Thin films: new physics and applications ?

Oberseminar 2007

Hao Tjeng

Lehrstuhl für Angewandte Physik II. Physikalisches Institut, Universität zu Köln

Can we use thin films to create new materials, new properties and new devices ?

Yes, but one needs to understand the 'physics', i.e. need to understand what happens to the electronic structure !

- Modification of material properties due to proximity of substrate:
 - strain
 - screening
 - charge donation
- New material compositions: non-existent in bulk, but stabilized in film
- New sample preparation routes: MBE combined with distillation and control of stoichiometry during growth by resistivity measurements

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Nature <u>394</u>, 453 (1998).

Doubling the critical temperature of La_{1.9}Sr_{0.1}CuO₄ using epitaxial strain

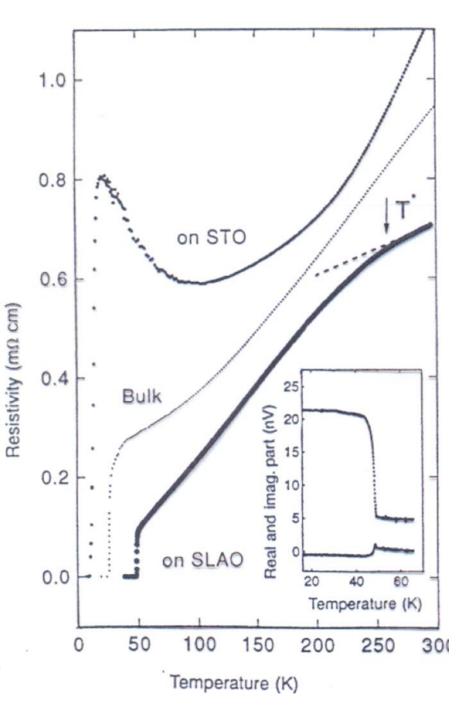
J.-P. Locquet*, J. Perret*†, J. Fompeyrine*‡, E. Mächler*, J. W. Seo*† & G. Van Tendeloo§

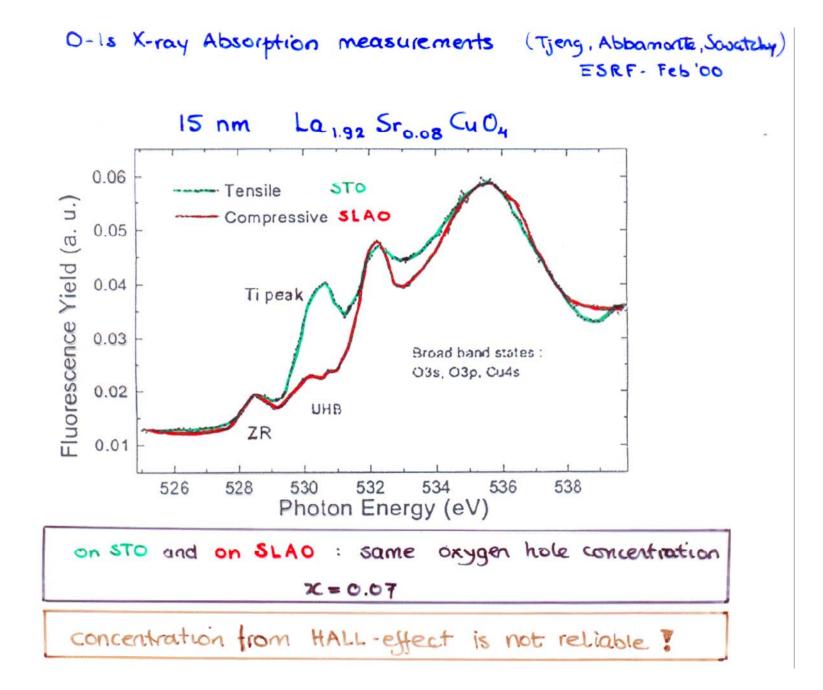
* IBM Research Division, Zurich Research Laboratory, CH-8803 Rüschlikon, Switzerland

† Institut de Physique, Université de Neuchâtel, CH-2000 Neuchâtel, Switzerland ‡ Institute of Inorganic Chemistry, University of Bern, CH-3012 Bern, Switzerland § EMAT, RUCA, University of Antwerp, B-2020 Antwerpen, Belgium

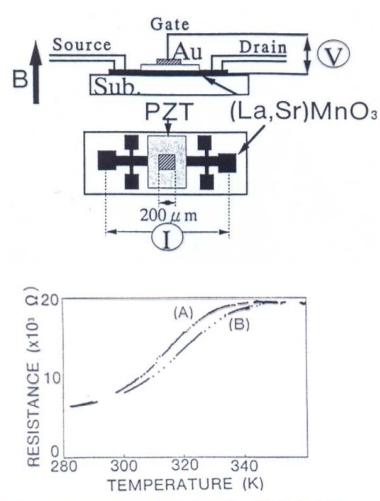
	X=0.10	X = 0.16 (opt.)
STO	Tc = IOK	
Bulk	$T_c = 25 K$	$T_c = 37 \text{ K}$
SLAO	Tc = 49 K	

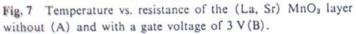
Figure 4 Resistivity versus temperature for the two films grown simultaneously and for the bulk x = 0.10 sample²⁶. Data were obtained using a four-point method. Inset, Real and imaginary parts of the a.c. susceptibility of the film on SLAO, which reveals a sharp, single-phase transition $\Delta T_c = 0.7$ K; the transition width of the film on STO is $\Delta T_c = 4$ K.





PAPER Special Issue on New Concept Device and Novel Architecture LSIs Novel Electronic Properties on Ferroelectric / Ferromagnetic Heterostructures





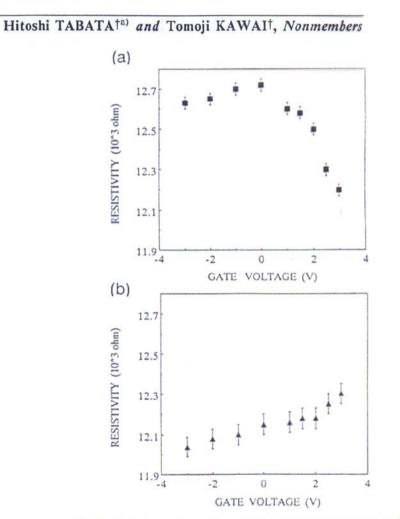
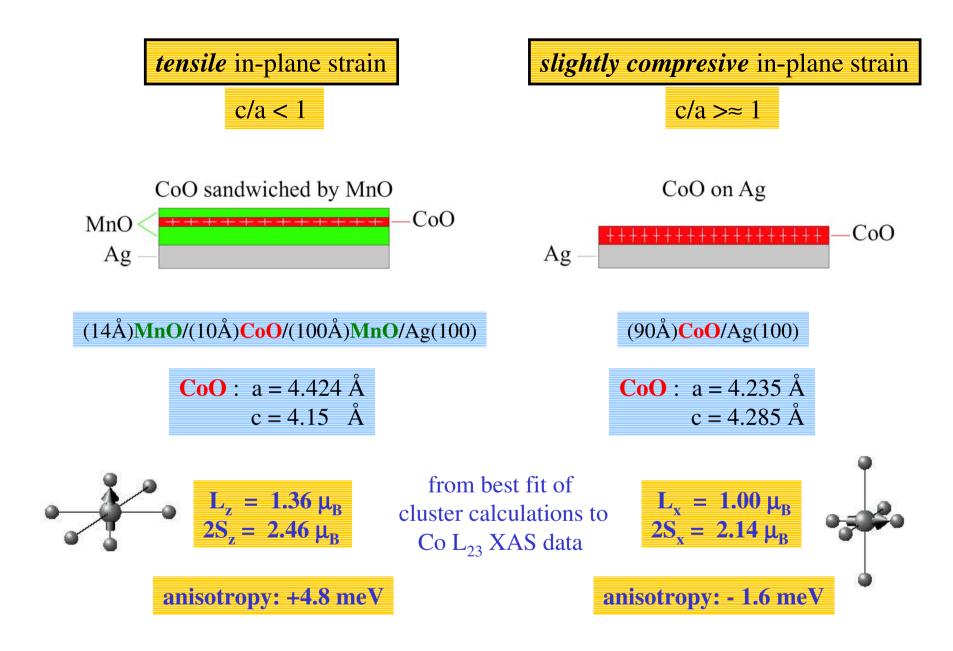
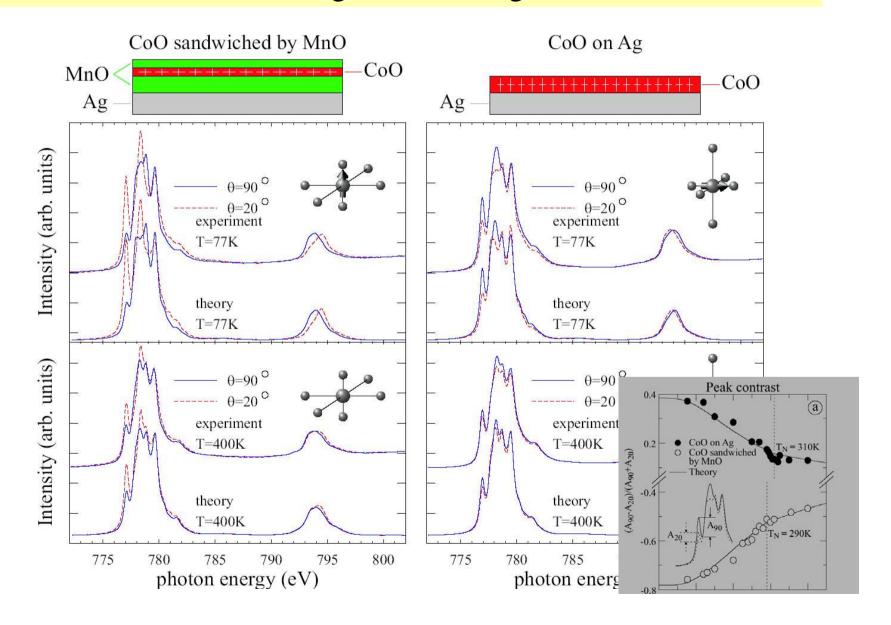
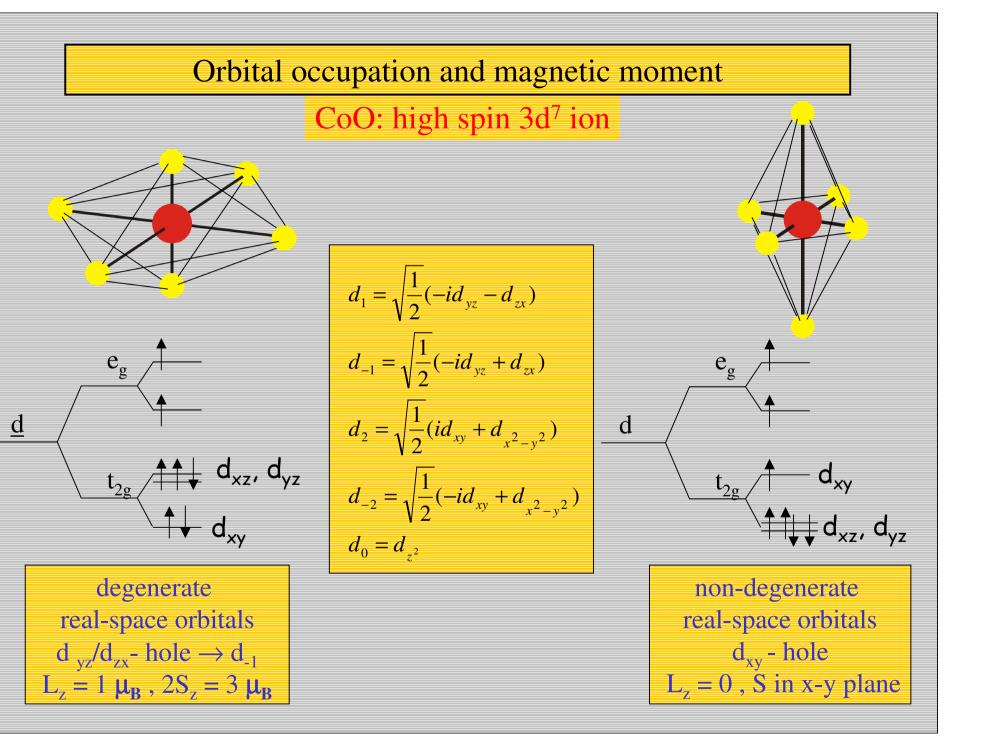


Fig. 8 Relation between the resistivity of ferroelectric LSMO layer and the gate voltage applied at a gate electrode (a) without magnetic filed and (b) with magnetic field of 0.3 T (3000 G).



Cluster calculations establish orientation and magnitude of magnetic moments





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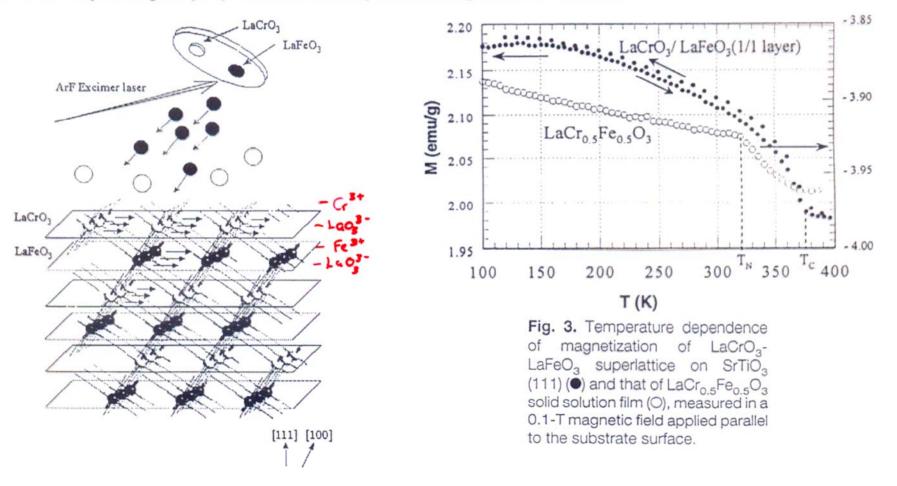
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Ferromagnetism in LaFeO₃-LaCrO₃ Superlattices

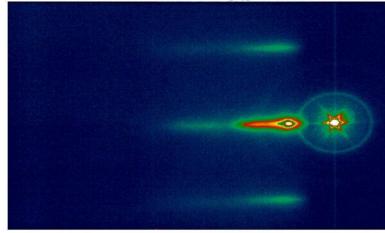
Kenji Ueda, Hitoshi Tabata, Tomoji Kawai*

Ferromagnetic spin order has been realized in the LaCrO₃-LaFeO₃ superlattices. Ferromagnetic coupling between Fe³⁺ and Cr³⁺ through oxygen has long been expected on the basis of Anderson, Goodenough, and Kanamori rules. Despite many studies of Fe-O-Cr-based compounds, random positioning of Fe³⁺ and Cr³⁺ ions has frustrated the observation of ferromagnetic properties. By creating artificial superlattices of Fe³⁺ and Cr³⁺ layer along the [111] direction, ferromagnetic ordering has been achieved.

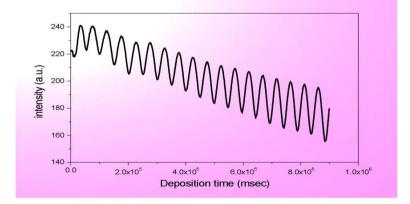


Stabilizing rocksalt $Cr_{1-x}O$ by epitaxial growth

RHEED on 18 ML Cr_{1-x}O on MgO(100)



RHEED intensity vs. deposition time



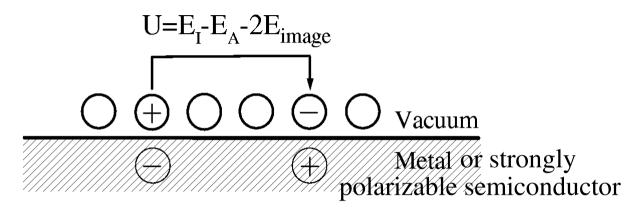
- 0 < x < 0.3
- defect structure (ordered)
- multilayers Cr_{1-x}O/MgO

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Modification of material properties using image charge screening



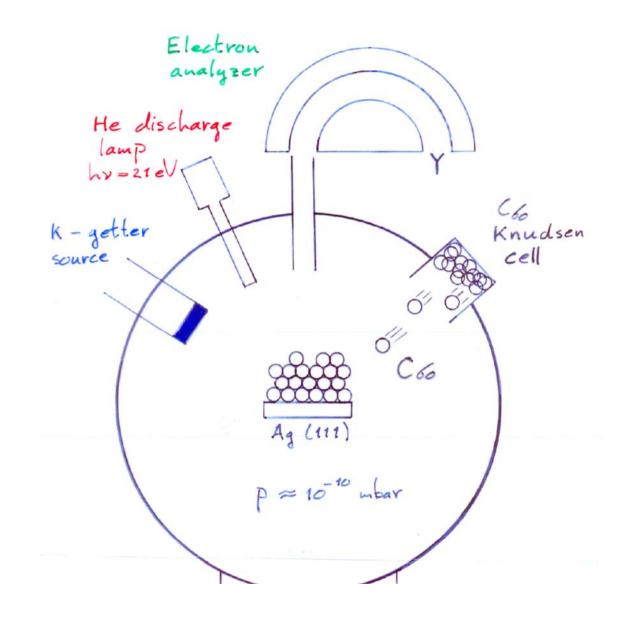
Reduction of charge excitation energies:

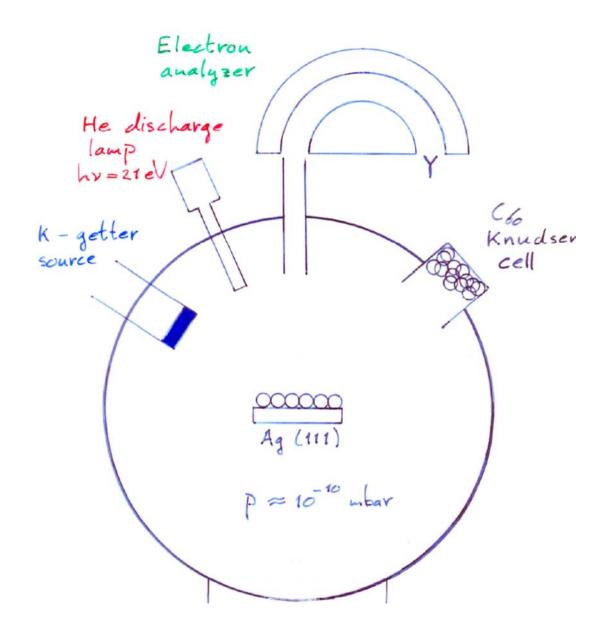
Examples from experiments:

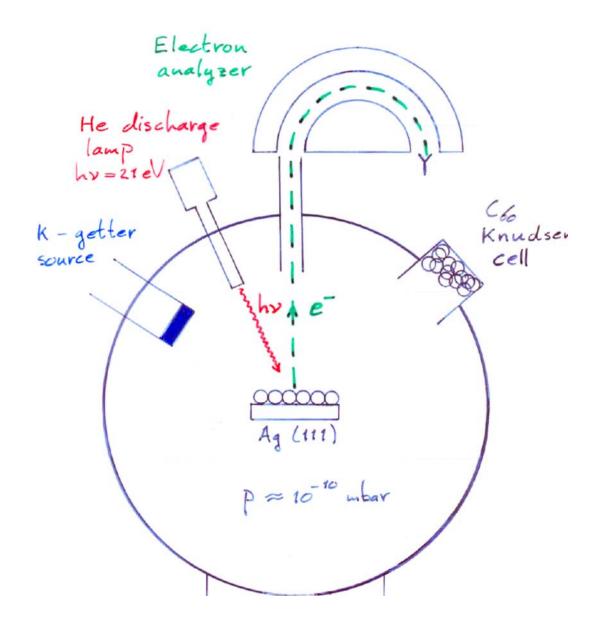
•Monolayer C_{60} on Ag : U and E_g reduced by 1 eV •thin oxide film on Ag : U and Δ reduced by 1-2 eV

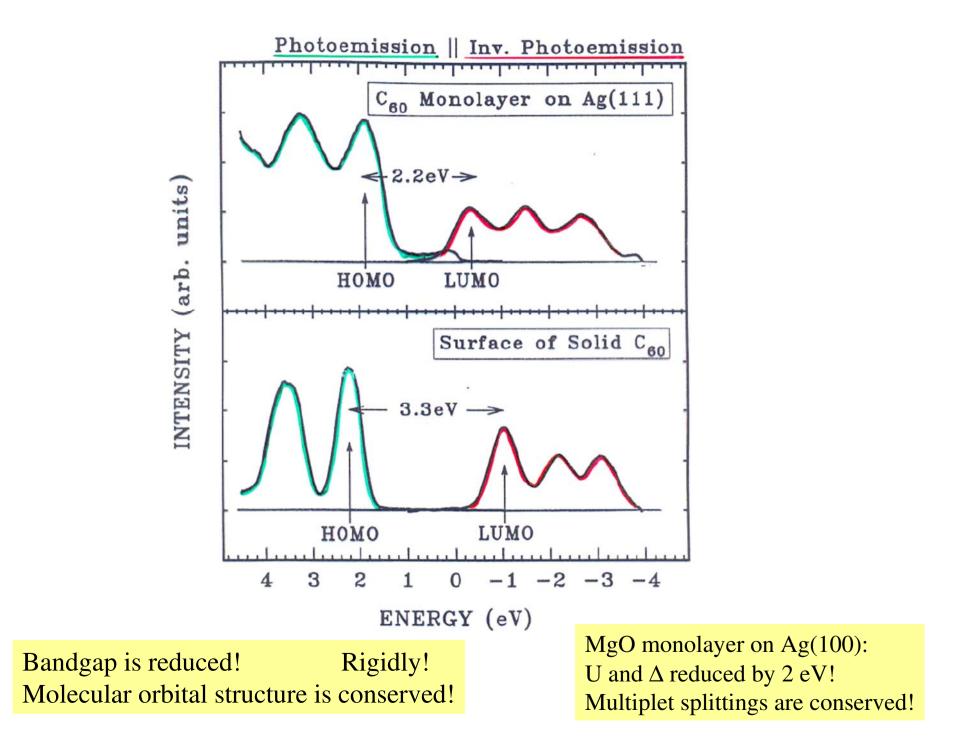
Expectations:

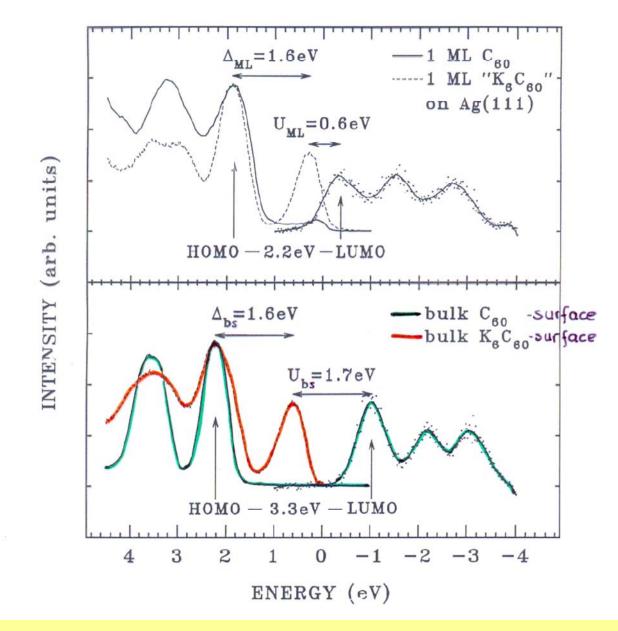
•Stronger (super)exchange interactions: $\sim t^2/U$; $\sim t^4/\Delta^2(1/U-1/\Delta)$ •Higher T_C and T_N ?!!











Bandgap is reduced because on-site Coulomb energy U is reduced!

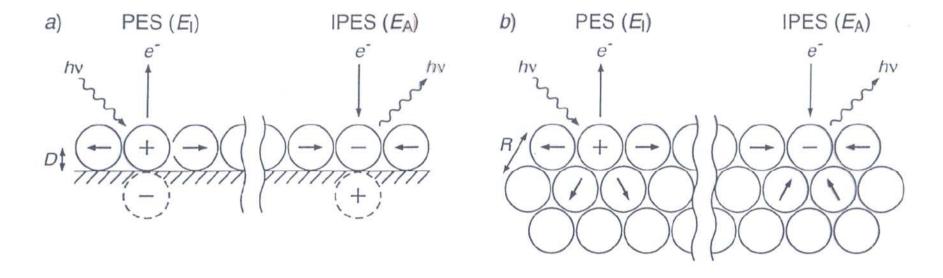
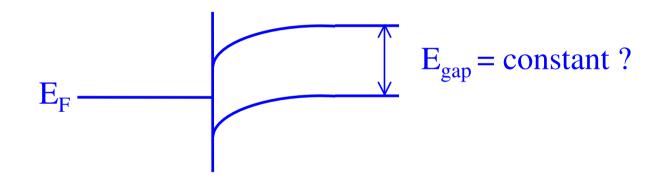
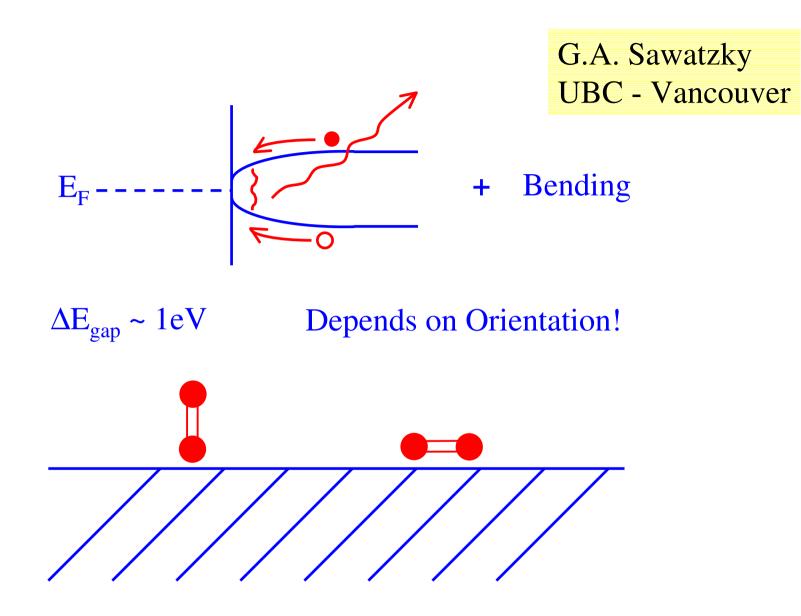


Fig. 3. – Photoemission and inverse photoemission processes for a monolayer of C_{60} on metal (a) and for the surface of bulk C_{60} (b). In both cases, the final state charges and polarizations of the bucky-balls are indicated.

G.A. Sawatzky UBC - Vancouver

What happens at a semiconductor –metal interface





Orientation changes the gap at interface Orientation disorder is really bad

Influence of STM tip on bandgap of solid C_{60} ?!

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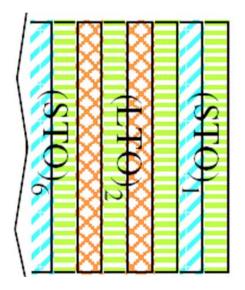
Electronic reconstruction at an interface between a Mott insulator and a band insulator

Satoshi Okamoto & Andrew J. Millis

Department of Physics, Columbia University 538 West 120th Street, New York, New York 10027, USA

Surface science is an important and well-established branch of materials science involving the study of changes in material properties near a surface or interface. A fundamental issue has been atomic reconstruction: how the surface lattice symmetry differs from the bulk. 'Correlated-electron compounds' are materials in which strong electron-electron and electron-lattice interactions produce new electronic phases, including interaction-induced (Mott) insulators, many forms of spin, charge and orbital ordering, and (presumably) high-transitiontemperature superconductivity^{1,2}. Here we propose that the fundamental issue for the new field of correlated-electron surface/interface science is 'electronic reconstruction': how does the surface/interface electronic phase differ from that in the bulk? As a step towards a general understanding of such phenomena, we present a theoretical study of an interface between a strongly correlated Mott insulator and a band insulator. We find dramatic interface-induced electronic reconstructions: in wide parameter

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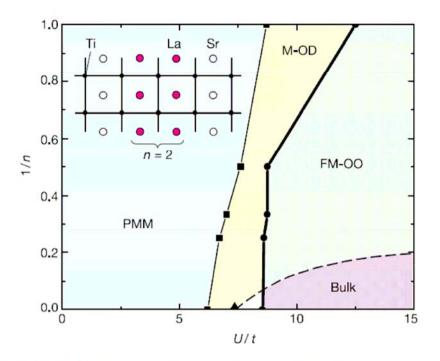
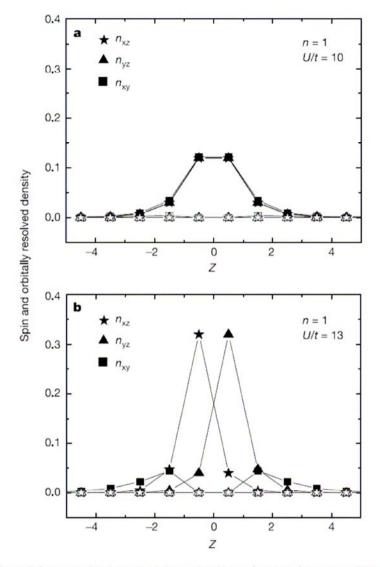
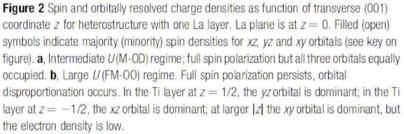


Figure 1 Ground-state phase diagram computed in Hartree-Fock approximation as a function of the on-site Coulomb interaction U and the inverse of the La layer number n. For small U values the ground state is a paramagnetic metal with no orbital ordering (PMM region; shaded blue). The solid line marked with squares denotes a second-order transition to a orbitally disordered magnetic state (M-OD; shaded yellow) that is ferromagnetic for n = 1; for n > 1 each (001) Ti layer is uniformly polarized, but the magnetization direction alternates from layer to layer, leading to a ferrimagnetic state (n = 2, 4, 6, ...; odd number of occupied Ti layers) or antiferromagnetic state (n = 3, 5, ...;7, ...; even number of occupied Ti layers). The solid line marked with circles denotes a first-order transition to a fully polarized ferromagnetic state with (00π) orbital order (FM-00; shaded green). For sufficiently thick samples (Bulk, shaded pink), the latter transition is pre-empted by a first-order transition to the bulk state, which, in the Hartree-Fock approximation used here, has ferromagnetic spin order and G-type ($\pi\pi\pi$) antiferroorbital order. The actual materials exhibit a G-type AF order and a complicated orbital order²⁰ apparently due to subtle lattice distortions neglected here²¹. Inset, schematic of plane perpendicular to (010) direction of (001) superlattice for the n = 2 case. Circles show the the positions of Sr (white) and La (red) ions respectively; small black dots show the positions of Ti ions.





ranges, the near-interface region is metallic and ferromagnetic, whereas the bulk phase on either side is insulating and antiferromagnetic. Extending the analysis to a wider range of interfaces and surfaces is a fundamental scientific challenge and may lead to new applications for correlated electron materials.

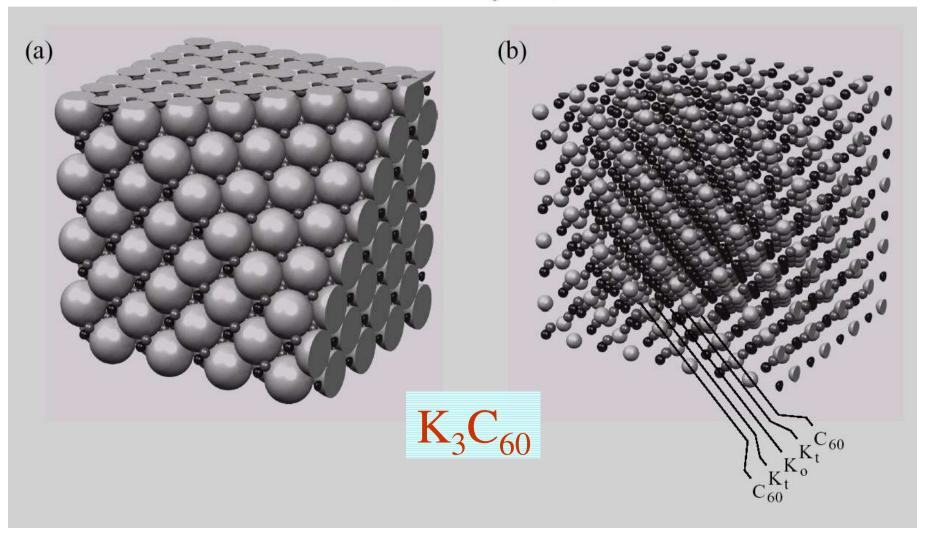
To assess the effects of a surface or interface on correlatedelectron behaviour we require to understand the changes in the parameters governing bulk correlated-electron behaviour. The three key factors are interaction strengths, bandwidths and electron densities^{1,3}, all of which may change near a surface or interface. In most cases, surface- or interface-induced changes in all three factors will contribute, but in developing a general understanding it is desirable first to study the different effects in isolation. Here we focus on the effect of electron-density variation caused by the spreading of charge across an interface. A different charge distribution effect-the compensation of a polar surface by electronic charge rearrangement-was argued to change the behaviour of C60 films⁴. (Indeed, Hesper *et al.*⁴ coined the term "electronic reconstruction" in reference to this specific effect; we suggest that this useful phrase be applied more generally to denote electronic phase behaviour that is fundamentally different at a surface from in bulk.) Proximity to a surface or interface can also change the electron interaction parameters^{5,6}, the electron bandwidth⁷, and level degeneracy⁸. Experimental studies of surfaces⁹⁻¹² and heterostructures¹³

- Hesper, R., Tjeng, L. H., Heeres, A. & Sawatzky, G. A. Photoemission evidence of electronic stabilization of polar surface in K₃C₆₀. *Phys. Rev. B* 62, 16046–16055 (2000).
- Altieri, S., Tjeng, L. H. & Sawatzky, G. A. Electronic structure and chemical reactivity of oxide-metal interfaces: MgO(100)/Ag(100). *Phys. Rev. B* 61, 16948–16955 (2000).

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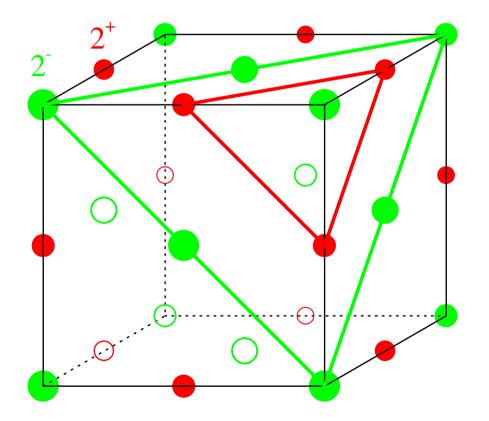
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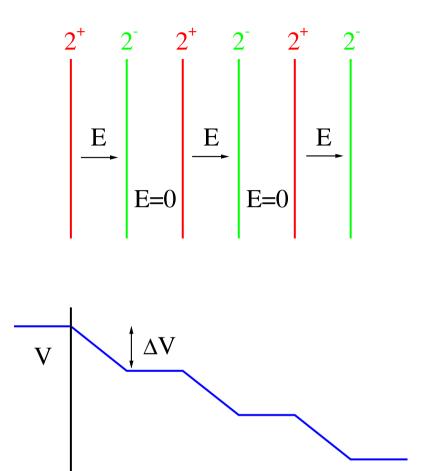
R. Hesper, L. H. Tjeng, A. Heeres, and G. A. Sawatzky Solid State Physics Laboratory, Materials Science Centre, University of Groningen, Nijenborgh 4, 9747 AG Groningen, the Netherlands (Received 19 April 2000)



Polar Surfaces

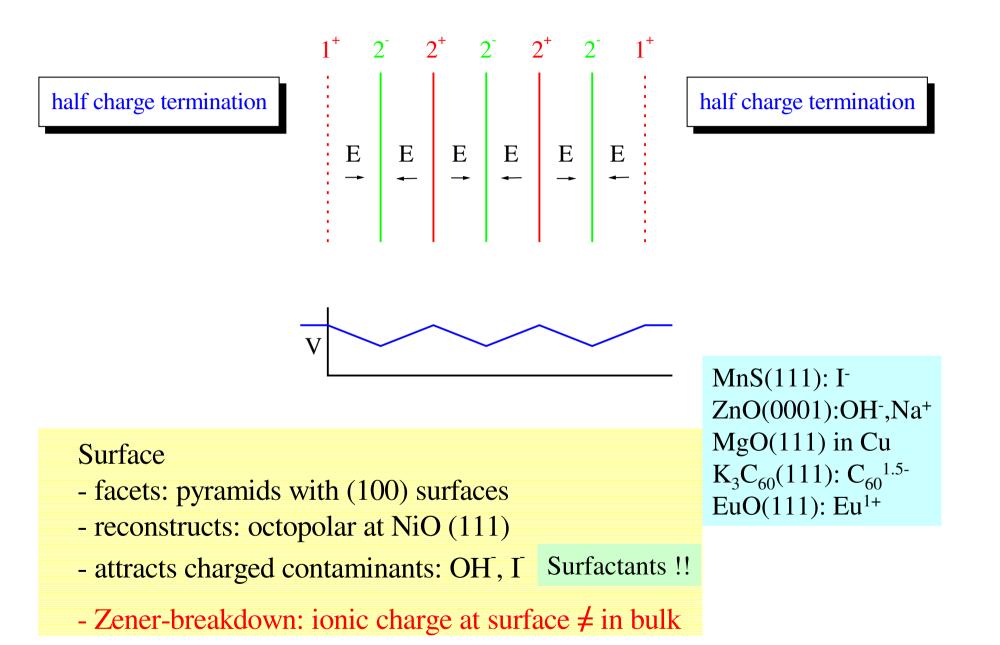
- Existence of non-neutral or charged planes in crystal structures
- Rocksalt (111) surfaces: MgO,NiO





 $\Delta V = 57.9$ Volt per MgO or NiO double layer

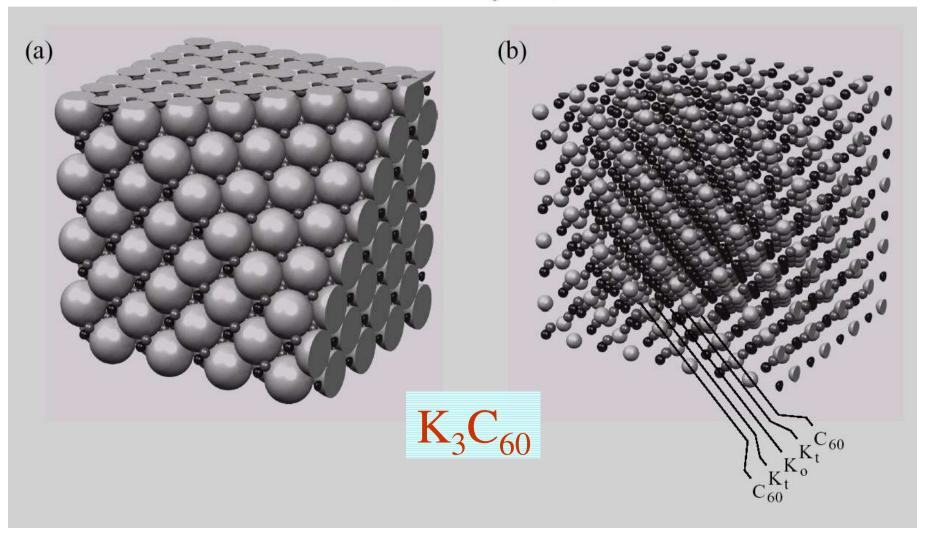
IMPOSSIBLE !!



VOLUME 62, NUMBER 23

Photoemission evidence of electronic stabilization of polar surfaces in K₃C₆₀

R. Hesper, L. H. Tjeng, A. Heeres, and G. A. Sawatzky Solid State Physics Laboratory, Materials Science Centre, University of Groningen, Nijenborgh 4, 9747 AG Groningen, the Netherlands (Received 19 April 2000)



ALKALI METAL FULLERIDES

Super conductors K3G0 : Tc= 19K Rb3G0 : Tc= 30K

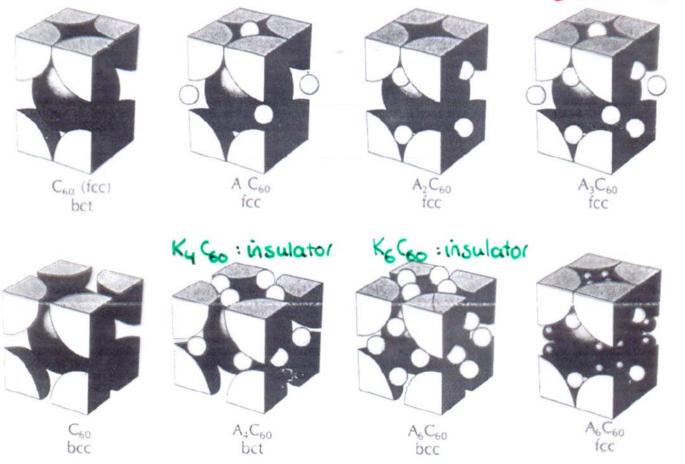
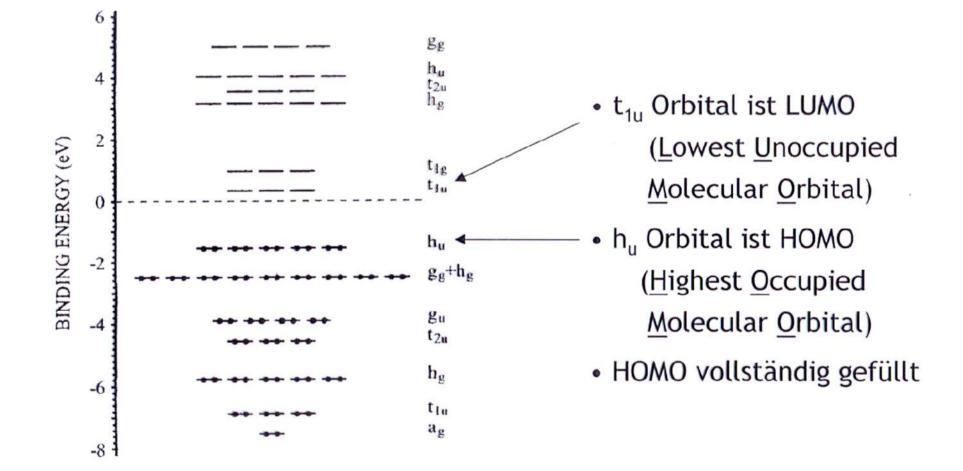


FIG. 21. The crystal structures of the fulleride family. The top row shows the fcc structure of undoped C_{60} , the A_1C_{60} structure with octahedral site occupancy, the A_2C_{60} structure with tetrahedral site occupancy, and the A_3C_{60} structure with tetrahedral and octahedral site occupancy. The bottom row shows C_{60} molecules arranged in the bcc structure, the filling of tetrahedral sites producing A_4C_{60} and A_6C_{60} . The bottom-right structure corresponds to

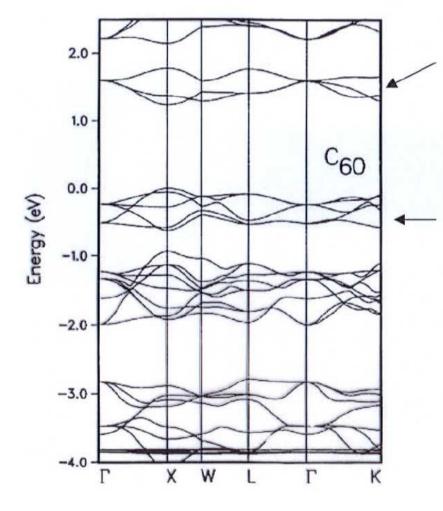
insulator

Elektronische Struktur eines C₆₀ Moleküls

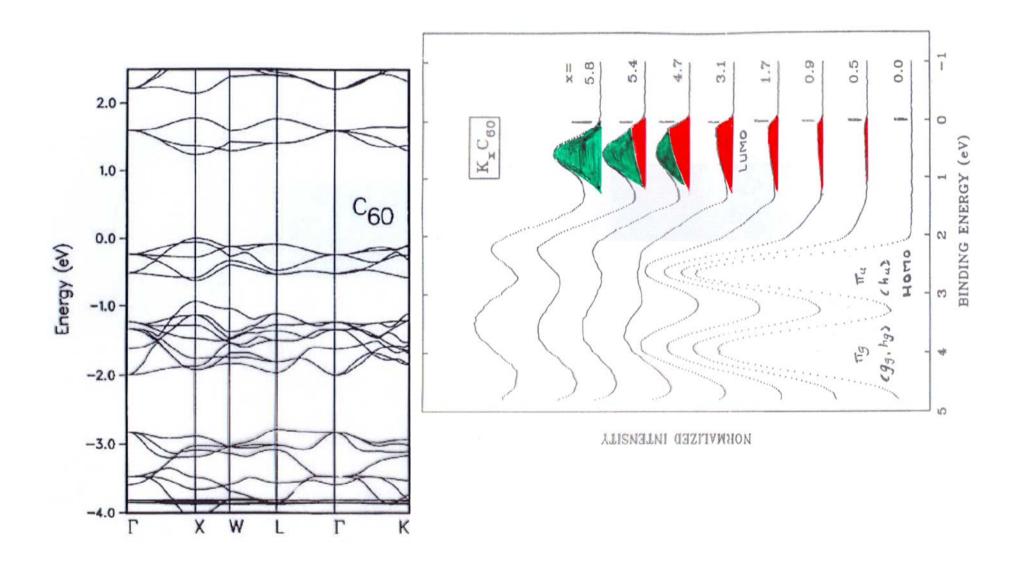


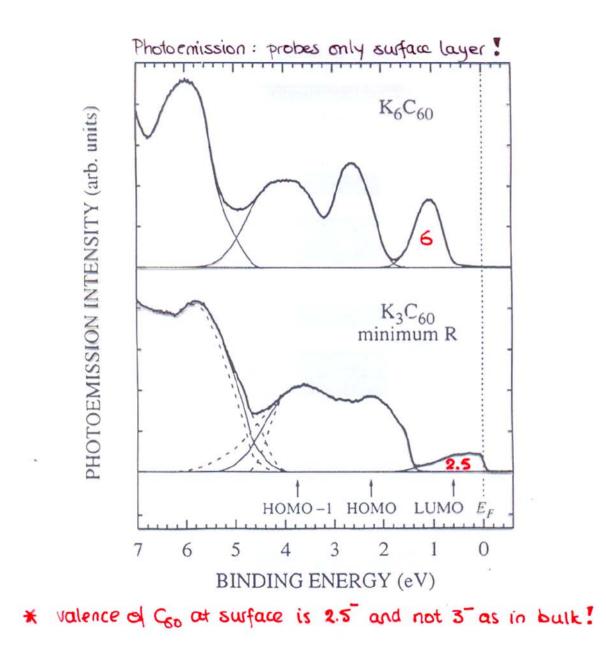
Bandstruktur eines C₆₀ Festkörpers

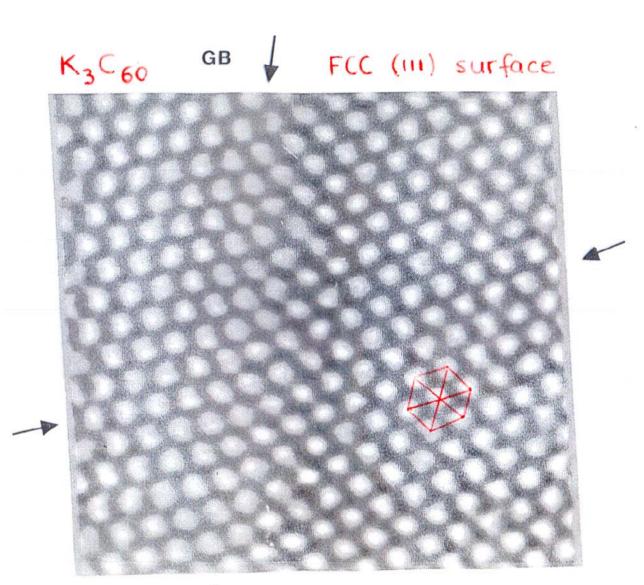
C₆₀ bandstructure



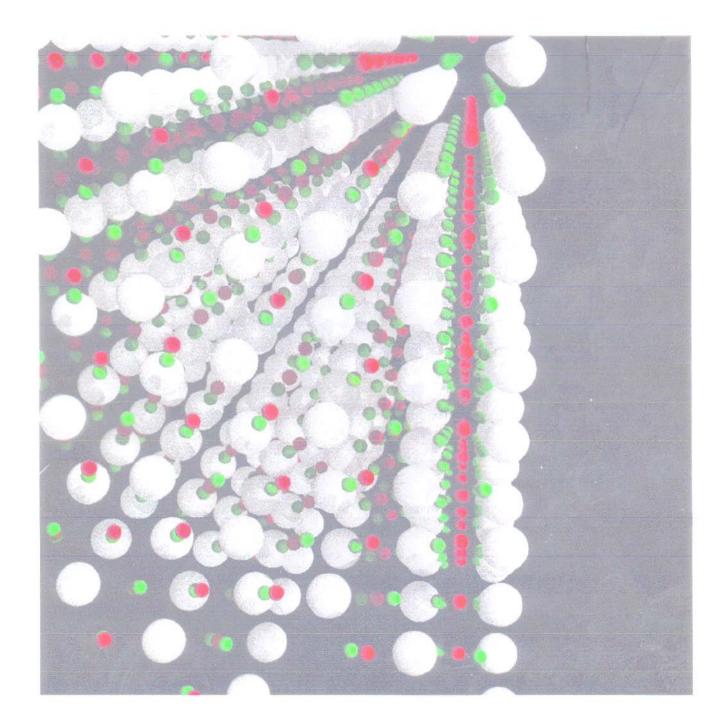
- t_{1u} Band ist LUMO
- t_{1u} Band ist dreifach entartet, kann 6 Elektronen aufnehmen
- h_u Band ist HOMO, vollständig gefüllt

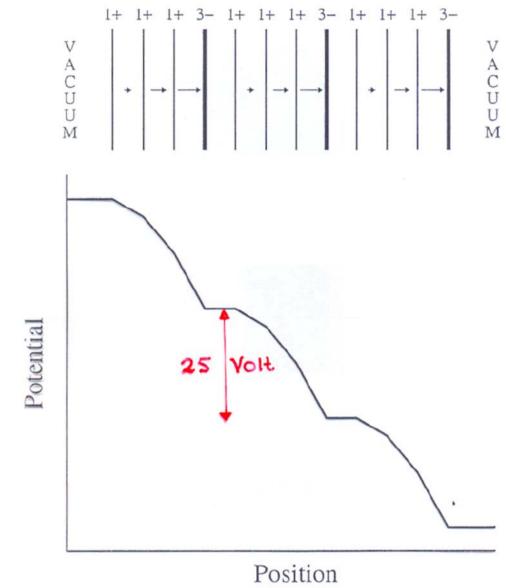


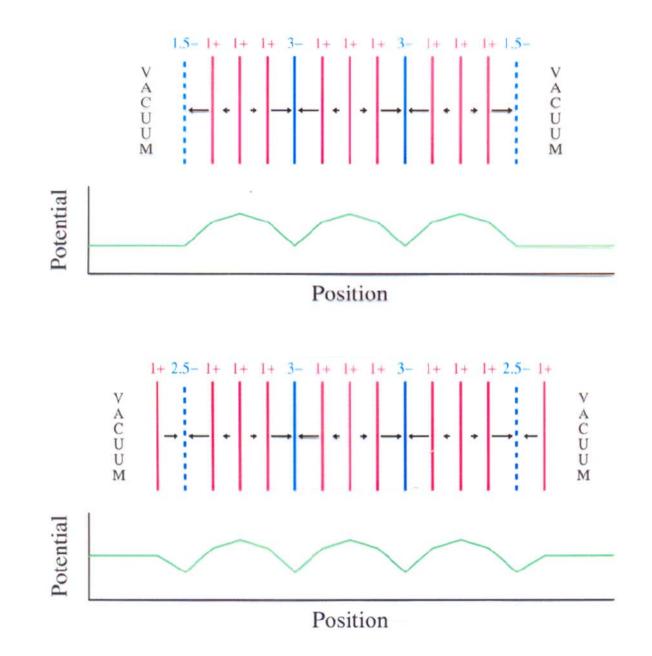


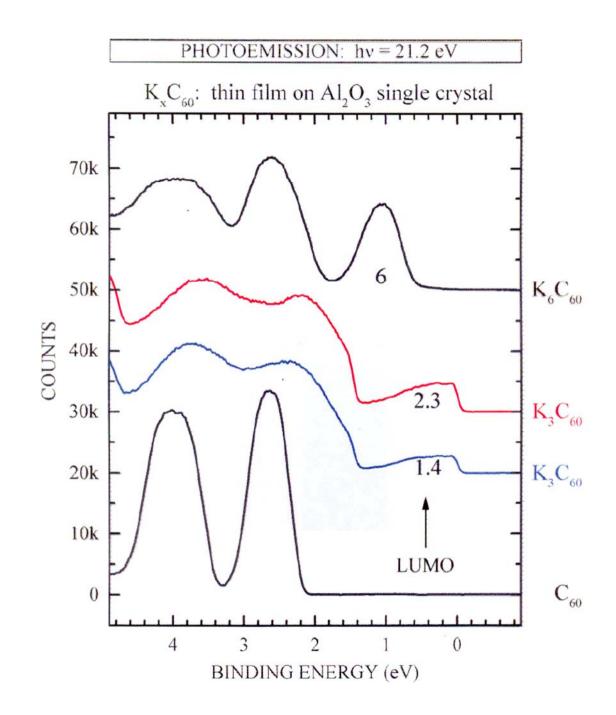


J.H. WEAVER AND D.M. POIRIER









Electronic Structure of K3(60 fcc (111) surface

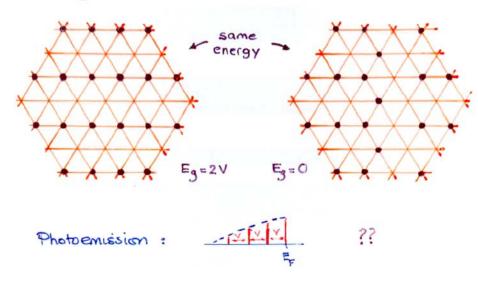
surface has larger U and smaller W than bulk !
 maive expectation: bulk is just metallic - surface is insulating

* Integer valence ~> 1/2 band filling non-degenerate Hubbard model Metal - insulator : U 2 W

★ Integer+1 valence ~> 1/4 band filling non-degenerate Hubbard model Metal - insulator: V ≥ W (U>V)

> U : on-site Coulomb interaction ≈ 1.7 eV Y : nearest neighbor Coulomb interaction ≈ 0.3~0.5 eV W : one-electron bandwidth ≈ 0.3~0.5 eV

* Triungular lattice, + band filling => Frustrated !



0.0

Photoemission from Buried Interfaces in SrTiO₃/LaTiO₃ Superlattices

M. Takizawa,¹ H. Wadati,¹ K. Tanaka,¹ M. Hashimoto,¹ T. Yoshida,¹ A. Fujimori,¹ A. Chikamatsu,² H. Kumigashira,² M. Oshima,² K. Shibuya,³ T. Mihara,⁴ T. Ohnishi,³ M. Lippmaa,³ M. Kawasaki,⁵ H. Koinuma,⁴ S. Okamoto,⁶ and A. J. Millis⁶

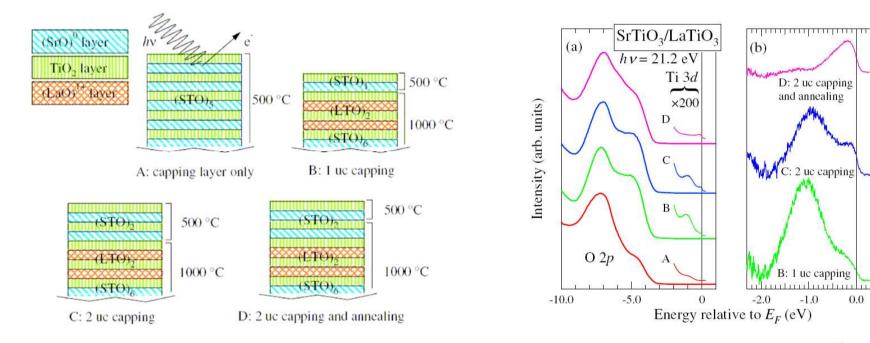
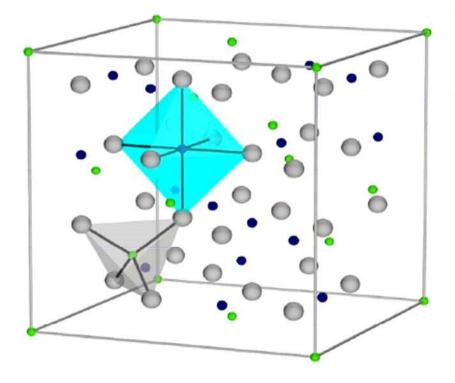


FIG. 1 (color online). Schematic views of the SrTiO₃/LaTiO₃ superlattice samples: capping layer only sample A; 1 uc capping sample B; 2 uc capping sample C; 2 uc capping and annealing sample D. Growth temperatures are also indicated.

FIG. 2 (color online). UPS spectra of the SrTiO₃/LaTiO₃ superlattice samples: the capping layer only sample A, the 1 uc capping sample B, the 2 uc capping sample C, and the 2 uc capping and annealing sample D. (a) Valence-band spectra over a wide energy range. (b) Near Fermi-level spectra after background subtraction (see text).

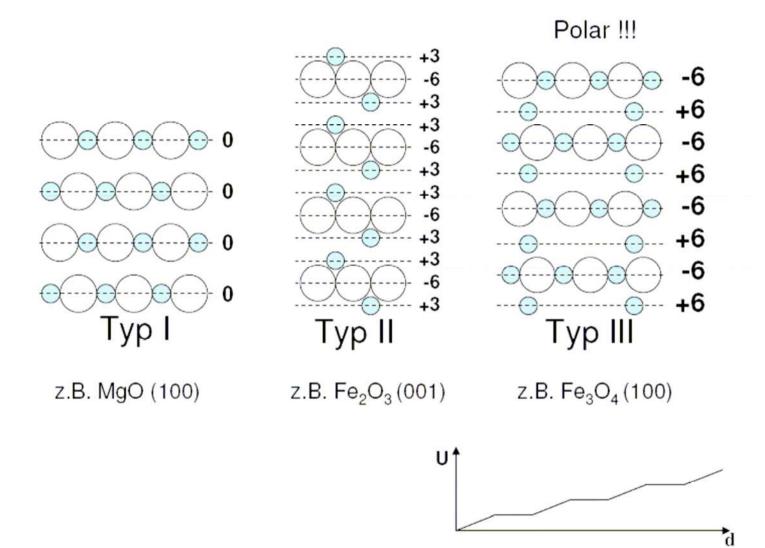






- Ältestes bekanntes magnetische Material
- Natürlich gewachsener Kristall zeigt Oktaederflächen
- Inverse Spinell-Struktur
- Sauerstoff bildet kubisch dichteste Packung
- Eisen füllt Löcher:
 - Trivalente Eisenionen (Fe³⁺) sind gleichmäßig auf Oktaeder- & Tetraeder-Plätze verteilt
 - Divalente Eisenionen (Fe²⁺) sind oktaedrisch von O umgeben
- a = 8.394 Å

Polar Surface of Fe_3O_4 (100)



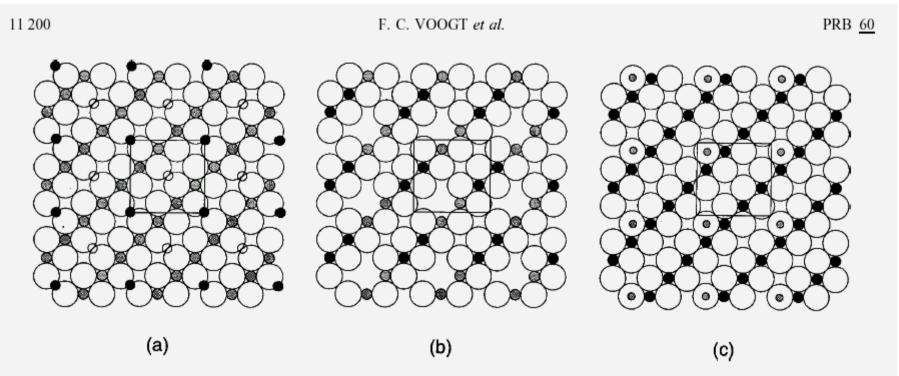
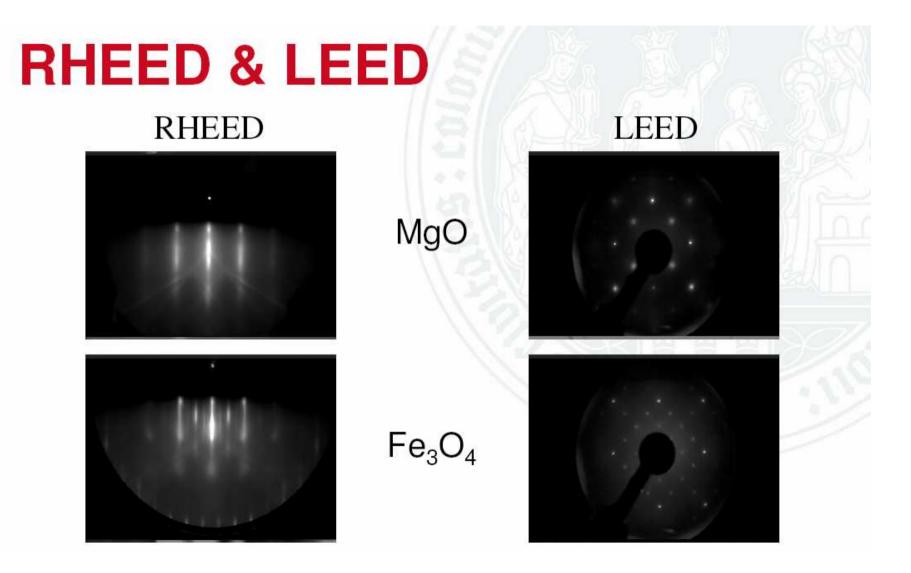


FIG. 7. Three possible surface structures for the $(\sqrt{2} \times \sqrt{2})$ R45° reconstructed Fe₃O₄(100) surface, in top view. (a) A termination at a half-filled *A* layer of Fe³⁺ ions. (b) A termination at a *B* layer of oxygen anions and octahedral Fe^{2.5+} ions. There is one oxygen vacancy per unit cell, accompanied by the oxidation of two Fe^{2.5+} ions to Fe³⁺. The remaining Fe^{2.5+} ions are trapped by the oxygen vacancies, resulting in charge ordering. (c) An alternative termination at a *B* layer. Here, the surface does not contain oxygen vacancies, but one hydroxyl group per unit cell. Furthermore, the surface is fully oxidized, containing only Fe³⁺ ions. Large open circles: oxygen anions; small open circles: missing Fe³⁺ ions; black filled circles: Fe³⁺ ions; large gray filled circles: Fe^{2.5+} ions; small gray filled circles: hydrogen. In each case, the bulk unit cell is outlined.



Work in progress

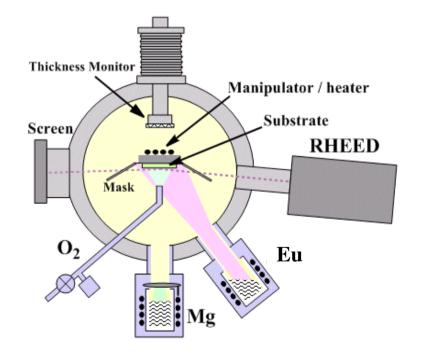
Thin films:

Lehrstuhl fur Angewandte Physik, II. Physikalisches Institut

Materials: binary oxides with precise stoichiometry control

Technique: <u>Molecular Beam Epitaxy</u> - control of oxygen stoichiometry - compatible with electron spectrocopies

ultra high vacuum (1x10⁻¹⁰ mbar)
effusion cells and e-beam evaporators
oxidizers: O₂, O₃, NO₂, O-radicals
co-evaporation and distillation
resistivity monitoring during growth !
in-situ RHEED and LEED
in-situ XPS and XAS



Mini-MBE at the home institute

Mini-MBE in Taiwan

Sample-transfer system

XPS

identical copies

MBE + *in-situ* ρ(T)

HBFG-MBE

HBFG-MBE: We have designed and constructed a new more versatile MBE system for the growth of binary oxide systems. It adds to the mini-MBE systems the capability to measure the resistivity of the thin films in situ and during growth for a wide range of temperatures. This allows to control the growth condition very accurately and to characterize the temperaturedependent transport properties of the thin films.

The system is equipped with a He flow cryostat, a RHEED gun and screen, and the system can accomodate up to 6 different effusion cells or e-beam evaporators. The design allows a full 360° azimuthal rotation of the sample in order to cover the angular range needed for a complete RHEED analysis.

For maximal flexibility both MBE systems are coupled via a sample-transfer system to each other, to an XPS system and to a loadlock.

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