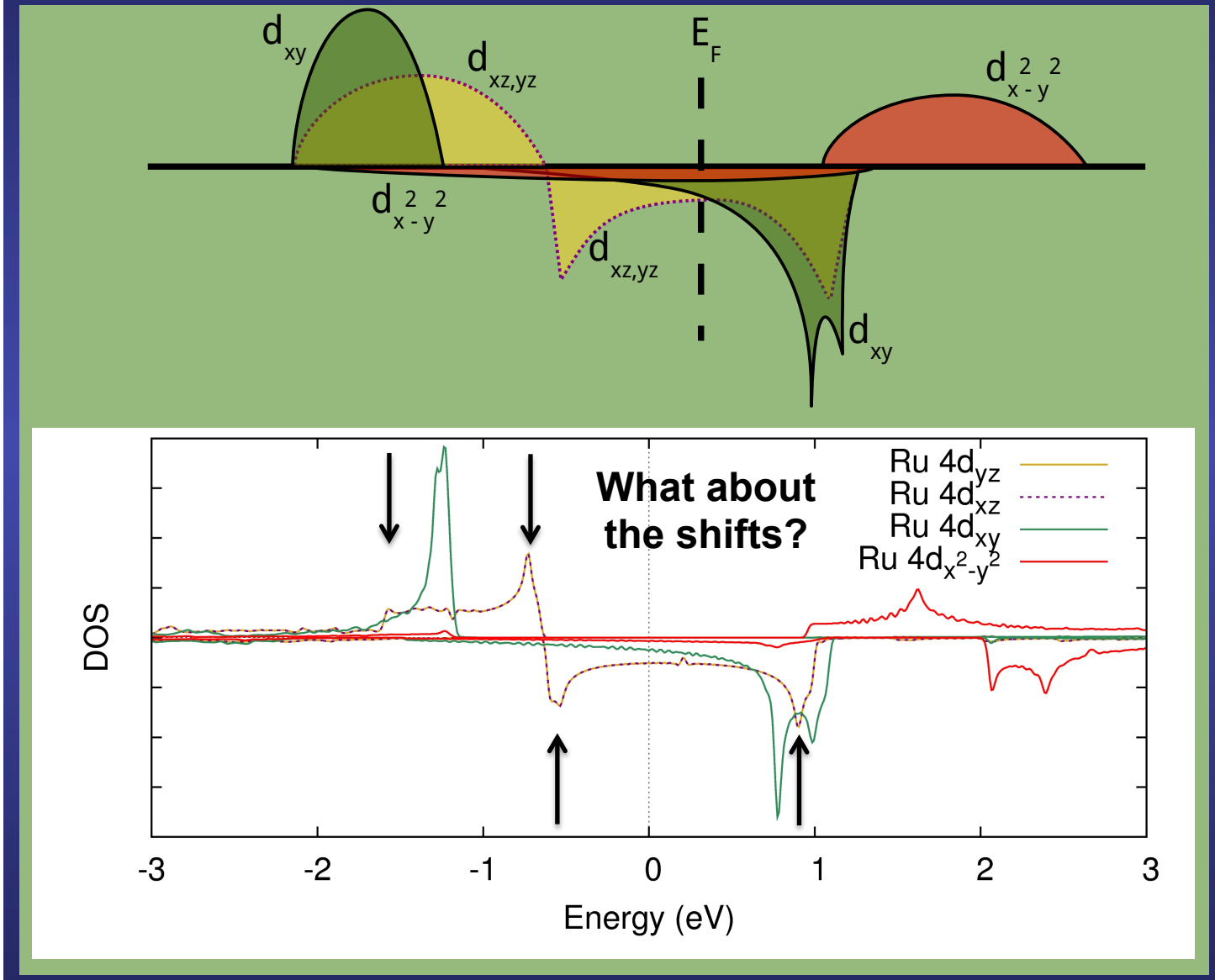
$d_{xz,yz}$ present two peaks in good agreement with first-principles

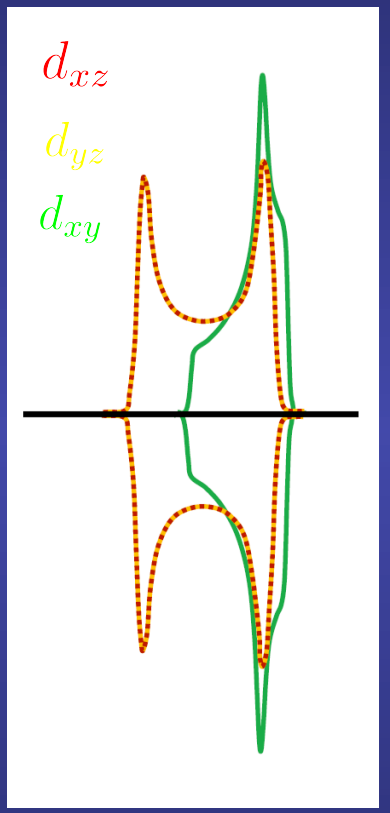
Reducing dimensionality (slab)



M. Verissimo-Alves *et al.*, Phys. Rev. Lett. 108, 107003 (2012)

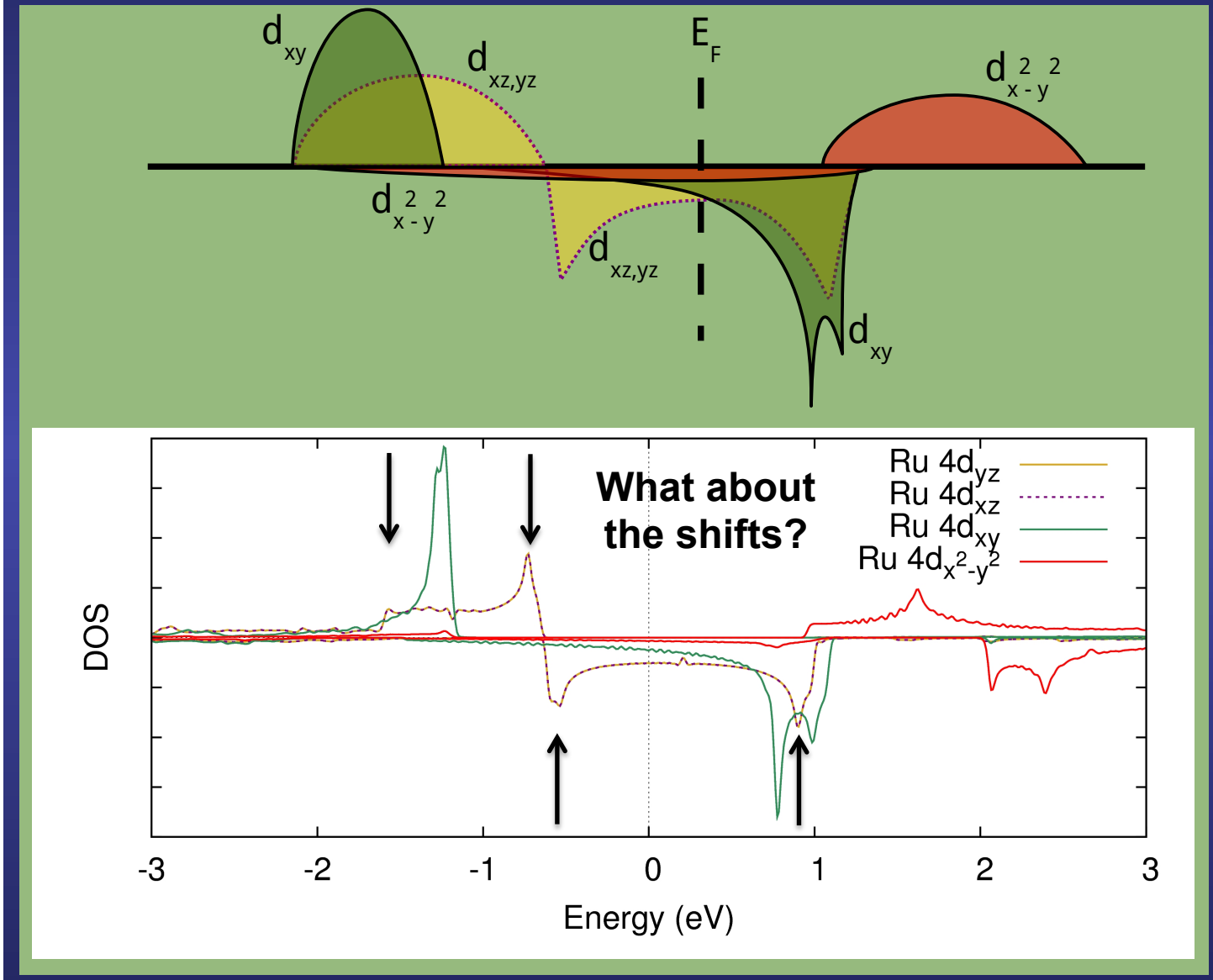
Good agreement between tight-binding and first-principles





M. Verissimo-Alves *et al.*, Phys. Rev. Lett. 108, 107003 (2012)

Two different effects to explain the shifts



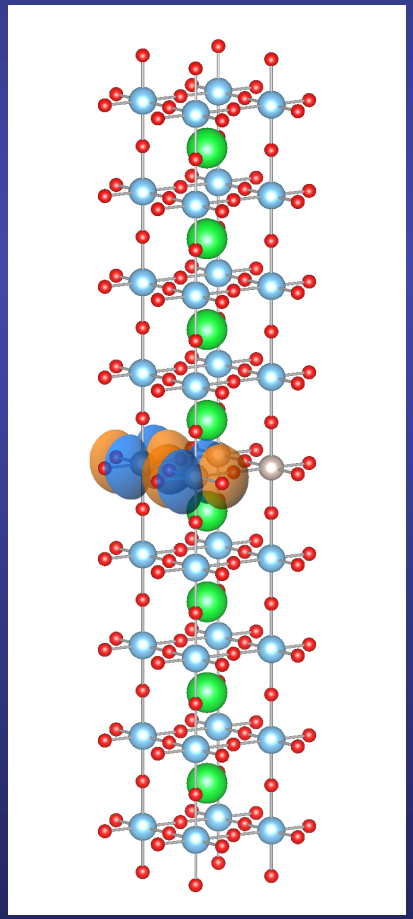
Different in bonding of the orbitals in-plane and out-of-plane neighbors

Strong correlation: the Hubbard U correction

M. Verissimo-Alves *et al.*, Phys. Rev. Lett. 108, 107003 (2012)

Explaining the shift: Different in bonding of the orbitals with in-plane and out-of-plane

d_{xy} orbitals only interact strongly with in-plane neighbors.
All of them are orbitals centered around Ru^{4+} atoms



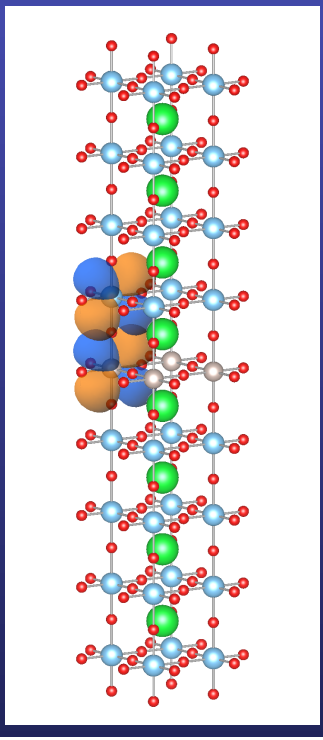
Explaining the shift: Different in bonding of the orbitals with in-plane and out-of-plane

d_{xy} orbitals only interact strongly with in-plane neighbors.
All of them are orbitals centered around Ru^{4+} atoms

$d_{yz,xz}$ orbitals interact:

In-plane with centers around Ru^{4+} ions.

Out-of-plane with functions centered on Ti^{4+} ions, mediated by O



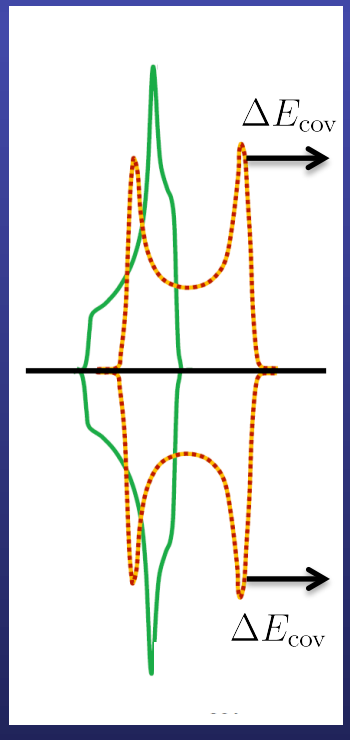
Explaining the shift: Different in bonding of the orbitals with in-plane and out-of-plane

d_{xy} orbitals only interact strongly with in-plane neighbors.
All of them are orbitals centered around Ru^{4+} atoms

$d_{yz,xz}$ orbitals interact:

In-plane with centers around Ru^{4+} ions.

Out-of-plane with functions centered on Ti^{4+} ions, mediated by O



Ru (2.20) is more electronegative than Ti (1.54)

⇓

Apical O are polarized toward Ru

⇓

Increase of covalency

⇓

Decrease in the energy of the bonding state and a increase of the antibonding levels ΔE_{cov}

Explaining the shift: strong correlation, the Hubbard U correction

LDA+U theory predicts that orbital energies are shifted by

$$U_{\mathrm{eff}}\left(\frac{1}{2}-\lambda\right)$$

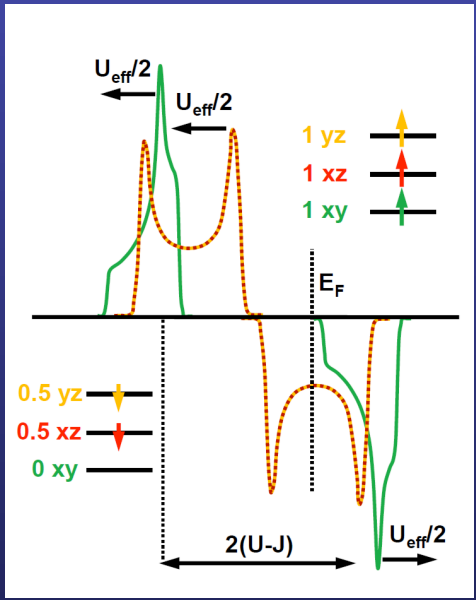
where λ is the occupation of the orbital

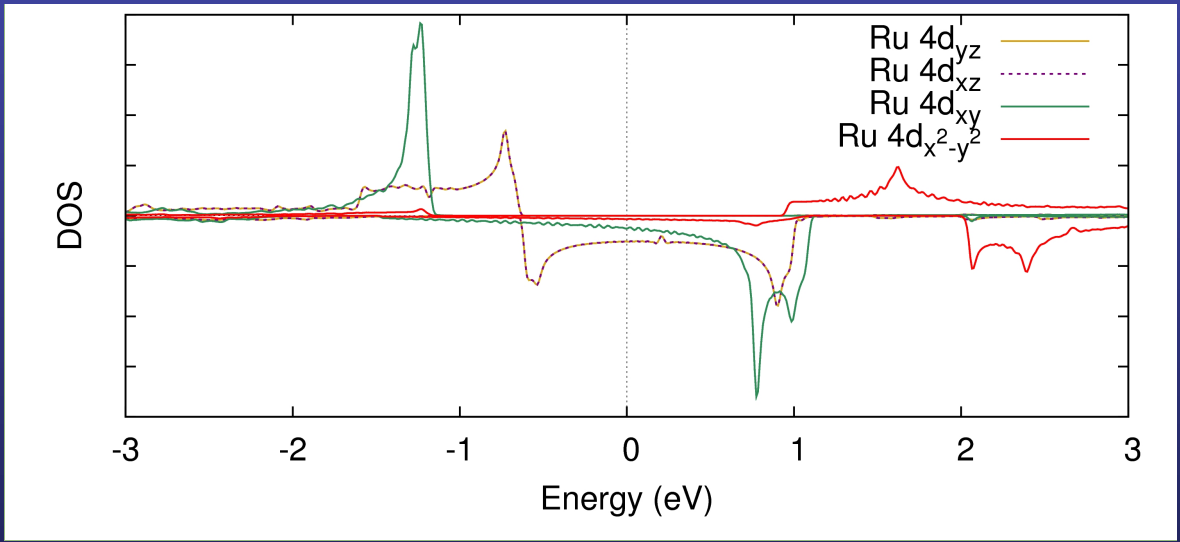
Assuming that:

the majority spin t_{2g} levels are full

the minority spin d_{xz}, d_{yz} and d_{xy} contain respectively 0.5, 0.5 and 0.0 e

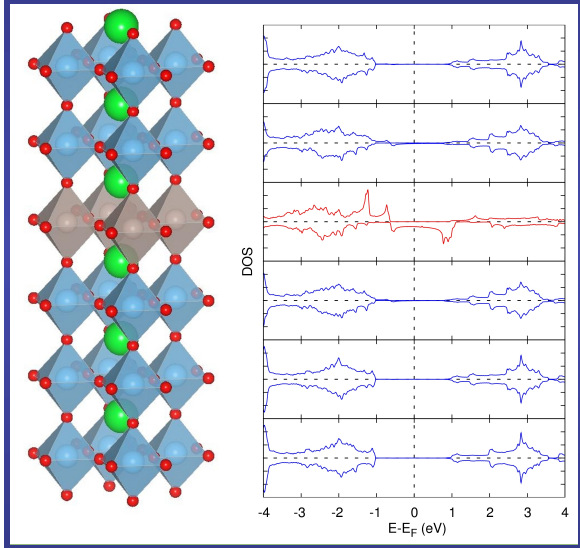
Good agreement between tight-binding and first-principles results





Conclusions

Highly confined (one monolayer thick) 2DEG at the $SrTiO_3/SrRuO_3$ interfaces in $(SrTiO_3)_5/(SrRuO_3)_1$ periodic superlattices



New origin for the 2DEG: due to electronegativity of Ru, and not to polar catastrophe

2DEG localized on d-orbitals of Ru and not on Ti

2DEG intrinsically magnetic (not dependent on O vacancies or defects, as in $LaAlO_3/SrTiO_3$)

M. Verissimo-Alves *et al.*, Phys. Rev. Lett. 108, 107003 (2012)

Two questions addressed in this talk

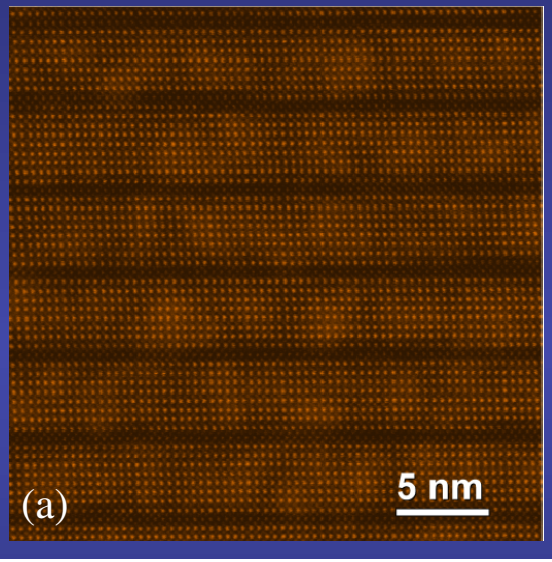
Question: Are there alternative mechanisms to generate two dimensional electron gases with new intrinsic functional properties?

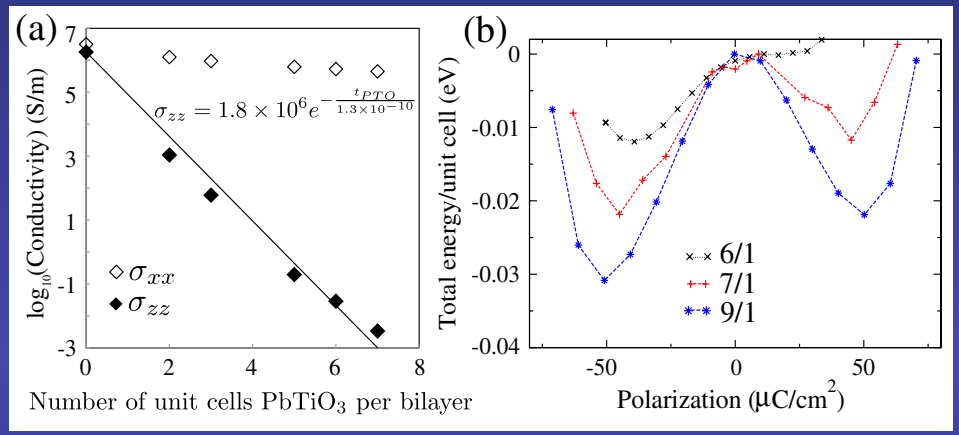
If so, what are they useful for?

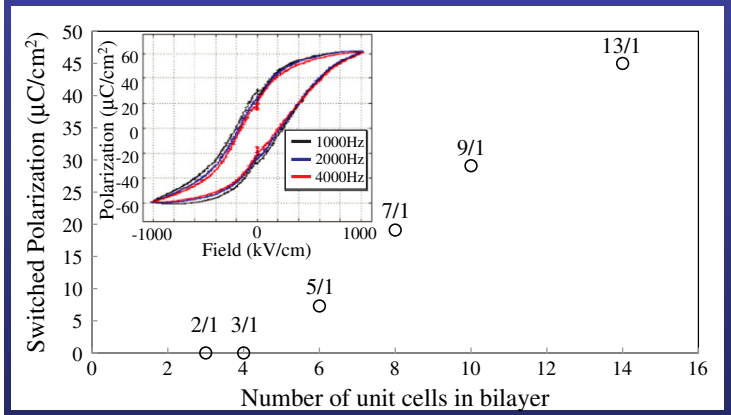
1. Coupling between magnetism and ferroelectricity

Ferroelectric $PbTiO_3/SrRuO_3$ superlattices with broken inversion symmetry

n-unit cells of $PbTiO_3$ / 1unit cell of $SrRuO_3$







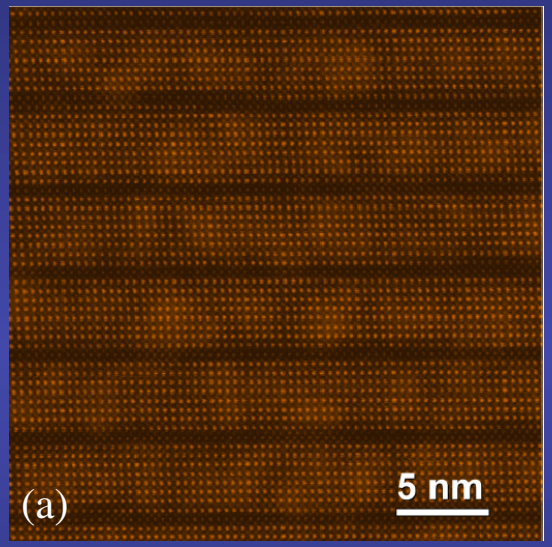
- The electrons are confined to the $SrRuO_3$ layer (σ_{xx} does not change dramatically with the spacing between layers)
- The out-of-plane conductivity decreases exponentially

- Inversion symmetry is artificially broken in a bicolor superlattice
- Hysteresis loops are measured

S. J. Callori *et al.*, Phys. Rev. Lett. 109, 067601 (2012)

Ferroelectric $PbTiO_3/SrRuO_3$ superlattices with broken inversion symmetry

n-unit cells of $PbTiO_3$ / 1unit cell of $SrRuO_3$



In simulations of superlattices with more than one unit cells thick of $SrRuO_3$, the magnetization is different for the two polarization directions

S. J. Callori *et al.*, Phys. Rev. Lett. 109, 067601 (2012)

Two questions addressed in this talk

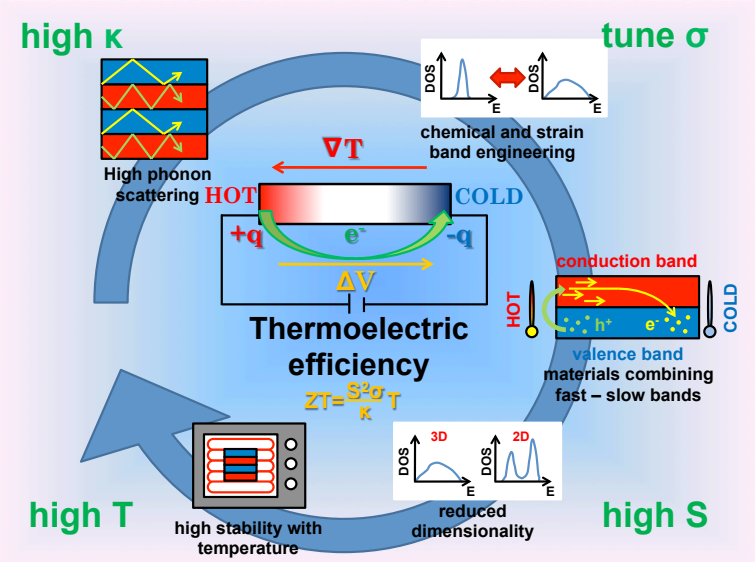
Question: Are there alternative mechanisms to generate two dimensional electron gases with new intrinsic functional properties?

If so, what are they useful for?

1. Coupling between magnetism and ferroelectricity

2. Use in thermoelectric devices

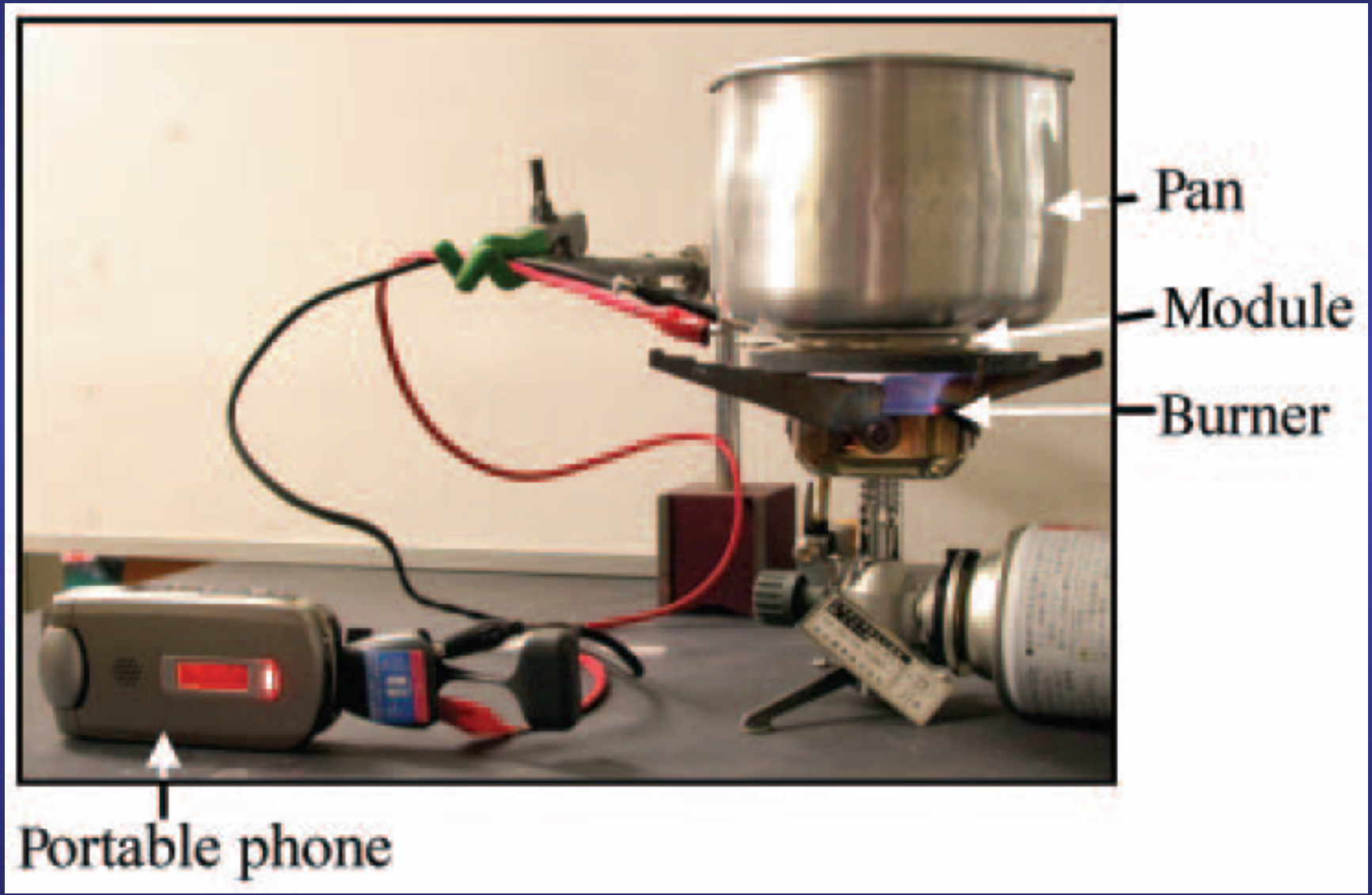
Analysis of the thermoelectric figure of merit for $SrTiO_3/SrRuO_3/SrTiO_3$ superlattices



The thermoelectric effect is the direct conversion of temperature differences to electric voltage and viceversa.

A good thermoelectric system could be used to convert waste heat into electricity without producing greenhouse gas emissions.

Thermoelectric materials might play a role on the solution of today's energy problem



K. Koumoto, I. Terasaki and R. Funahashi, MRS Bulletin 31 206 (2006)

Performance of a thermoelectric material evaluated through the dimensionless figure of merit

$$ZT = \frac{S^2 \sigma T}{\kappa}$$

Z	Figure of merit
T	Absolute temperature
S	Seebeck coefficient
σ	Electrical conductivity
κ	Thermal conductivity

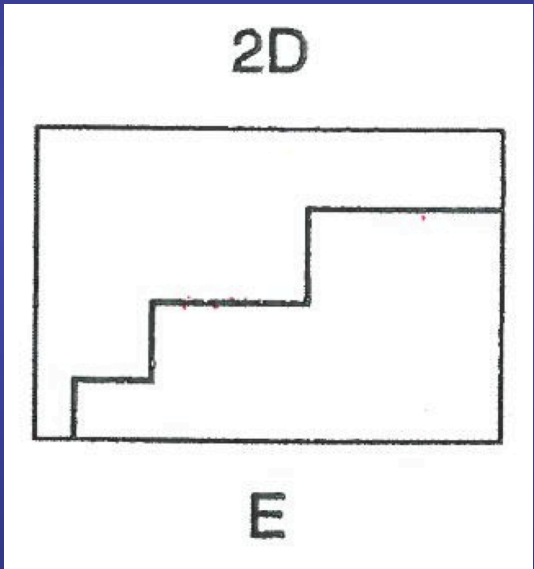
For a material to be useful for electronic devices, $ZT > 1$ at room temperature

With conventional solids, a limit is rapidly obtained, where a modification to any one of these parameters adversely affects the other transport coefficients so the resulting Z does not vary significantly.

It might be possible to increase Z of certain materials preparing them in quantum-well superlattices

Electrons confined to move in two dimensions.

Change in the band structure and the electronic density of states



Two-dimensional density of states in the free-electron model

An increase in the carrier density per unit volume can be obtained without changing the Fermi energy, i.e. without a change in the Seebeck coefficient S

L. D. Hicks and M. S. Dresselhaus, Phys. Rev. B 47, 12727 (1993)

It might be possible to increase Z of certain materials preparing them in quantum-well superlattices

The best thermoelectric

G. D. MAHAN*† AND J. O. SOFO‡

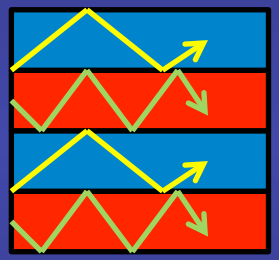
Proc. Natl. Acad. Sci. USA
Vol. 93, pp. 7436–7439, July 1996
Applied Physical Sciences

The transport distribution that maximizes the figure of merit is the Dirac delta function. An ideal delta function is not achievable in real materials. However, electronic *f*-levels are tightly bound in atoms, and bind little in solids (10–11). They give a contribution to the density of states in solids, which is a Lorentzian of very narrow width. This is nature's closest approximation to a delta function.

It might be possible to increase Z of certain materials preparing them in quantum-well superlattices

Electrons confined to move in two dimensions.

Layering may reduce the phonon themal conductivity



Degrees of freedom to play with in superlattices:

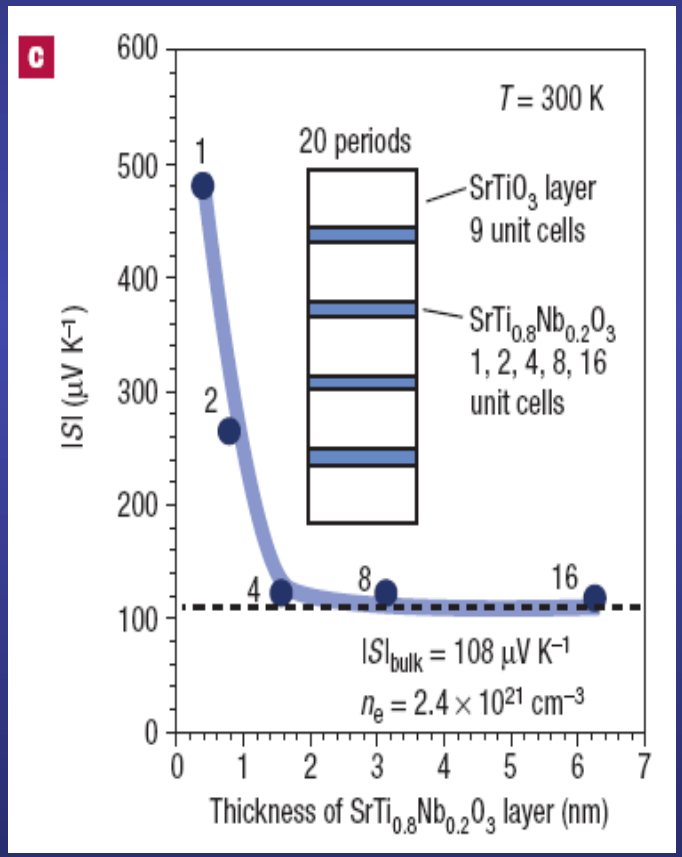
- Layer thickness (the thinnest the better)
- Orientation in which make the layers
- Optimum current direction
- Anisotropy effective-mass tensor

L. D. Hicks and M. S. Dresselhaus, Phys. Rev. B 47, 12727 (1993)

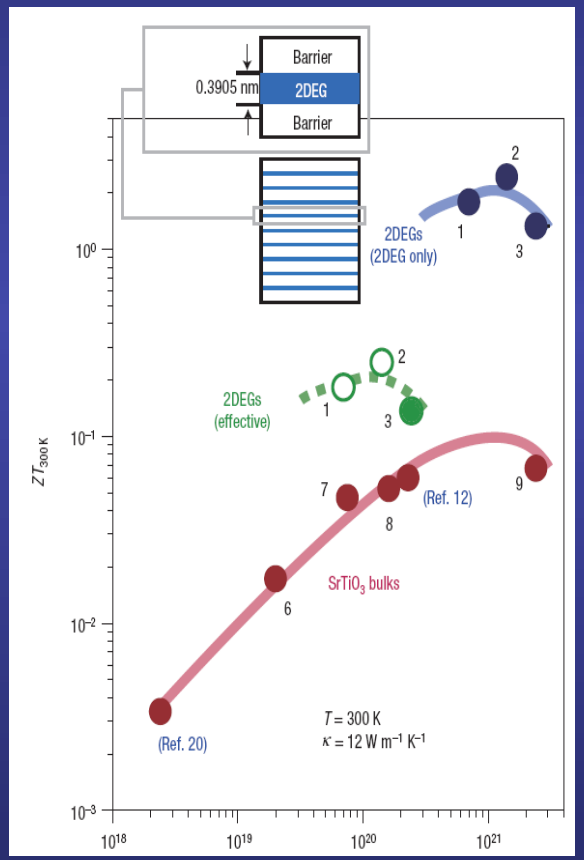
A new class of thermoelectric materials: 2DEG confined within the thickness of a unit cell in $SrTiO_3$

$SrTiO_3$ (9 unit cells) / $SrTi_{0.8}Nb_{0.2}O_3$ / $SrTiO_3$ (9 unit cells)

Dramatic increase in the Seebeck coefficient



Thermoelectric figure of merit



H. Ohta *et al.*, Nature Materials 6, 129 (2007)

H. Ohta, Materials Today, 10, 44 (2007)

Simulations of the thermoelectric figure of merit: transition from first to second-principles methods

First-principles

WIEN-2K

SIESTA

CRYSTAL

…

Input required:

Atomic structure

Symmetry space group

Electronic band structure

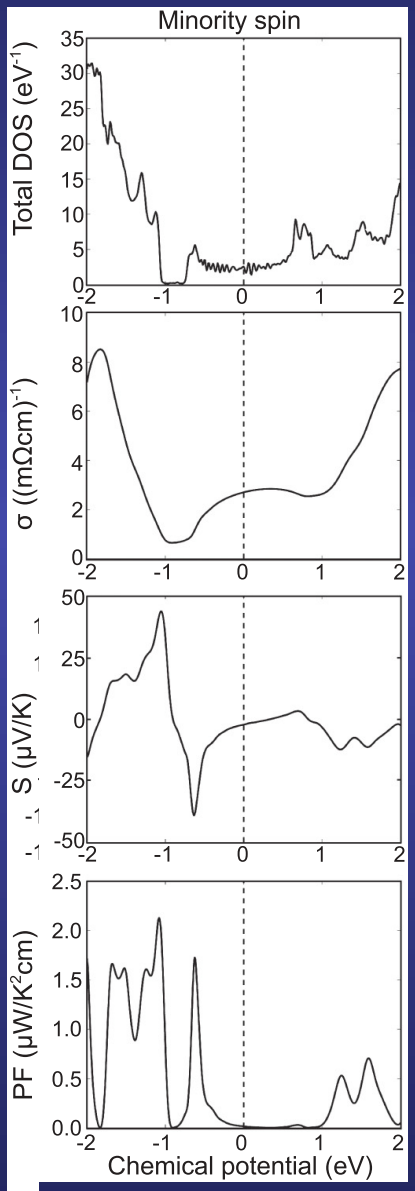
Second-principles

BOLTZTRAP

G. H. Madsen and D. J. Singh, Computer Physics Communications 175, 67 (2006)

Solves the semiclassical Bloch-Boltzman transport equations within the constant relaxation time approximation

Transport tensors in $SrTiO_3/SrRuO_3/SrTiO_3$: minority spin



Behavior around Fermi energy at zero doping is different for each spin component

System is metallic

Conductivity presents a local maximum close to $\mu = 0$

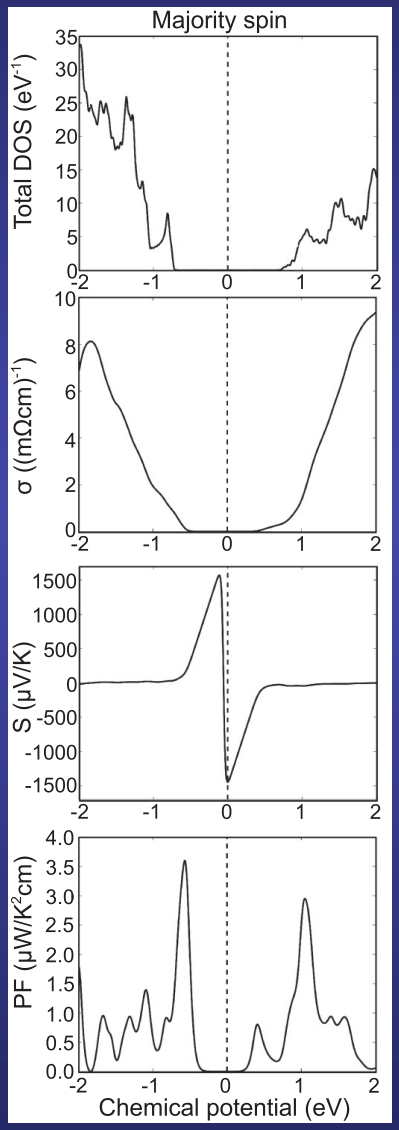
σ decreases as the chemical potential gets closer to the $d_{xz,yz}$ band edge

Seebeck coefficient is very small at $\mu = 0$

When the system is doped, the absolute value increase lineary with the chemical potential

M. Verissimo-Alves *et al.* Phys. Rev. B 86, 085305 (2012)

Transport tensors in $SrTiO_3/SrRuO_3/SrTiO_3$: majority spin



Behavior around Fermi energy at zero doping is different for each spin component

System is semiconducting

Small contribution to σ

Seebeck coefficient displays large values

$1500\mu\mathrm{V/K}$

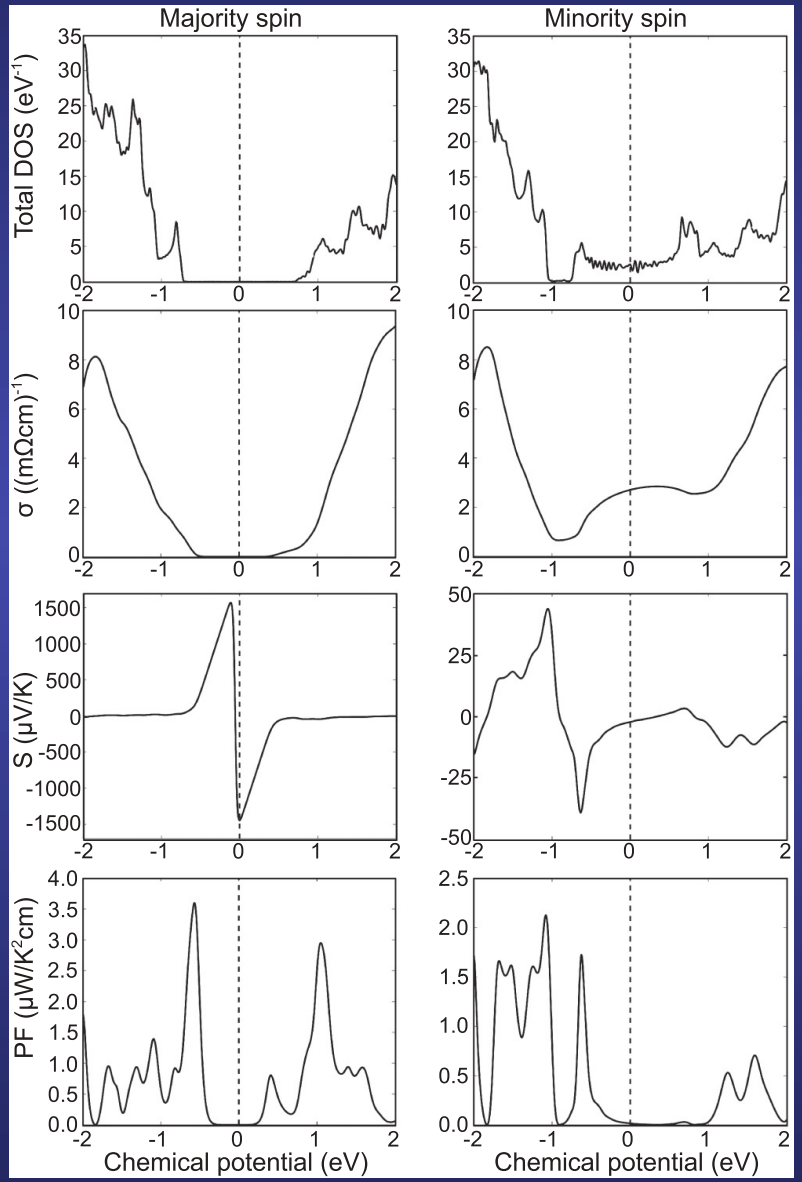
For comparison one monolayer of Nb-doped $SrTiO_3$ embedded into a $SrTiO_3$ matrix

$500\ \mu\mathrm{V/K}$

W. S. Choi *et al.*, Phys. Rev. B 82, 024301 (2010)

M. Verissimo-Alves *et al.* Phys. Rev. B 86, 085305 (2012)

Transport tensors in $SrTiO_3/SrRuO_3/SrTiO_3$:



The power factor shows strong compensation of the Seebeck coefficient and conductivity in both channels

$$\mathrm{PF} = S^2\sigma$$

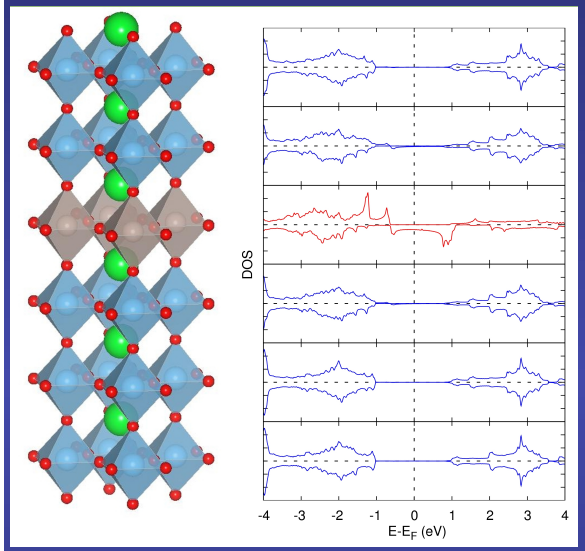
Wherever the Seebeck coefficient is large the electrical conductivity is very small (or even zero)

Only for very strong hole doping (1 hole per Ru atom) an appreciable enhancement is observed

M. Verissimo-Alves *et al.* Phys. Rev. B 86, 085305 (2012)

Conclusions

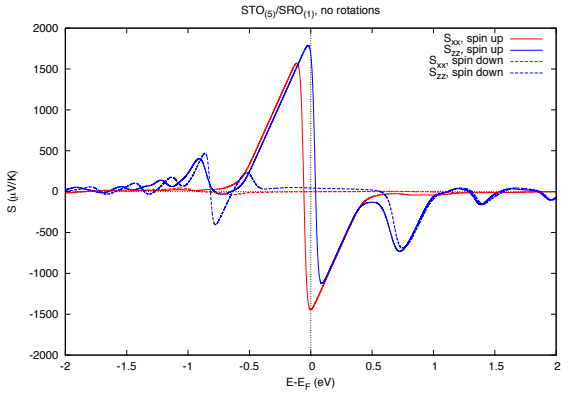
Highly confined (one monolayer thick) 2DEG at the $SrTiO_3/SrRuO_3$ interfaces in $(SrTiO_3)_5/(SrRuO_3)_1$ periodic superlattices

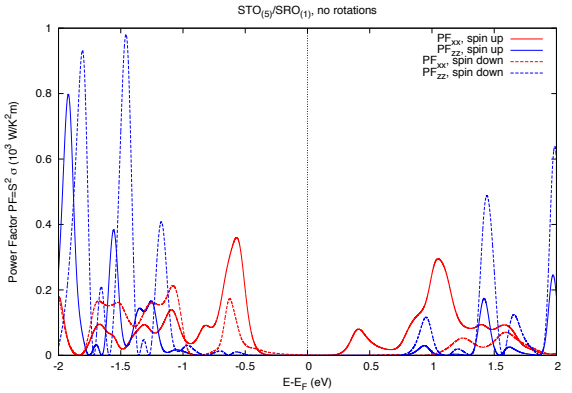


New **origin** for the 2DEG: due to **electronegativity of Ru**, and not to polar catastrophe

2DEG **localized on** d-orbitals of **Ru** and not on Ti

2DEG **intrinsically magnetic** (not dependent on O vacancies or defects, as in $LaAlO_3/SrTiO_3$)





Large enhancement of the Seebeck coefficient, but without the concomitant increase of the figure of merit

Many thanks to

Pablo García-Fernández

Marcos Verissimo-Alves

Philippe Ghosez

Daniel I. Bilc

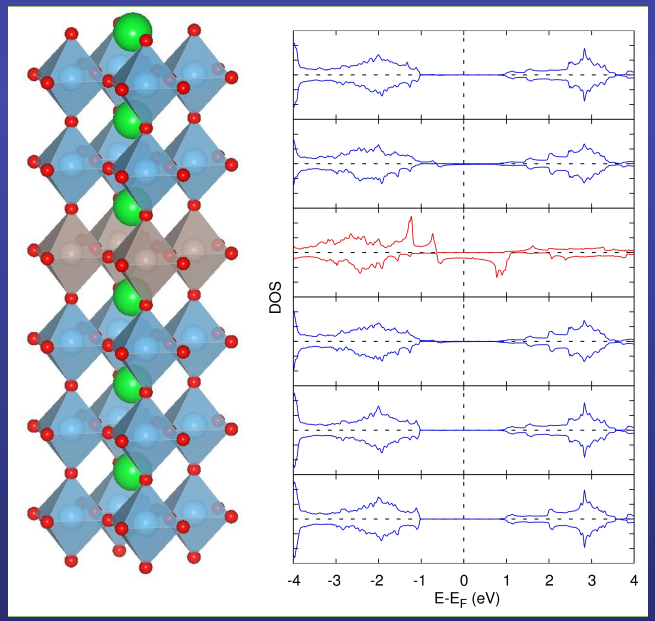
Finantial support

Engineering Exotic Phenomena
Ox/Des
at Oxide Interfaces

Computer time

RES
RED ESPAÑOLA DE SUPERCOMPUTACIÓN

Supplemental information



Javier Junquera

UNIVERSIDAD DE CANTABRIA

Bulk $SrRuO_3$: a well known ferromagnetic metal

Highly correlated, narrow d-band metal

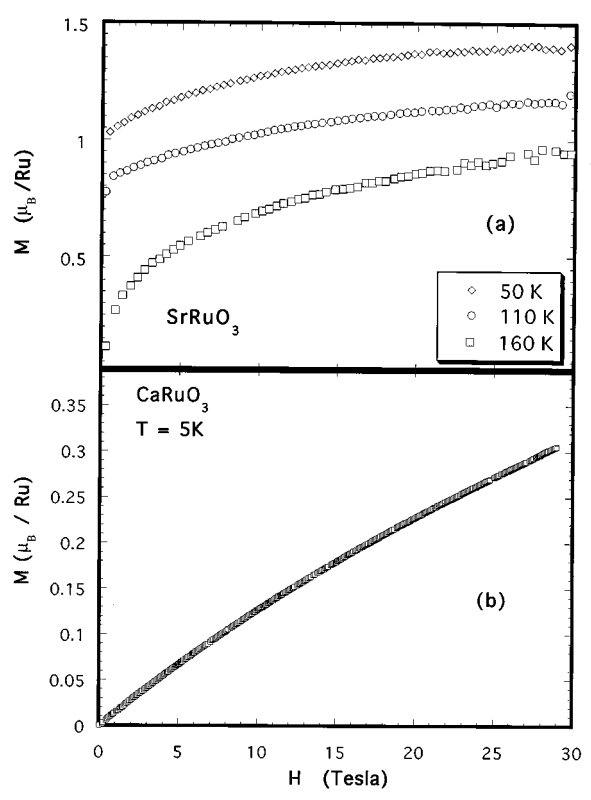
Ferromagnetic, with a transition temperature around 160 K

In bulk, crystallizes in the **$GdFeO_3$ structure** (Pbnm crystal structure; $a^-a^-c^+$ rot.)

Magnetic properties in bulk **difficult to characterize**:

Difficulty of making single domain crystal samples
Large magnetocrystalline anysotropy

Magnetization does not saturate even for 30 T



G. Cao *et al.*, Phys. Rev. B 56, 321 (1997)

Bulk $SrRuO_3$: a well known ferromagnetic metal

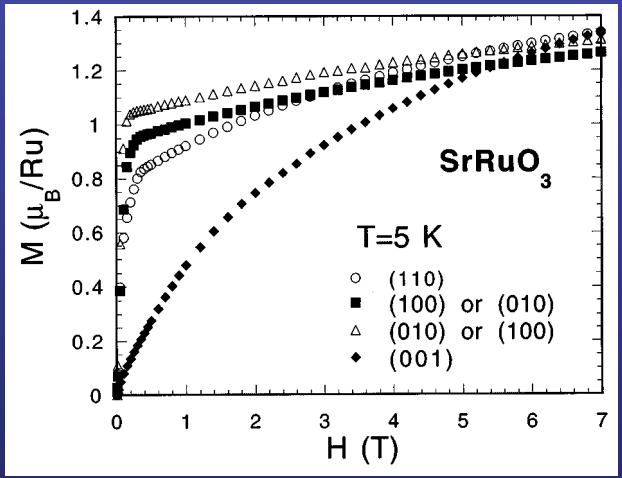
Highly correlated, narrow *d*-band metal

Ferromagnetic, with a transition temperature around 160 K

In bulk, crystallizes in the **$GdFeO_3$ structure** (Pbnm crystal structure; $a^-a^-c^+$ rot.)

Magnetic properties in bulk **difficult to characterize**:

- Difficulty of making single domain crystal samples
- Large spin-orbit coupling of the magnetic 4*d* Ru atom (900 cm^{-1})
- Large magnetocrystalline anysotropy



G. Cao *et al.*, Phys. Rev. B 56, 321 (1997)

When the field is applied along the direction of these minima, the applied field H cannot overcome the magnetic anisotropy and the magnetization does not follow the direction of H. Thus, the hard in-plane axis of the magnetization coincides with the direction at which the minima appear.[11] Note that this means that even at 9 T the magnetic anisotropy is not overcome.

Dramatic anysotropy of the magnetization in plane vs out-of-plane

G. Herranz *et al.*,
J. Appl. Phys. 97, 10M321 (2005)

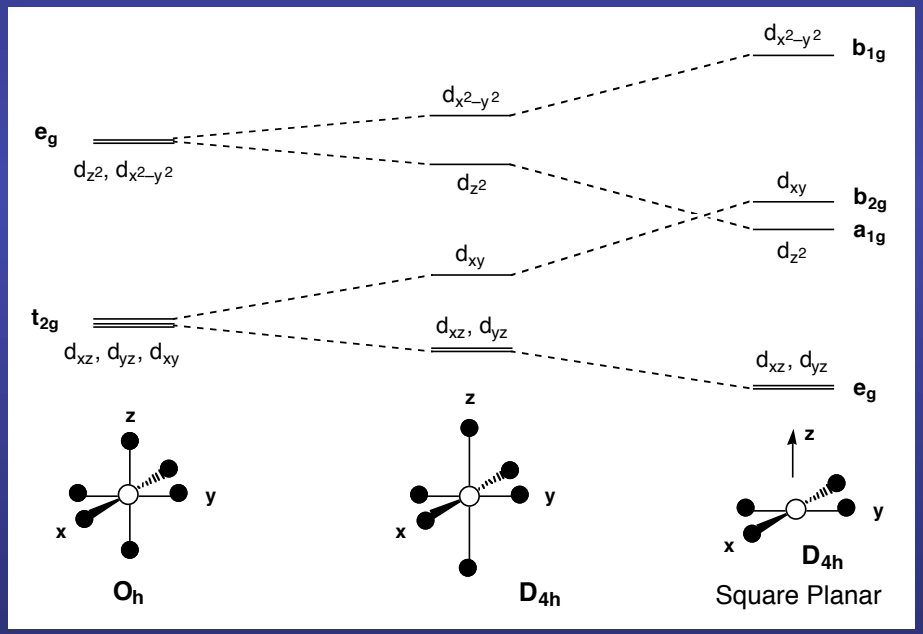
Electronic structure of $SrRuO_3$ thin films and superlattices are very different

Superlattice:

Local structure is cubic-like
The chemical environment of the Ru ions is preserved up to second nearest neighbours (nearly the same as in bulk)

Thin-films:

Loose of ligands $\Longrightarrow$ Tetragonal structure
Influence of reconstruction is much larger



$(t_{2g}^3 \uparrow, t_{2g}^1 \downarrow)$

Moment of $2\mu_B/\mathrm{f.u.}$

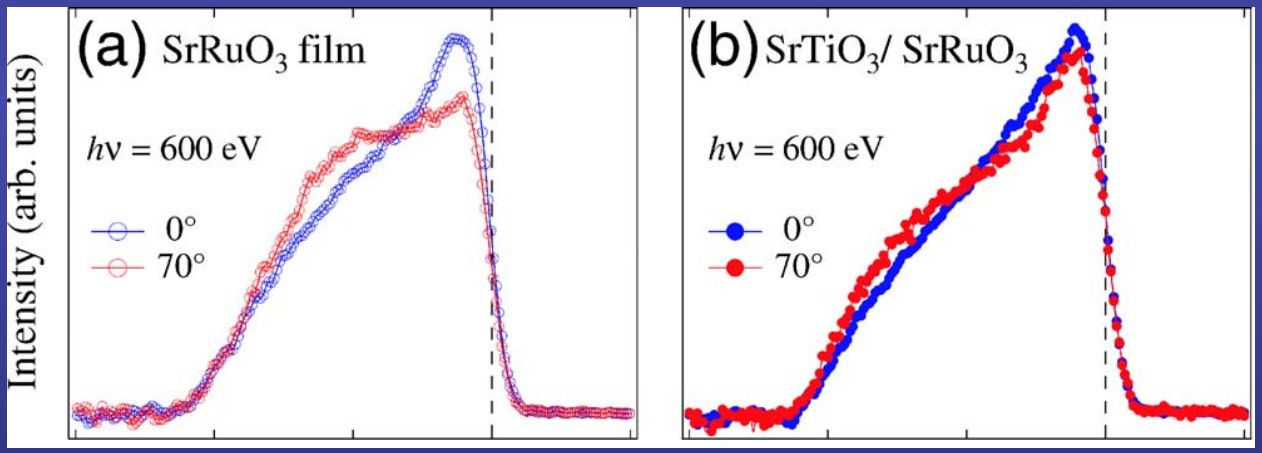
$(e_g^2 \uparrow, a_{1g}^1 \uparrow, b_{2g}^1 \uparrow)$

Moment of $4.0\mu_B/\mathrm{f.u.}$

Electronic structure of $SrRuO_3$ thin films and superlattices are very different

Superlattice:
Local structure is cubic-like
The chemical environment of the Ru ions is preserved up to second nearest neighbours (nearly the same as in bulk)

Thin-films:
Loose of ligands $\Rightarrow$ Tetragonal structure
Influence of reconstruction is much larger

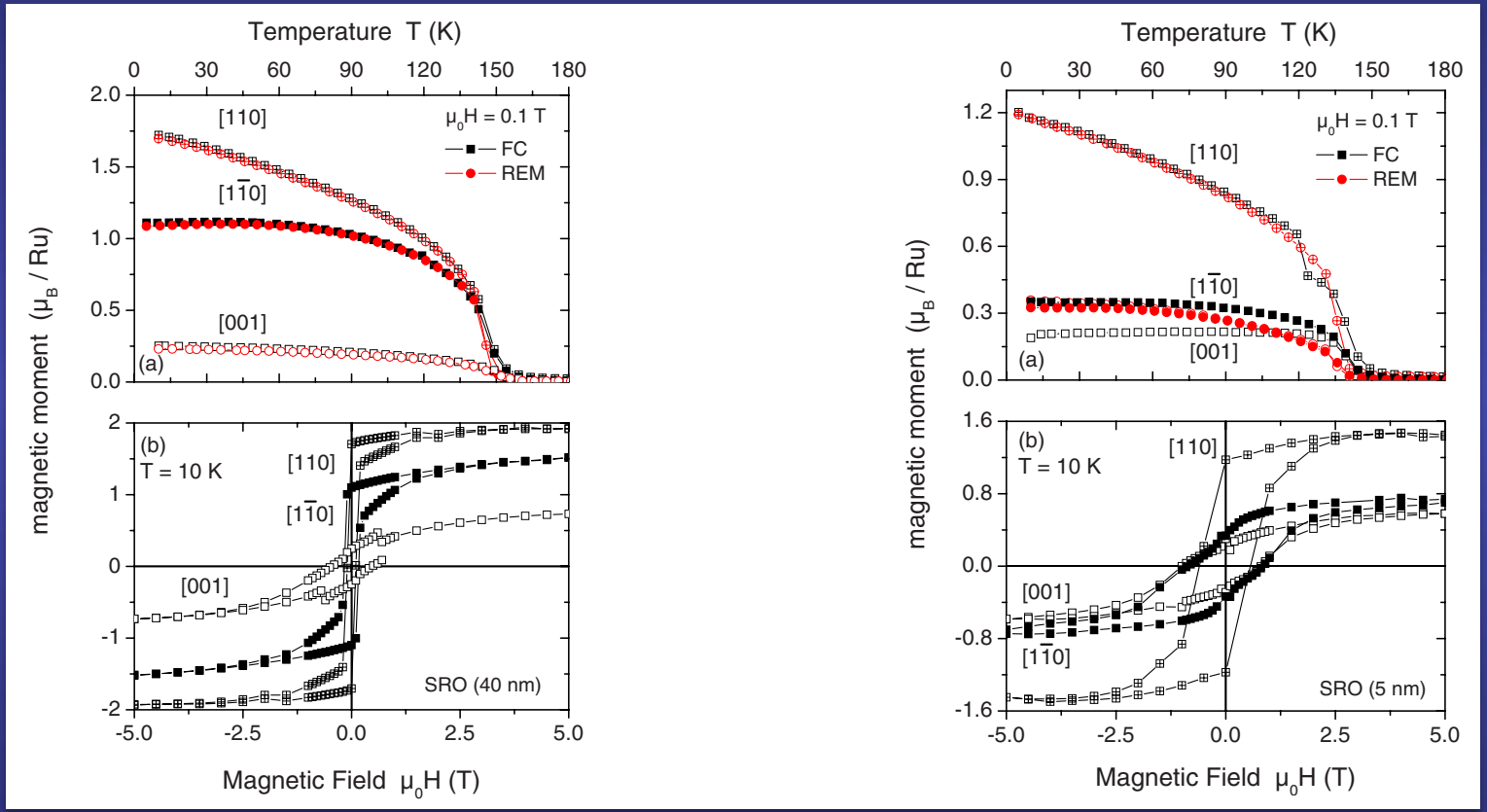


Some spectral weight is transferred from the sharp peak at E_F to a broad structure at -1.5 eV.

More remarkable for the thin film than for the superlattice

H. Kumigashira *et al.* Appl. Phys. Lett. 92, 122105 (2008)

Thin films of $SrRuO_3$ on $SrTiO_3$



40 nm thick $SrRuO_3$

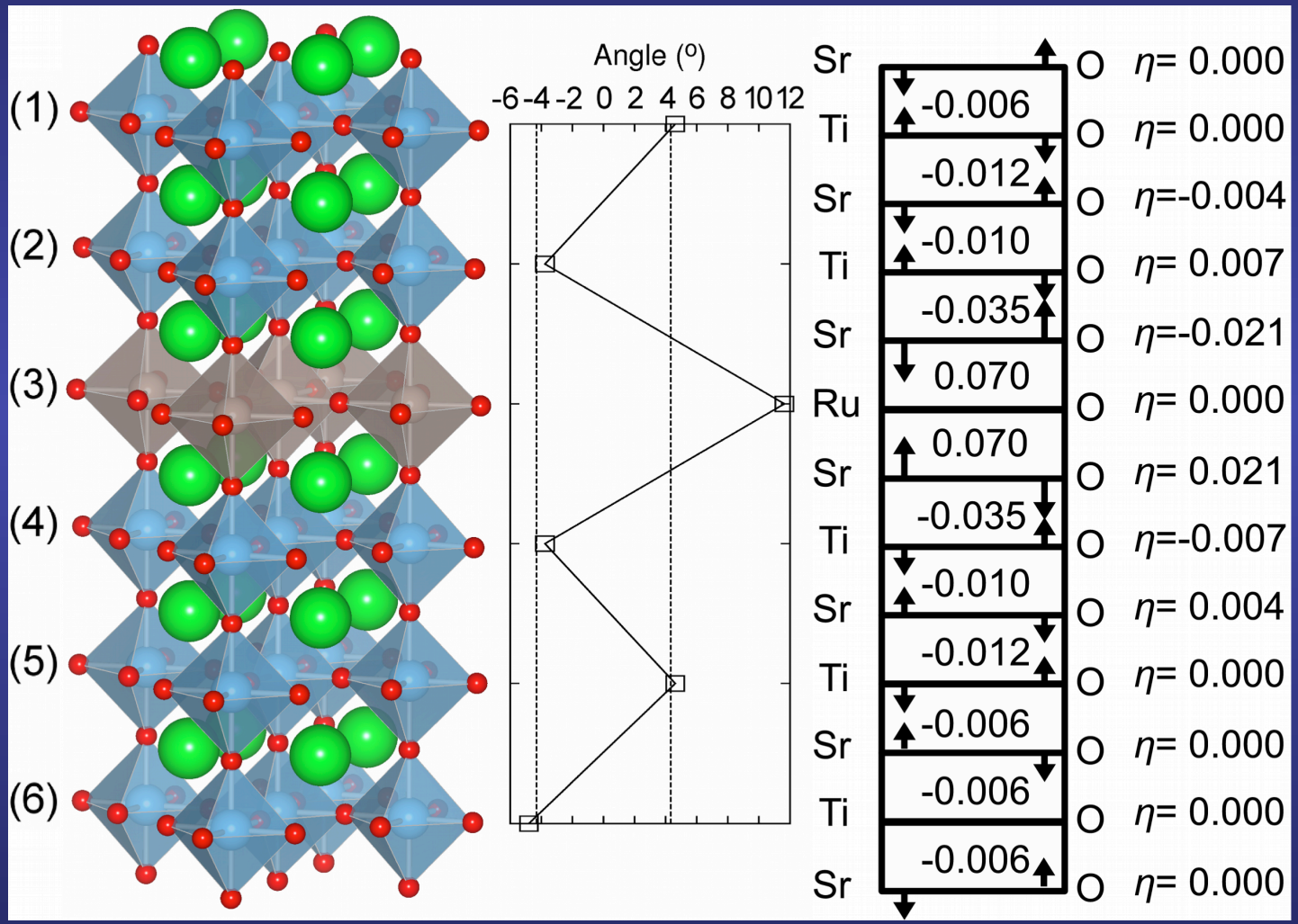
5 nm thick $SrRuO_3$

M. Ziese *et al.*, Phys. Rev. B 81, 184418 (2010)

Atomic structure of periodic $(SrTiO_3)_5/(SrRuO_3)_1$ superlattices

LSDA+U results

Units in Å



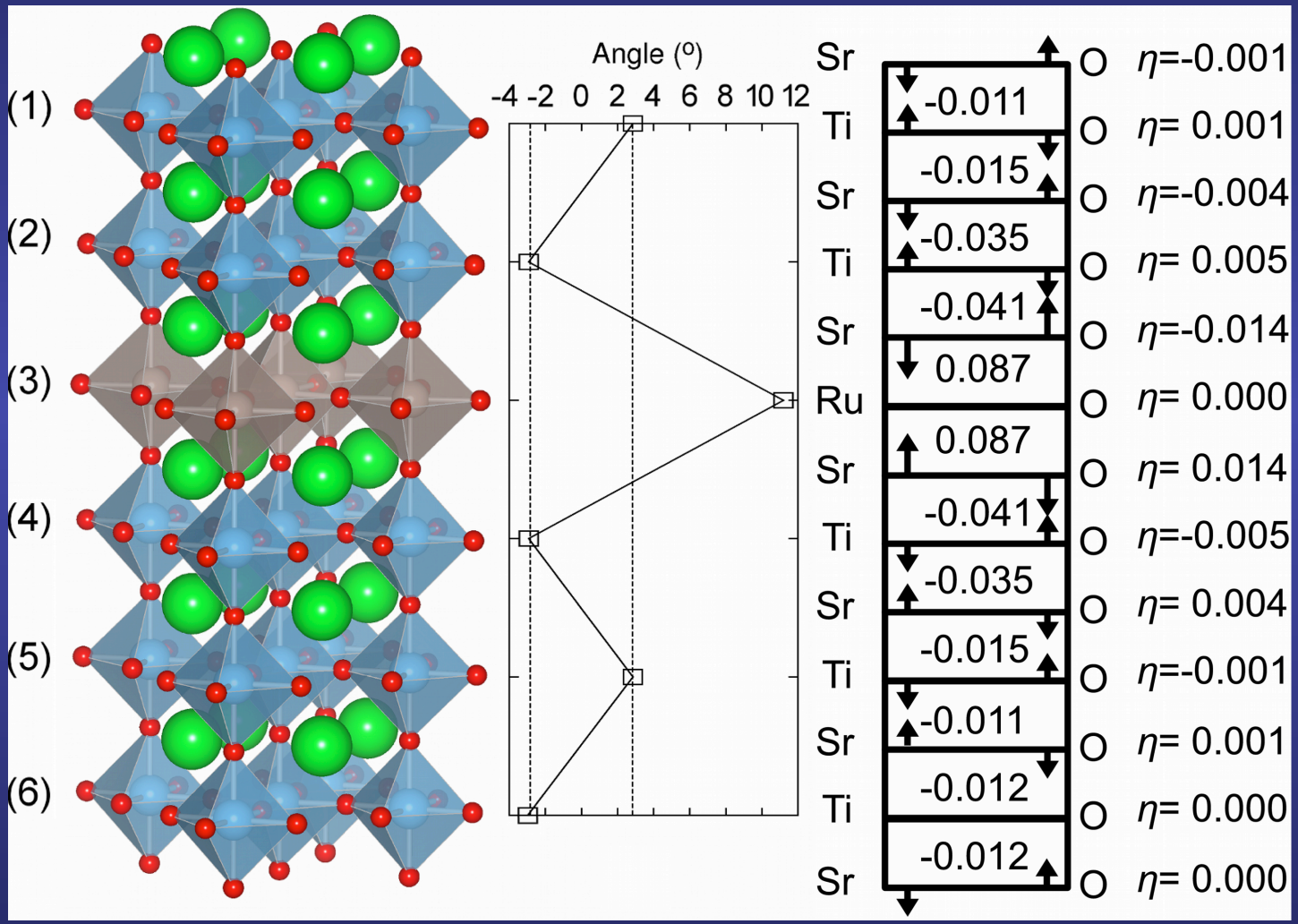
Small atomic rumplings and changes in the interplanar distances

M. Verissimo-Alves *et al.*,
Physical Review Letters 108, 107003 (2012)

Atomic structure of periodic $(SrTiO_3)_5/(SrRuO_3)_1$ superlattices

Hybrid functional B1-WC results CRYSTAL

Units in Å

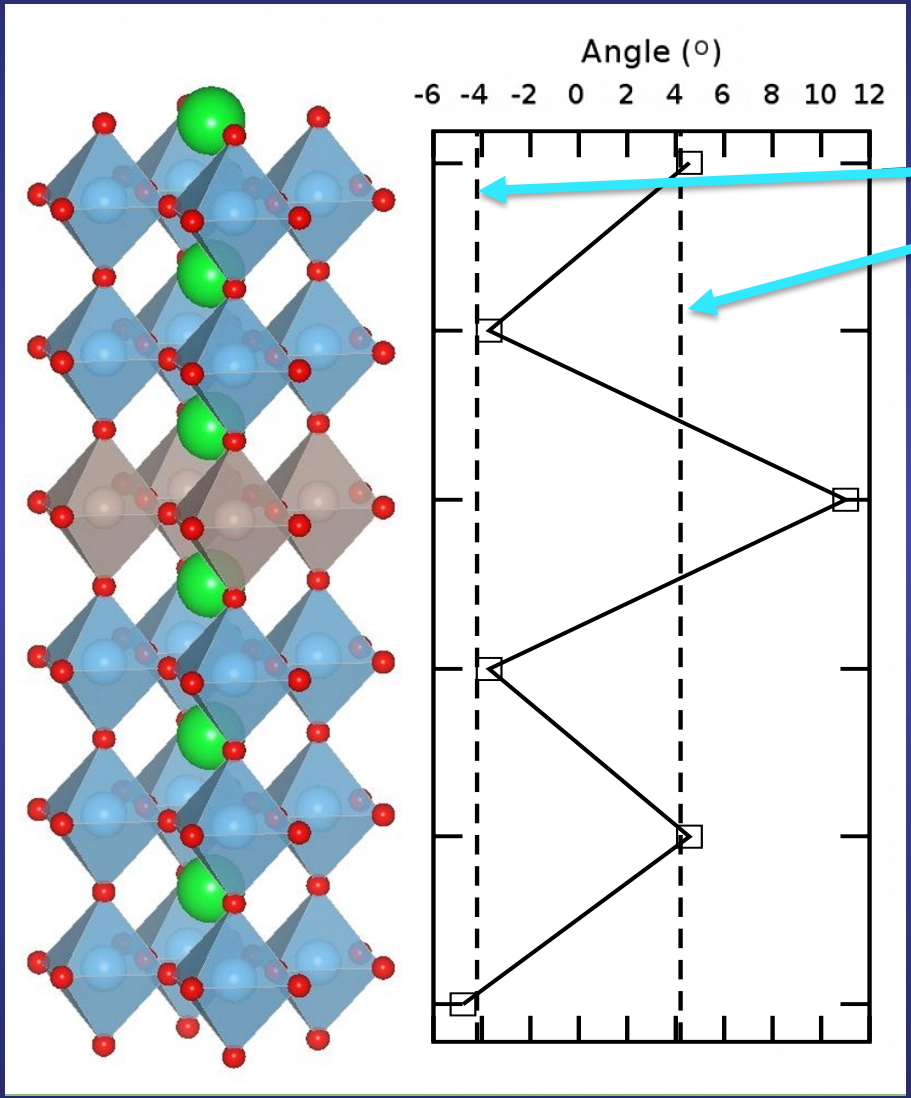


Small atomic rumplings and changes in the interplanar distances

M. Verissimo-Alves *et al.*,
Physical Review Letters 108, 107003 (2012)

Atomic structure of periodic $(SrTiO_3)_5/(SrRuO_3)_1$ superlattices

Bare LDA



Theoretical LDA value

$$\theta_{\text{bulk}}^{\text{SrTiO}_3} = 4.2^\circ$$

RuO_6 oxygen octahedra rotates 11.02°
bulk tetragonal $SrRuO_3$ under the same strain conditions rotates 11.3°

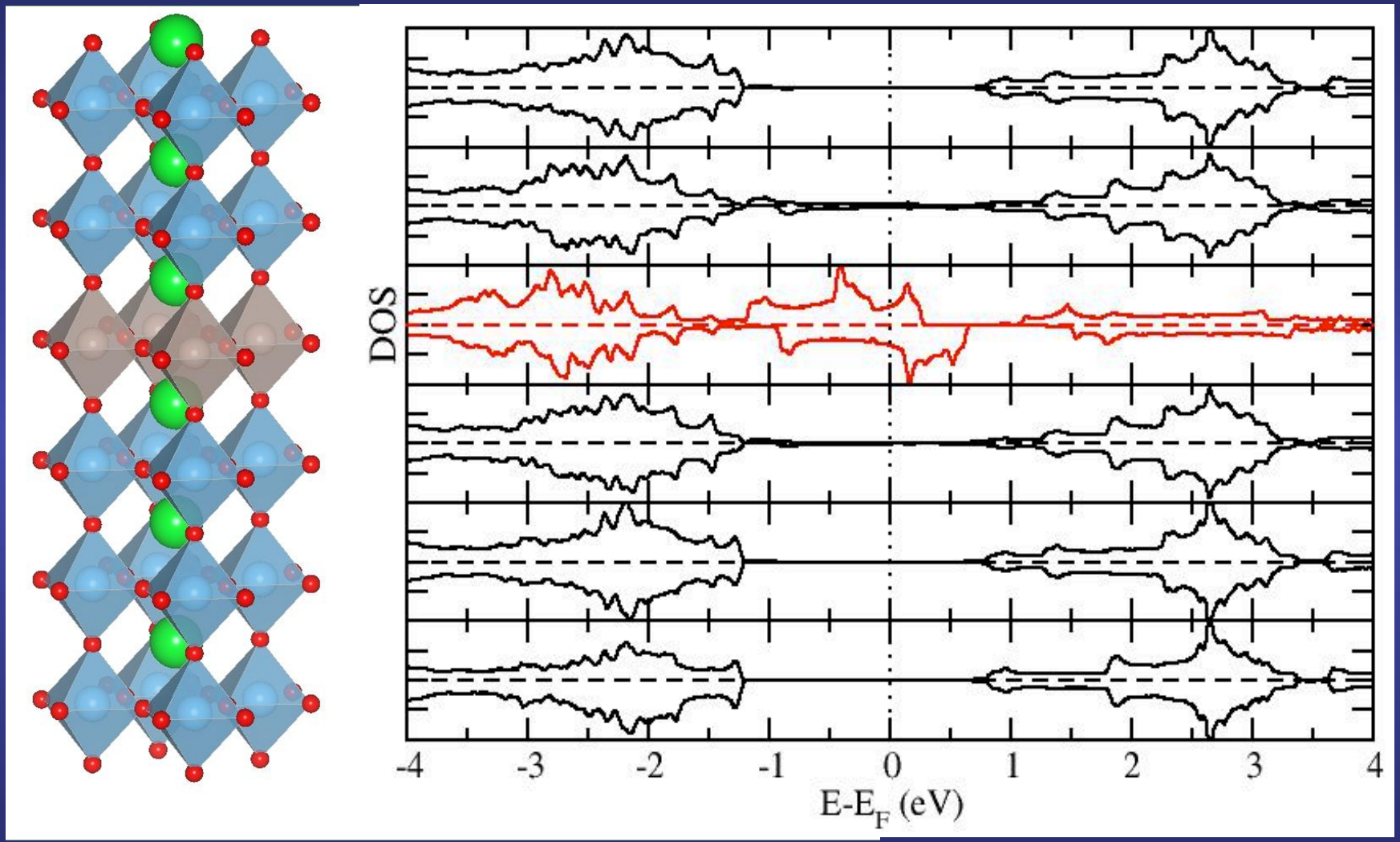
Interactions between RuO_2 planes well screened already with 5 layers of $SrTiO_3$

M. Verissimo-Alves *et al.*,
Physical Review Letters 108, 107003 (2012)

Electronic structure of periodic $(SrTiO_3)_5/(SrRuO_3)_1$ superlattices

Bare LDA

$\mu_{\mathrm{Ru}} = 0.7\mu_{\mathrm{B}}$

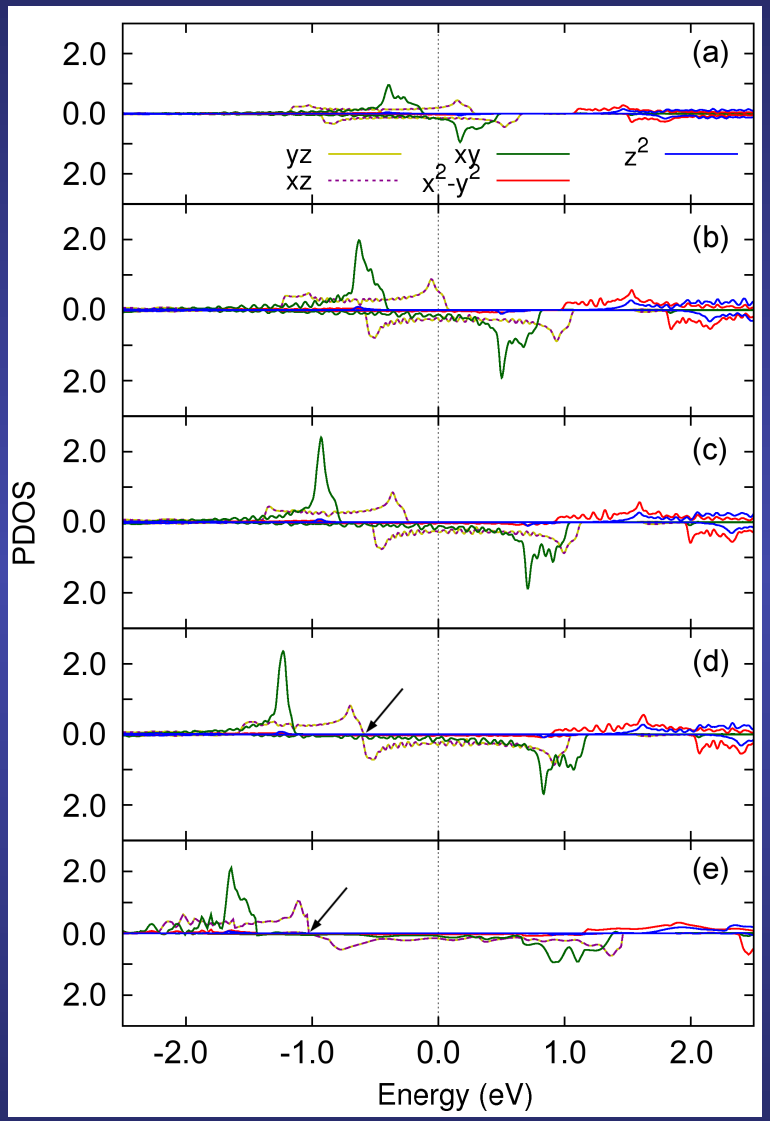


M. Verissimo-Alves *et al.*,
Physical Review Letters 108, 107003 (2012)

2DEG exhibit magnetism with magnetic moment $\mu = 1.0\mu_{\mathrm{B}}$ per $SrRuO_3$ unit cell

Effect of the U_{eff}

PDOS on the atomic orbitals of Ru atom



U_{eff} = 0.0 eV

U_{eff} = 1.0 eV

U_{eff} = 2.5 eV

U_{eff} = 4.0 eV

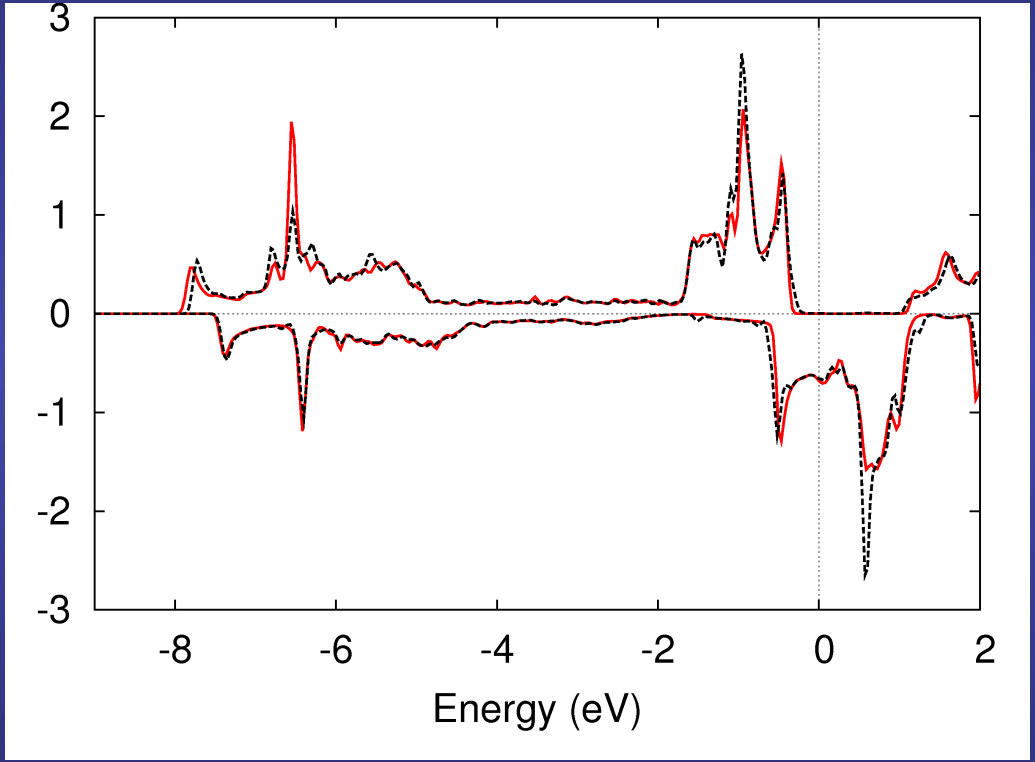
B1-WC functional

Calculations carried out at the frozen LSDA relaxed geometry

M. Verissimo-Alves *et al.*,
Physical Review Letters 108, 107003 (2012)

Effect of the spin-orbit interaction

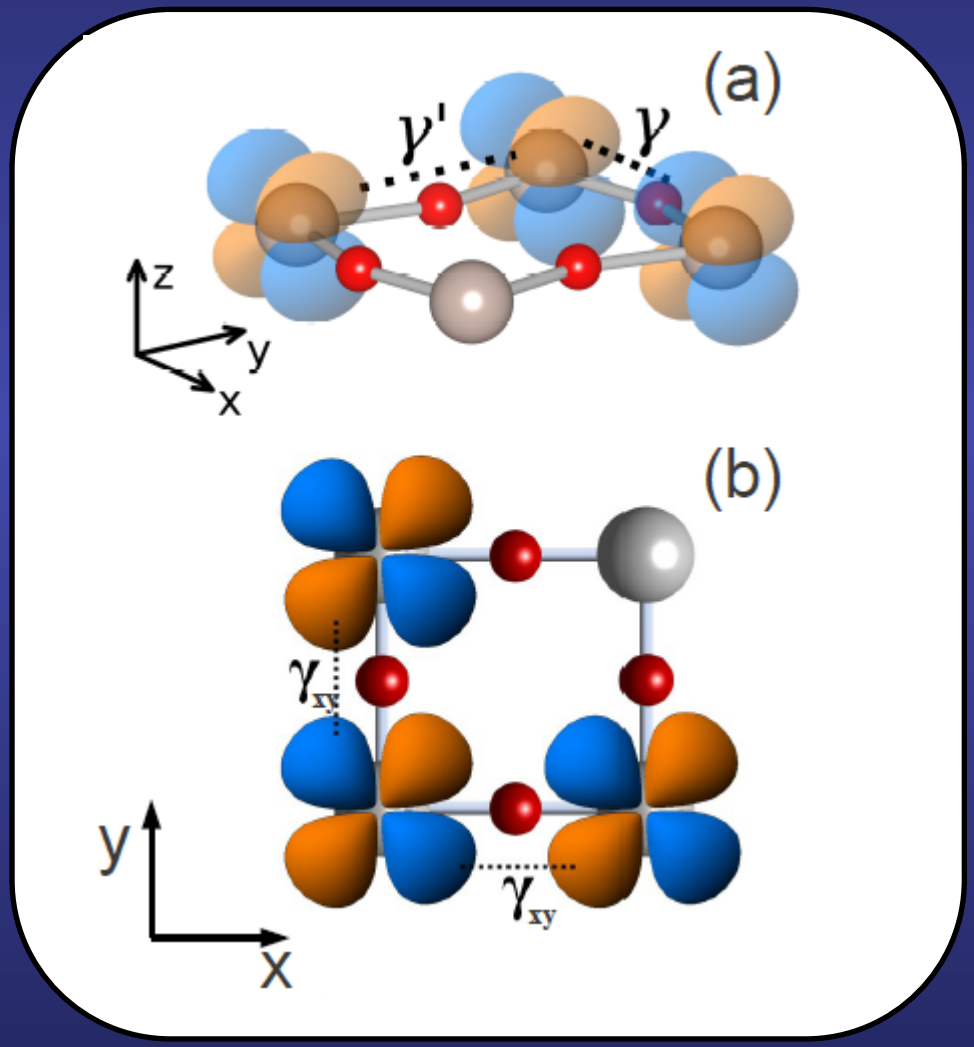
Hybrid functional B1-WC results WIEN-2K



M. Verissimo-Alves *et al.*,
Physical Review Letters 108, 107003 (2012)

Is the electron gas a 2DEG or 1DEG?

The minority spin DOS resembles that of a 1D tight-binding model



The xz bands have only a large TB constant along x

The 2DEG is formed of degenerate orthogonal 1DEGs (xz, yz)

The in-plane xy band has two large TB constants

Electrons would form a 2DEG

BOLTZTRAP approach to compute the transport tensors

BOLTZTRAP

G. H. Madsen and D. J. Singh, Computer Physics Communications 175, 67 (2006)

From the electronic band structure, we can compute the group velocities

$$v_\alpha(i,\vec{k}) = \frac{1}{\hbar}\frac{\partial \varepsilon_{i,\vec{k}}}{\partial k_\alpha}$$

and then the conductivity tensors

$$\sigma_{\alpha\beta}(i,\vec{k}) = e^2 \tau_{i,\vec{k}} v_\alpha(i,\vec{k}) v_\beta(i,\vec{k})$$

Simplest approximation for the relaxation time: keep it constant

The transport tensors can then be calculated from the conductivity distributions

$$\sigma_{\alpha\beta}(T;\mu) = \frac{1}{\Omega}\int \sigma_{\alpha\beta}(\varepsilon)\left[-\frac{\partial f_\mu(T;\varepsilon)}{\partial \varepsilon}\right] d\varepsilon \qquad \nu_{\alpha\beta}(T;\mu) = \frac{1}{eT\Omega}\int \sigma_{\alpha\beta}(\varepsilon)(\varepsilon-\mu)\left[-\frac{\partial f_\mu(T;\varepsilon)}{\partial \varepsilon}\right] d\varepsilon$$

Finally, the Seebeck coefficient can be easily calculated

$$S_{ij} = \frac{\mathcal{E}_i}{\nabla_j T} = \sum_\alpha \frac{\nu_{\alpha j}}{\sigma_{\alpha i}}$$

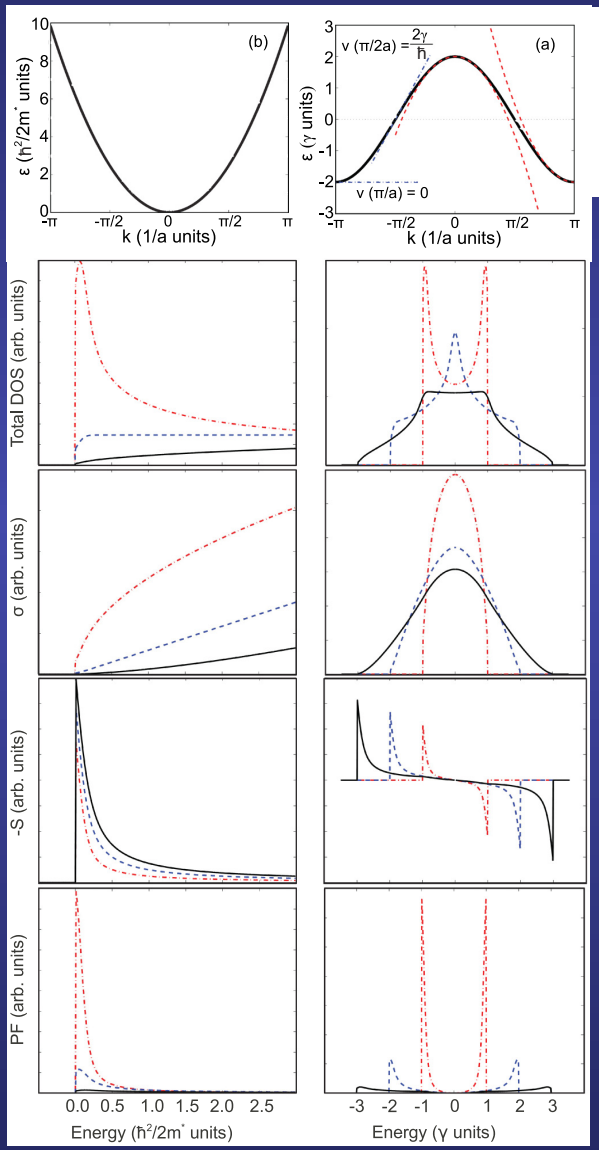
Simple models to explain the dependence of the transport functions: free-electron vs tight-binding

One band free-electron model

$$\varepsilon(\vec{k}) = \frac{\hbar^2}{2m^*}\sum_i k_i^2$$

DOS corresponds with the textbooks examples of the corresponding models

… while the free-electron ones are not



Tight-binding model

$$\varepsilon(\vec{k}) = 2\gamma\sum_i \cos(k_i a)$$

At the band bottom, both models are quite similar

The tight-binding bands are symmetrical around the center of the band…

More appropriate to describe the narrow 4d band

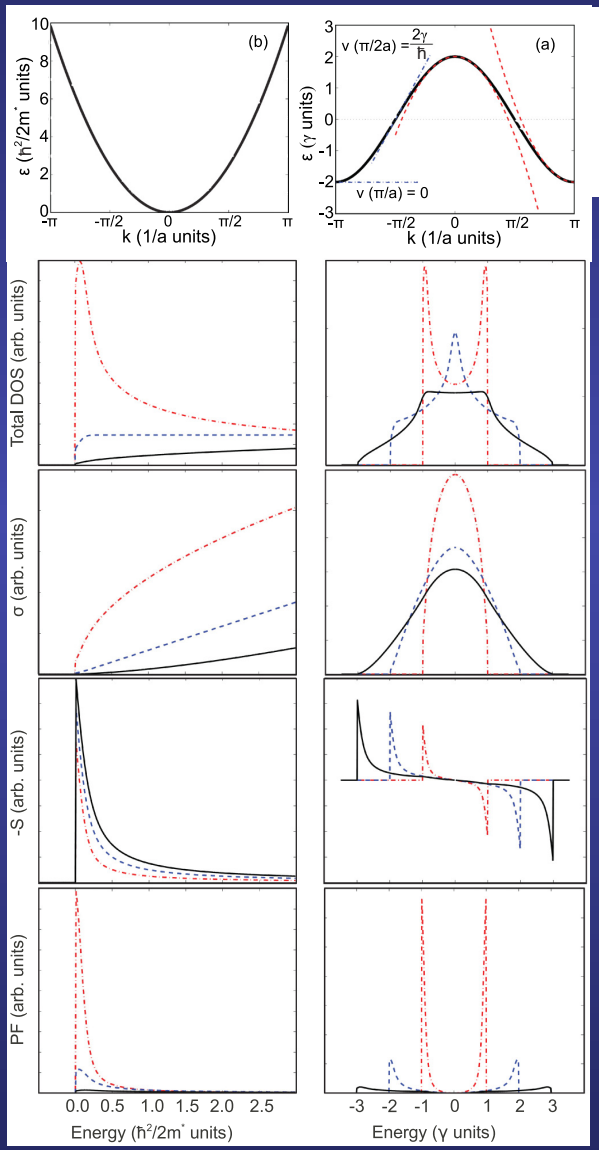
M. Verissimo-Alves *et al.* Phys. Rev. B 86, 085305 (2012)

Simple models to explain the dependence of the transport functions: free-electron vs tight-binding

One band free-electron model

$$\varepsilon(\vec{k}) = \frac{\hbar^2}{2m^*}\sum_i k_i^2$$

Conductivities are equivalent at the band bottom



1D
2D
3D

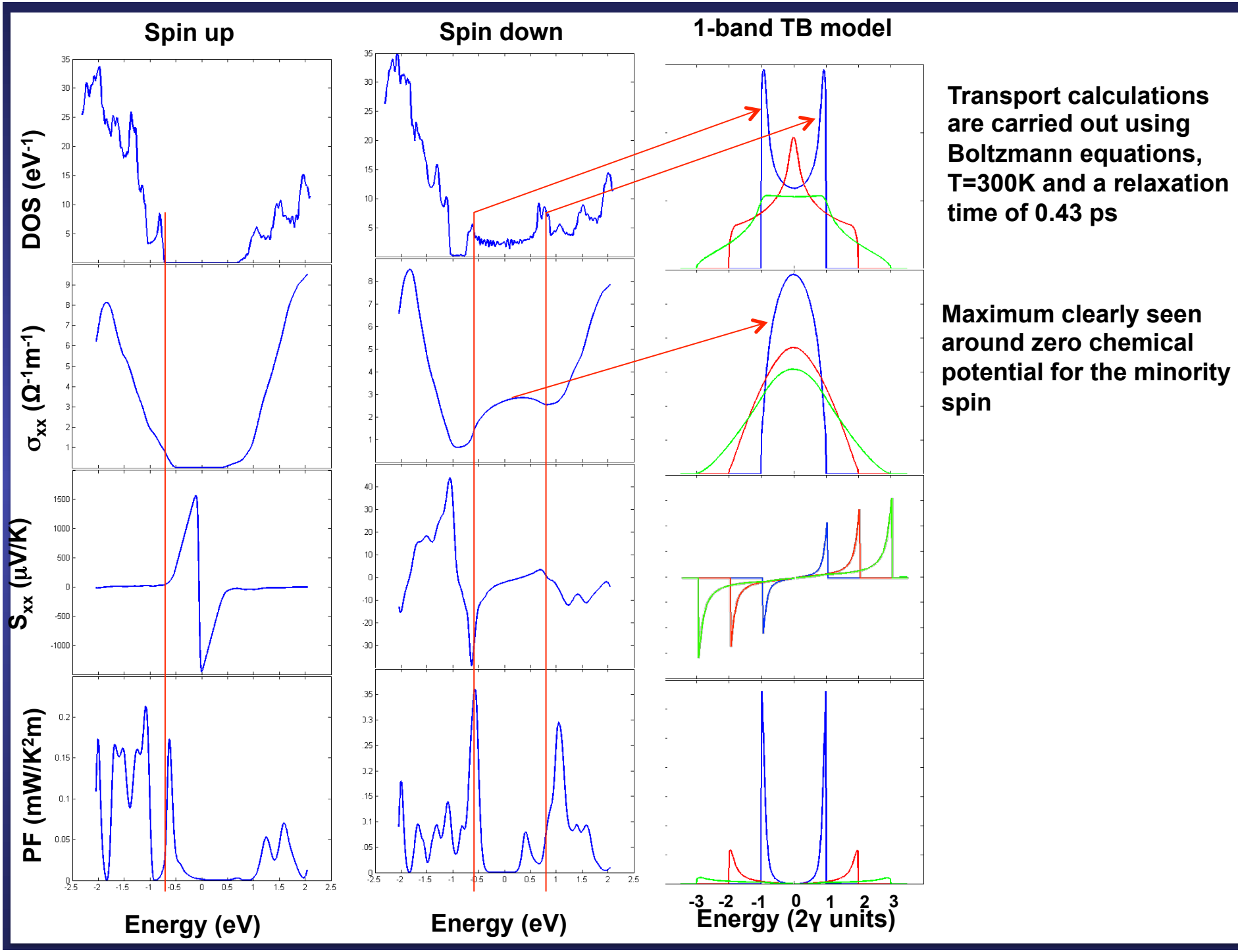
Tight-binding model

$$\varepsilon(\vec{k}) = 2\gamma\sum_i \cos(k_i a)$$

Conductivity decays in a quicker way as we approach the band bottom

Presents a maximum of the conductivity at the center of the gap (maximum of the group velocity)

M. Verissimo-Alves *et al.* Phys. Rev. B 86, 085305 (2012)



Transport calculations are carried out using Boltzmann equations, T=300K and a relaxation time of 0.43 ps

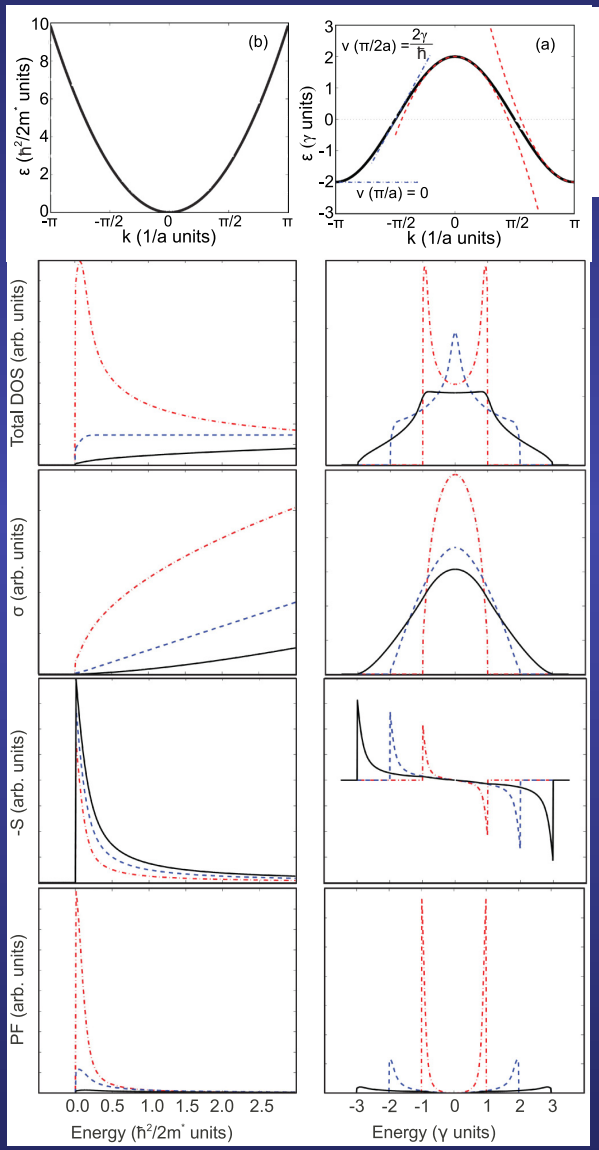
Maximum clearly seen around zero chemical potential for the minority spin

Simple models to explain the dependence of the transport functions: free-electron vs tight-binding

One band free-electron model

$$\varepsilon(\vec{k}) = \frac{\hbar^2}{2m^*}\sum_i k_i^2$$

Seebeck coefficient closely matches each other at the band bottom



1D
2D
3D

Tight-binding model

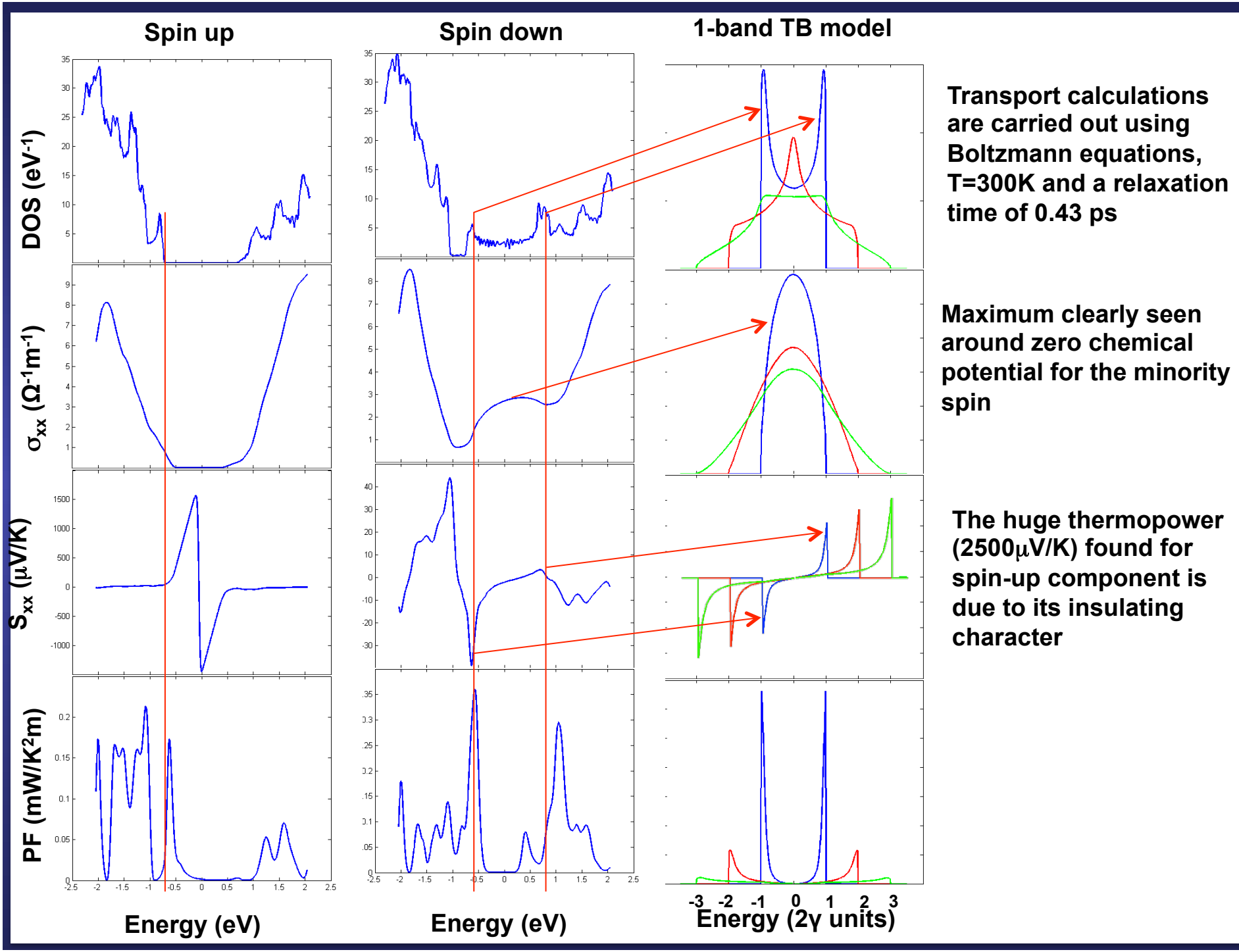
$$\varepsilon(\vec{k}) = 2\gamma\sum_i \cos(k_i a)$$

Seebeck coefficient increases with reduced dimensionality

The Seebeck coefficient changes from electrons to hole dominated behaviour

S = 0 right at the center of the band (half-filling), explaining the poor results in first-principles sim.

M. Verissimo-Alves *et al.* Phys. Rev. B 86, 085305 (2012)



Transport calculations are carried out using Boltzmann equations, T=300K and a relaxation time of 0.43 ps

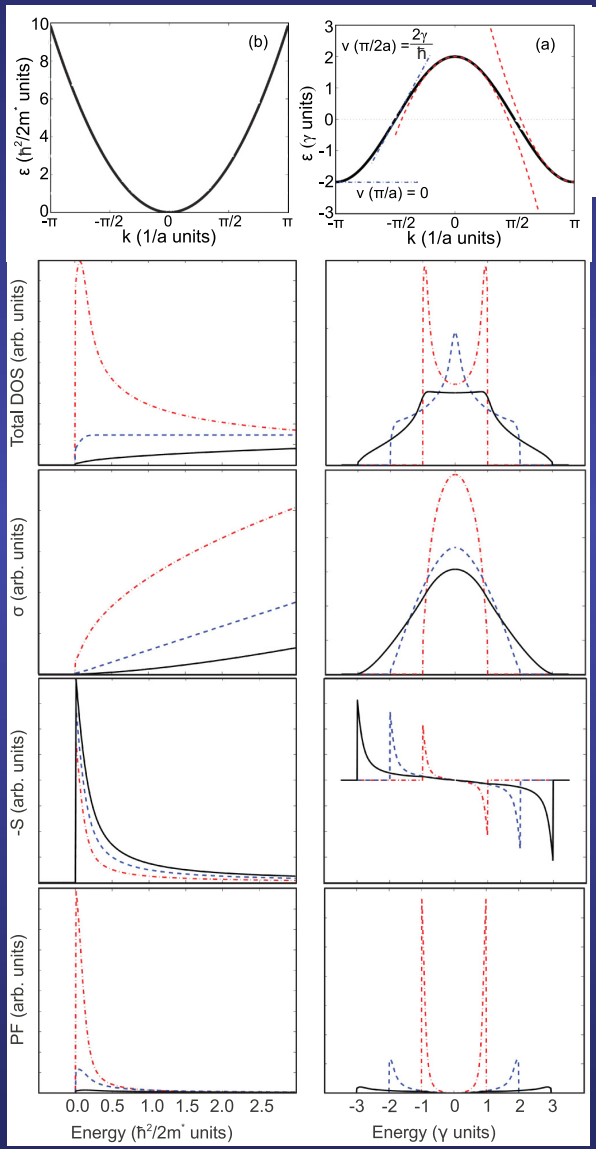
Maximum clearly seen around zero chemical potential for the minority spin

The huge thermopower (2500μV/K) found for spin-up component is due to its insulating character

Simple models to explain the dependence of the transport functions: free-electron vs tight-binding

One band free-electron model

$$\varepsilon(\vec{k}) = \frac{\hbar^2}{2m^*}\sum_i k_i^2$$



1D
2D
3D

Tight-binding model

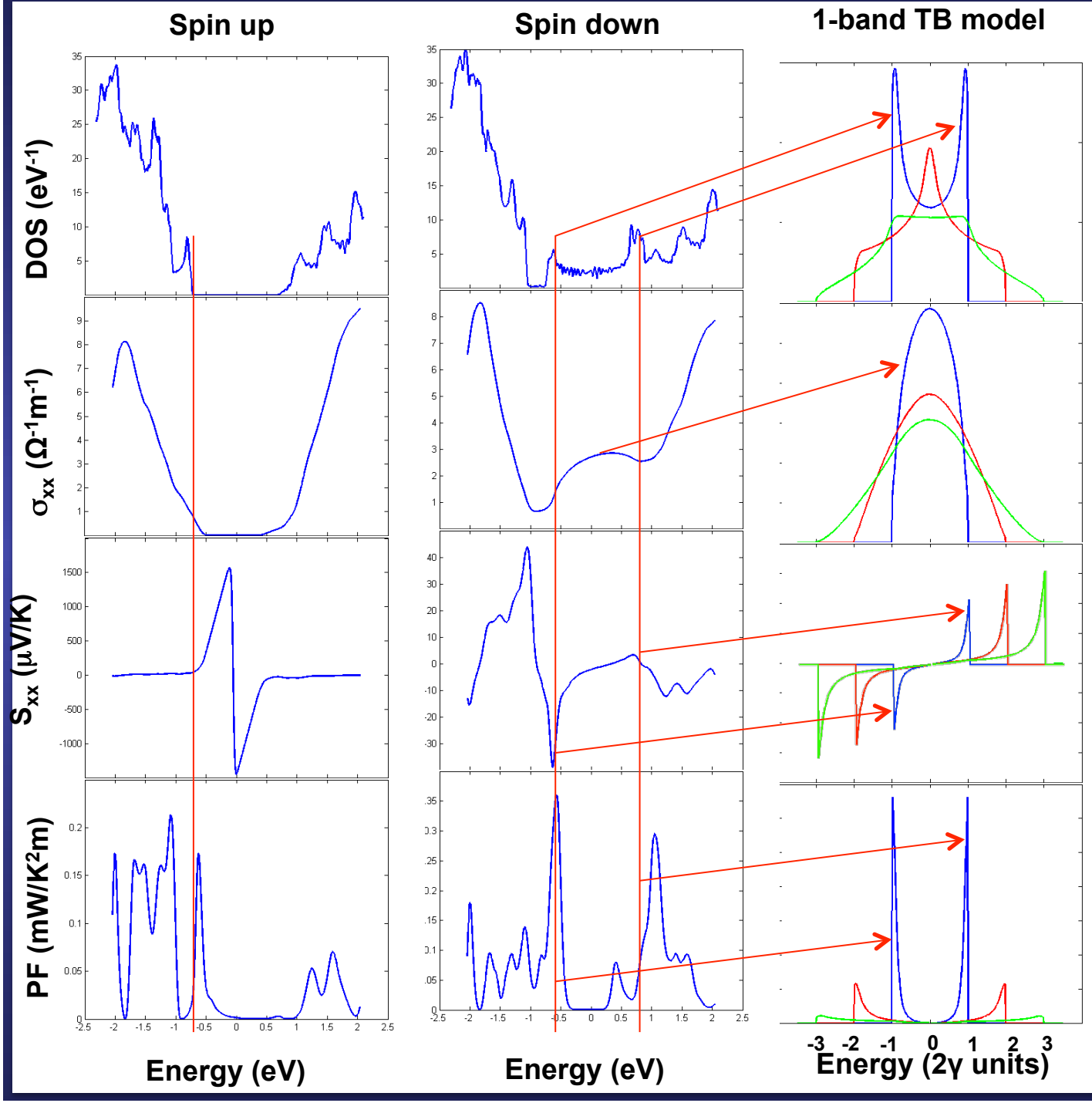
$$\varepsilon(\vec{k}) = 2\gamma\sum_i \cos(k_i a)$$

Enhancement of the power factor at optimal doping, locating the chemical potential close to the band bottom

The power factor is significantly enhanced when the dimensionality is reduced (as in the Hicks and Dresselhaus)

No large enough to use STO/SRO/STO as thermoelectric

M. Verissimo-Alves *et al.* Phys. Rev. B 86, 085305 (2012)

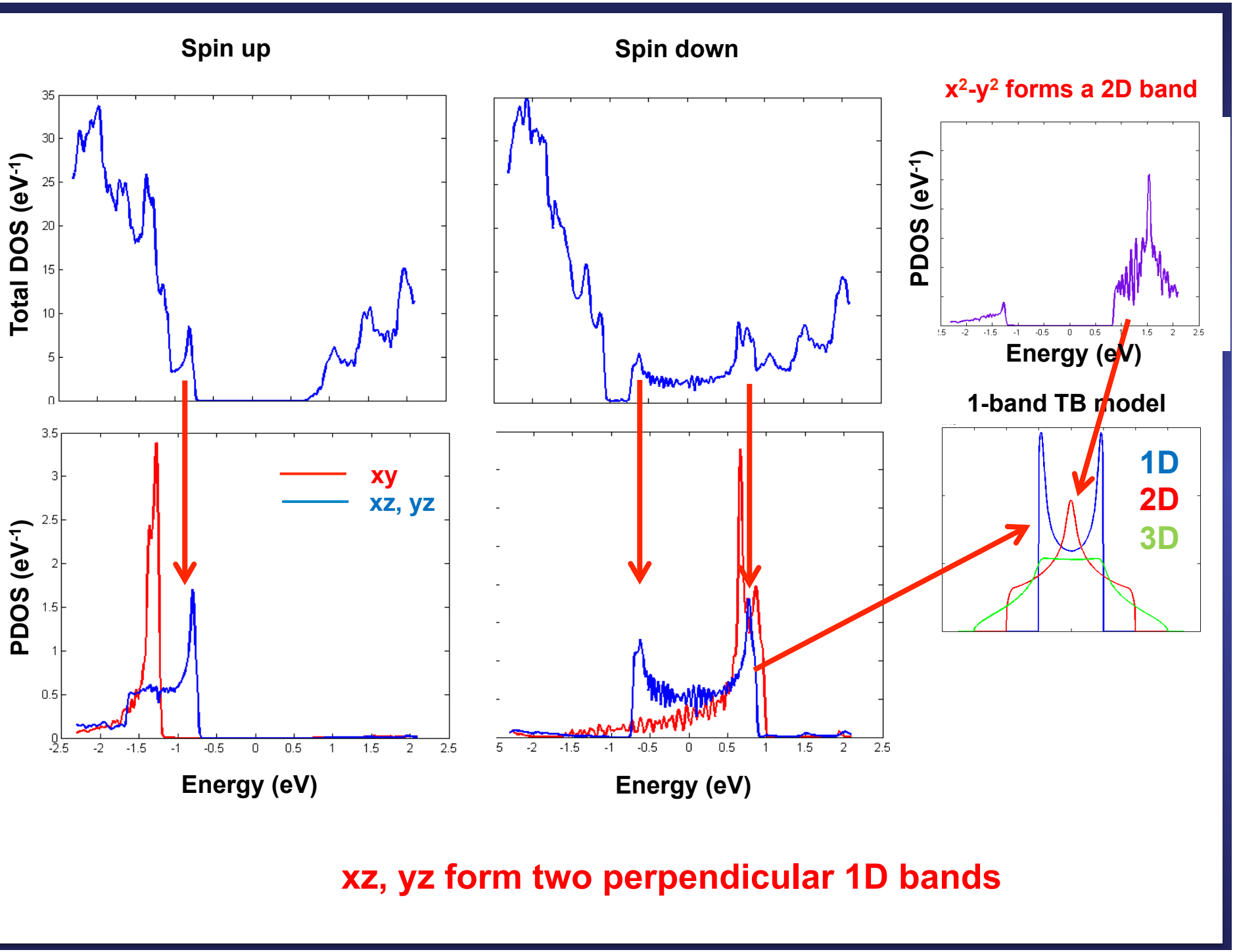


Transport calculations are carried out using Boltzmann equations, T=300K and a relaxation time of 0.43 ps

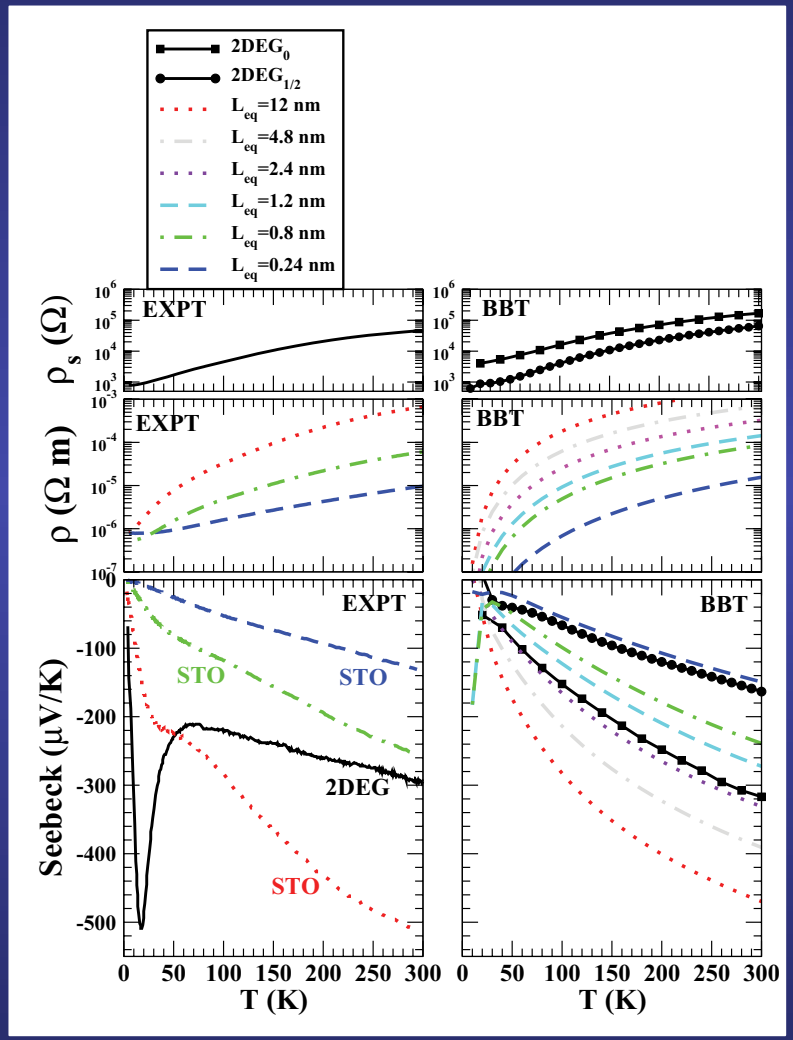
Maximum clearly seen around zero chemical potential for the minority spin

The huge thermopower (2500μV/K) found for spin-up component is due to its insulating character

While at the Fermi energy the Power Factor is very low a huge increase is found at the band edge to 0.35mW/K^{2}m


Spin up
Spin down
Total DOS (eV-1)
PDOS (eV-1)
xy
xz, yz
Energy (eV)
Energy (eV)
x2-y2 forms a 2D band
PDOS (eV-1)
Energy (eV)
1-band TB model
1D
2D
3D
xz, yz form two perpendicular 1D bands

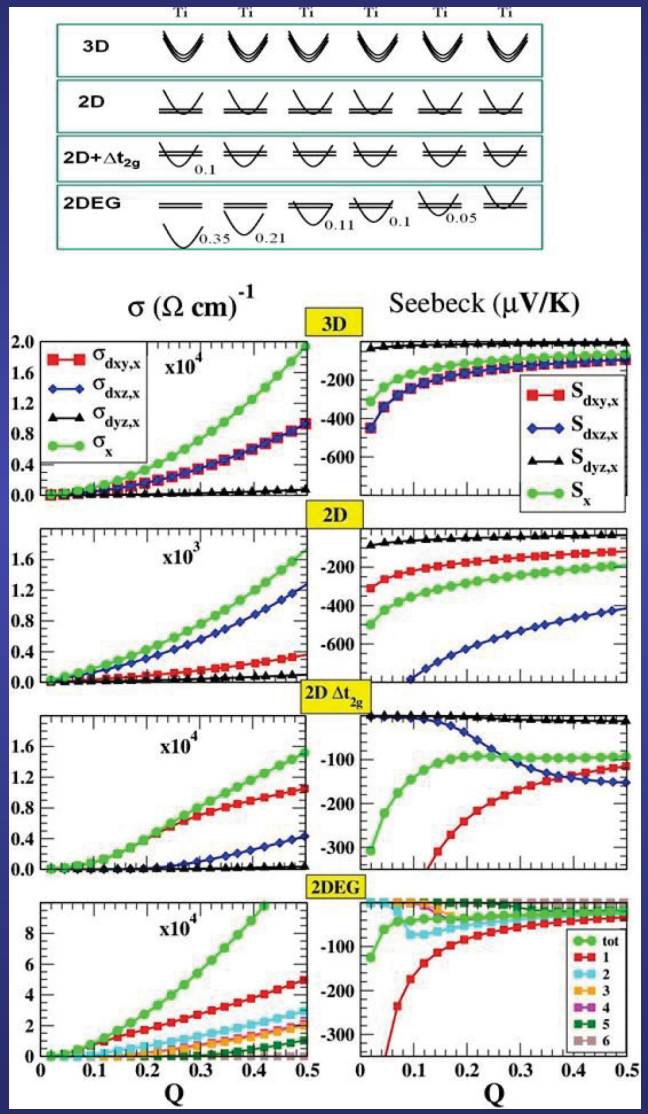
Quantum confinement does not enhance the thermoelectric power of 2DEG at $SrTiO_3/LaAlO_3$



Experiment and theory coherently report Seebeck coefficients larger in bulk $SrTiO_3$ than in $SrTiO_3/LaAlO_3$

A. Filippetti *et al.* Phys. Rev. B 86, 195301 (2012)
I. Pallecchi *et al.* Phys. Rev. B 81, 085414 (2010)

Quantum confinement does not enhance the thermoelectric power of 2DEG at $SrTiO_3/LaAlO_3$



Two dimensions: the different effective masses change occupancy, reduce chemical potential and increase the Seebeck coefficient

On-site splitting: d_{xy} orbitals occupied, increase of the chemical potential and reduction of the Seebeck

Inter-site splitting: only the d_{xy} of the interfacial layer contribute orbitals occupied, increase of the chemical potential and reduction of the Seebeck

A. Filippetti *et al.* Phys. Rev. B 86, 195301 (2012)
I. Pallecchi *et al.* Phys. Rev. B 81, 085414 (2010)