Screening of excitations and small polarons in strongly correlated solids and solid surfaces

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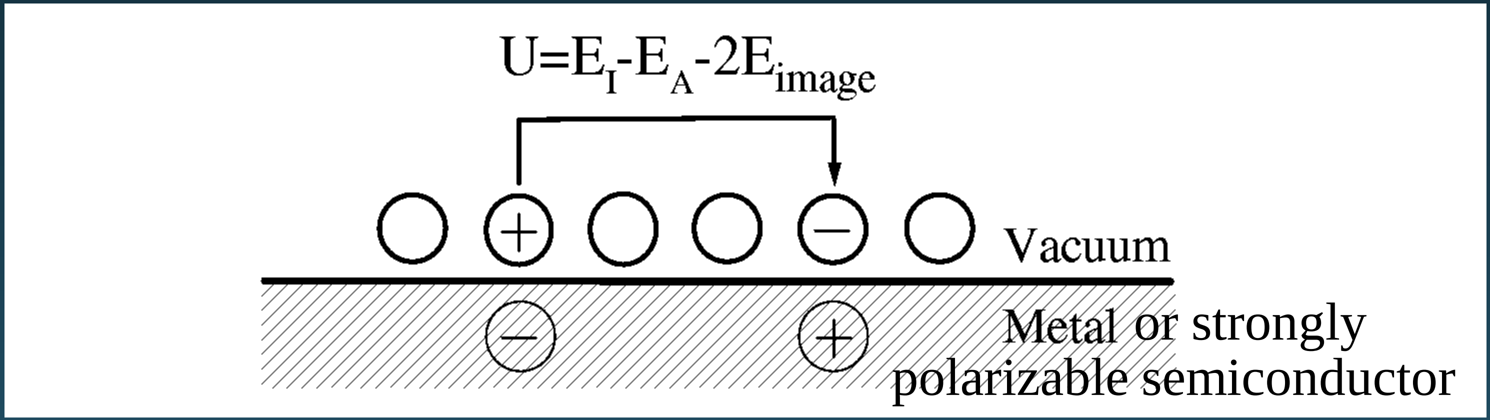
Chemical Physics of Solids
Dresden

- Salvatore Altieri, Ronald Hesper, George Sawatzky – *Univ. Groningen*
- Tim Haupricht, Thomas Lorenz – *Univ. Cologne*
- Andreas Reisner, Katharina Höfer, Christoph Becker, Roger Chang, Maurits Haverkort, Zhiwei Hu – *MPI Dresden*
- Yen-Fa Liao, Ku-Ding Tsuei, Hong-Ji Lin, Chien-Te Chen – *NSRRC, Taiwan*

Modification of material properties using image charge screening



Reduction of charge excitation energies:

- Coulomb energy: $U = U_o - 2E_{image}$
- Charge transfer energy: $\Delta = \Delta_o - 2E_{image}$
- Bandgap: $E_g = E_{go} - 2E_{image}$

Expectations:

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

Strongly reduced band gap in a correlated insulator in close proximity to a metal

Europhys. Lett., **40** (2), pp. 177-182 (1997)

R. Hesper, L. H. Tjeng and G. A. Sawatzky

Solid State Physics Laboratory, Materials Science Centre, University of Groningen Nijenborgh 4, 9747 AG Groningen, The Netherlands

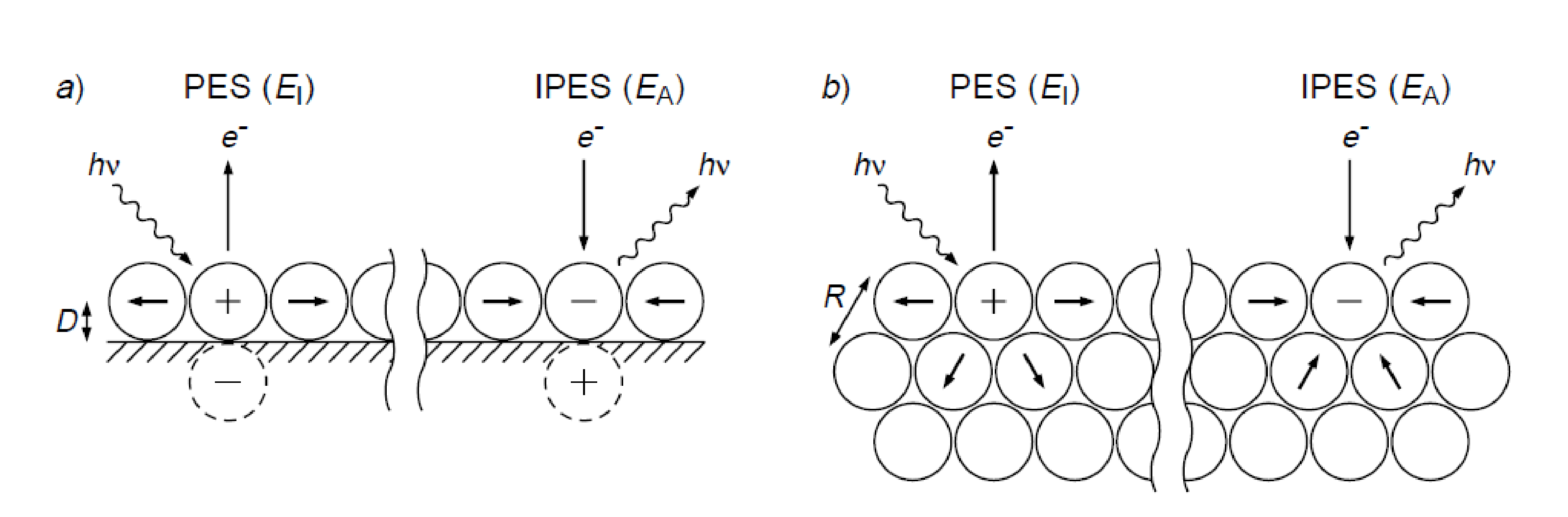
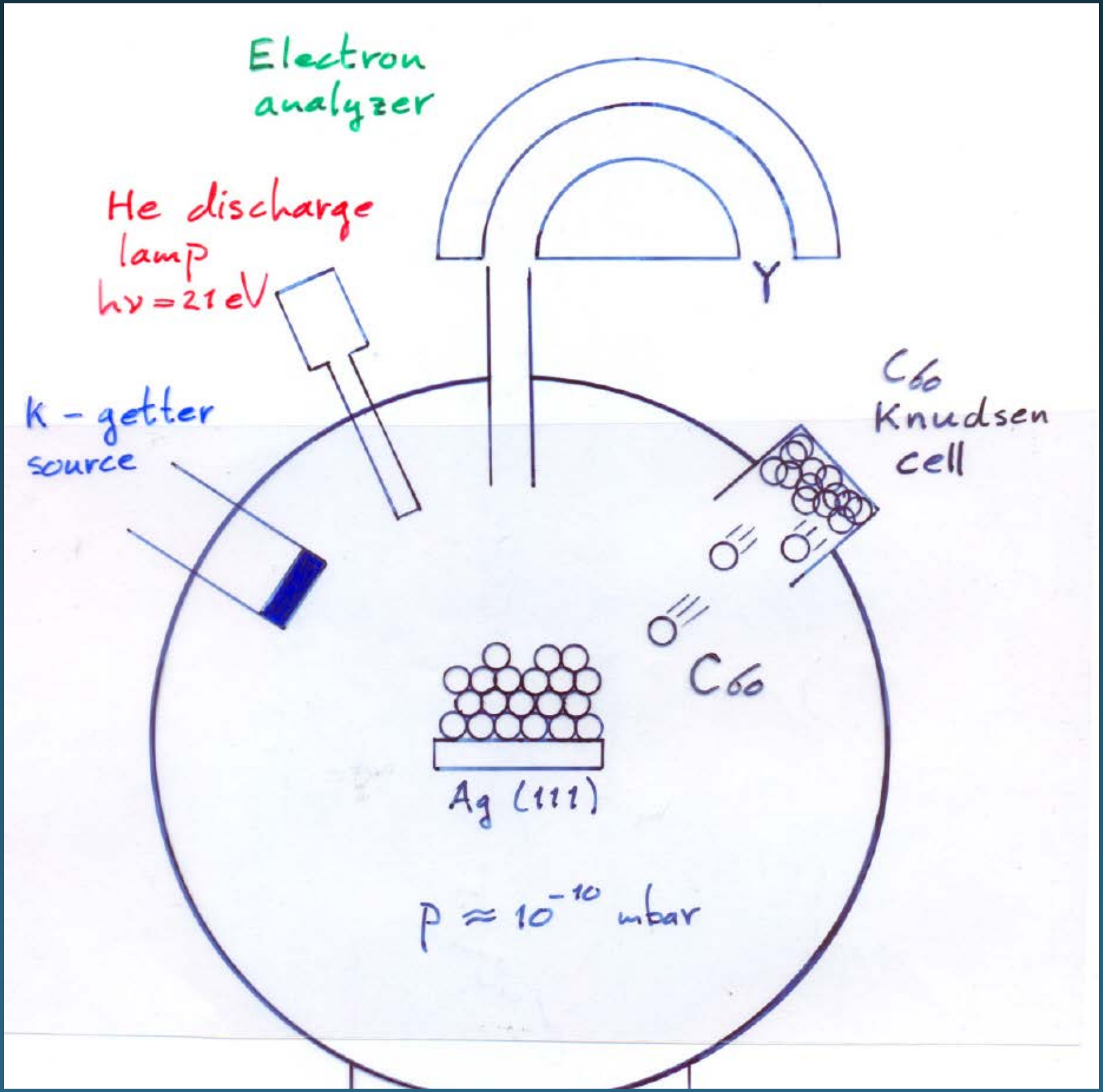
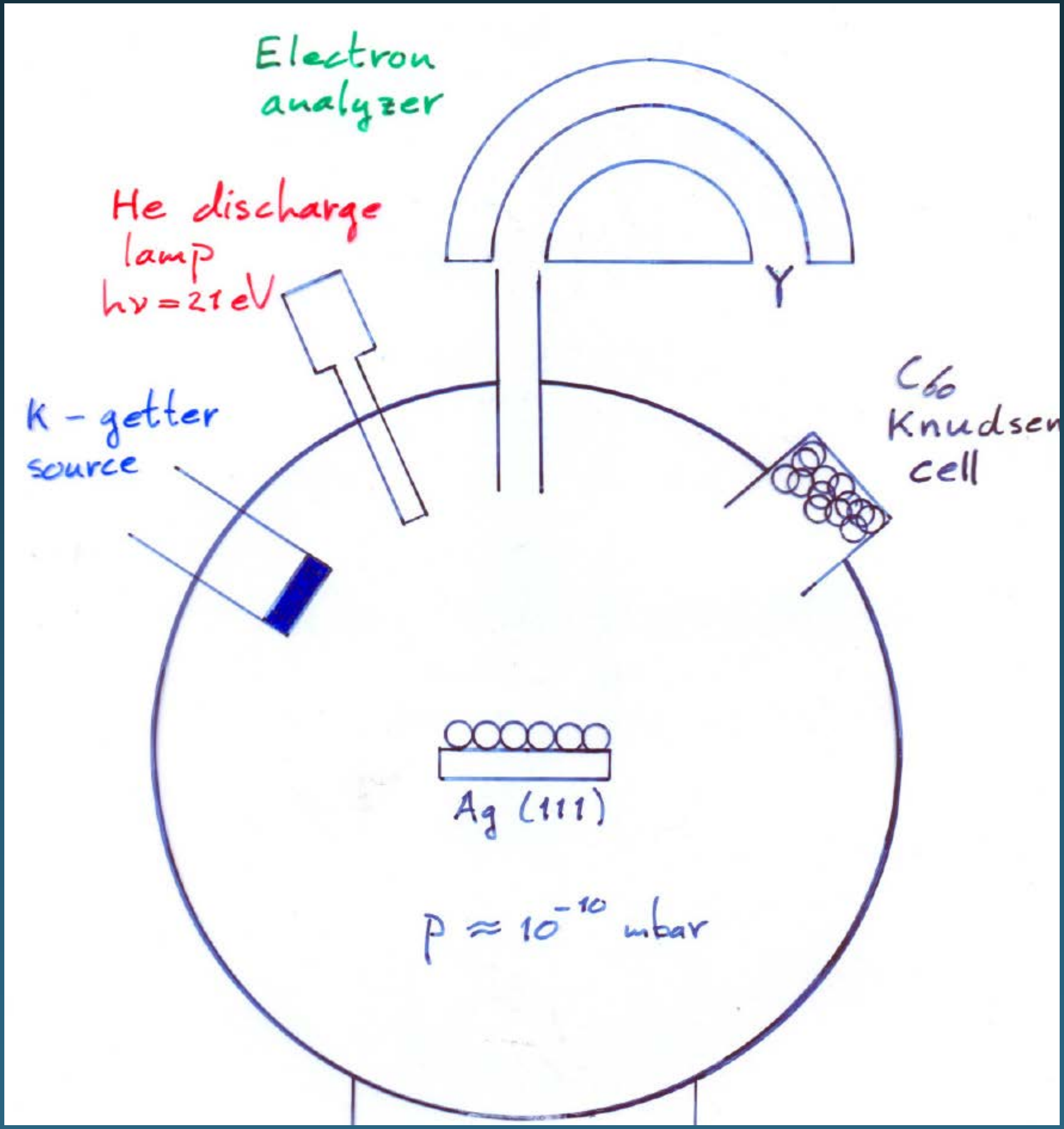


Fig. 3. – Photoemission and inverse photoemission processes for a monolayer of C_{60} on metal (*a*) and for the surface of bulk C_{60} (*b*). In both cases, the final state charges and polarizations of the bucky-balls are indicated.



Electron analyzer
He discharge lamp
$h\nu = 21$ eV
K - getter source
C_{60} Knudsen cell
C_{60}
Ag (111)
$p \approx 10^{-10}$ mbar



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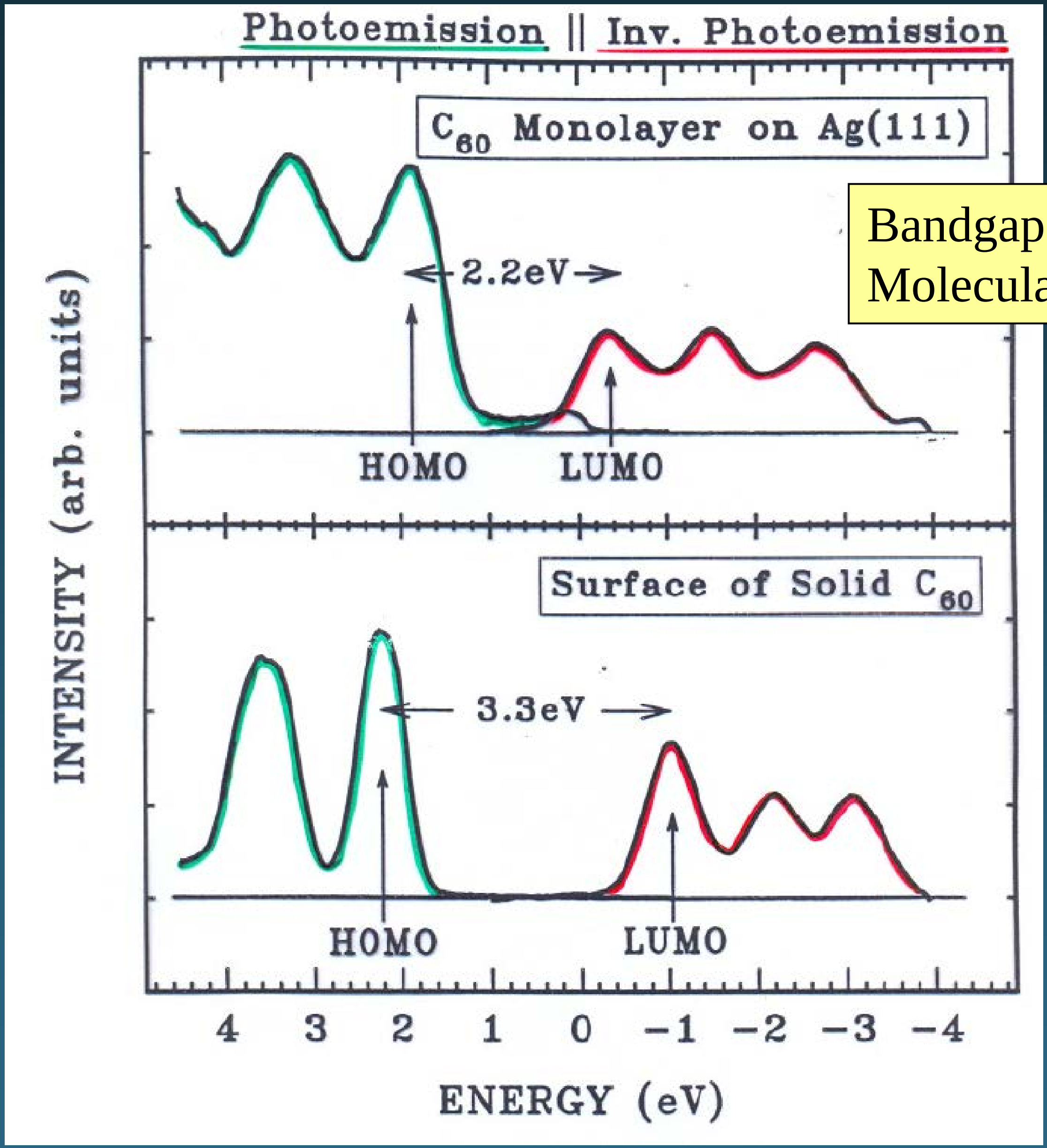
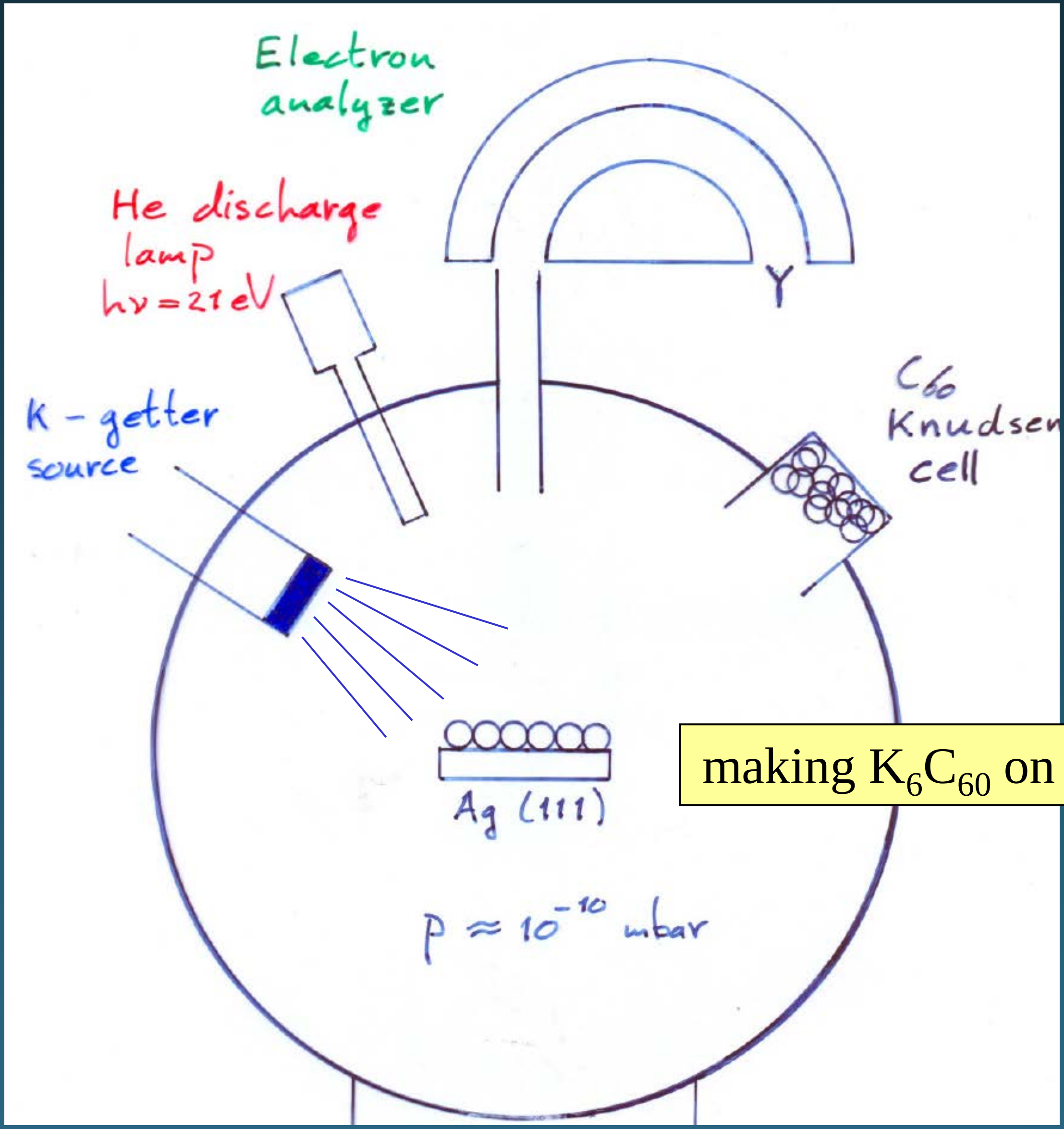
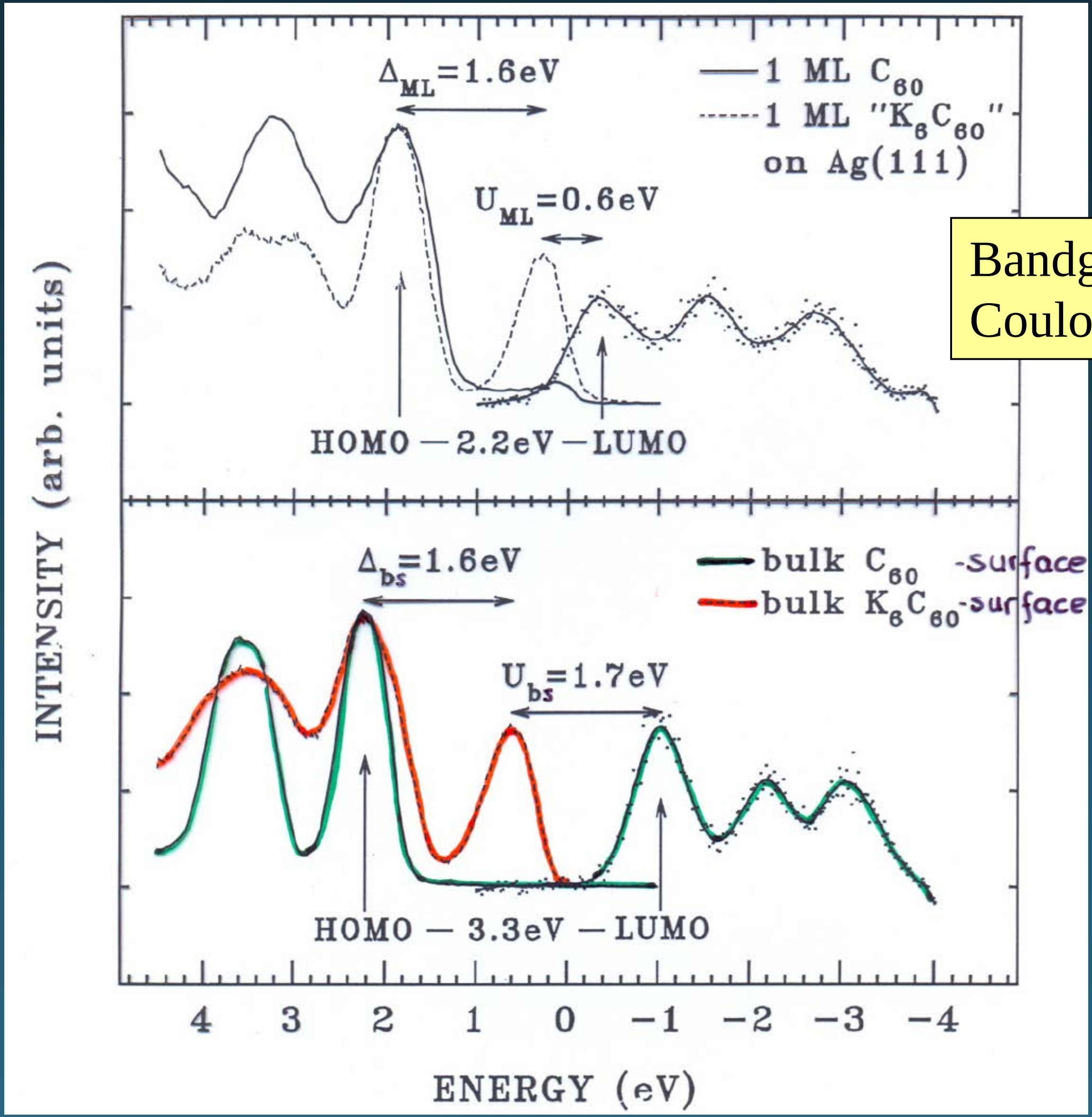


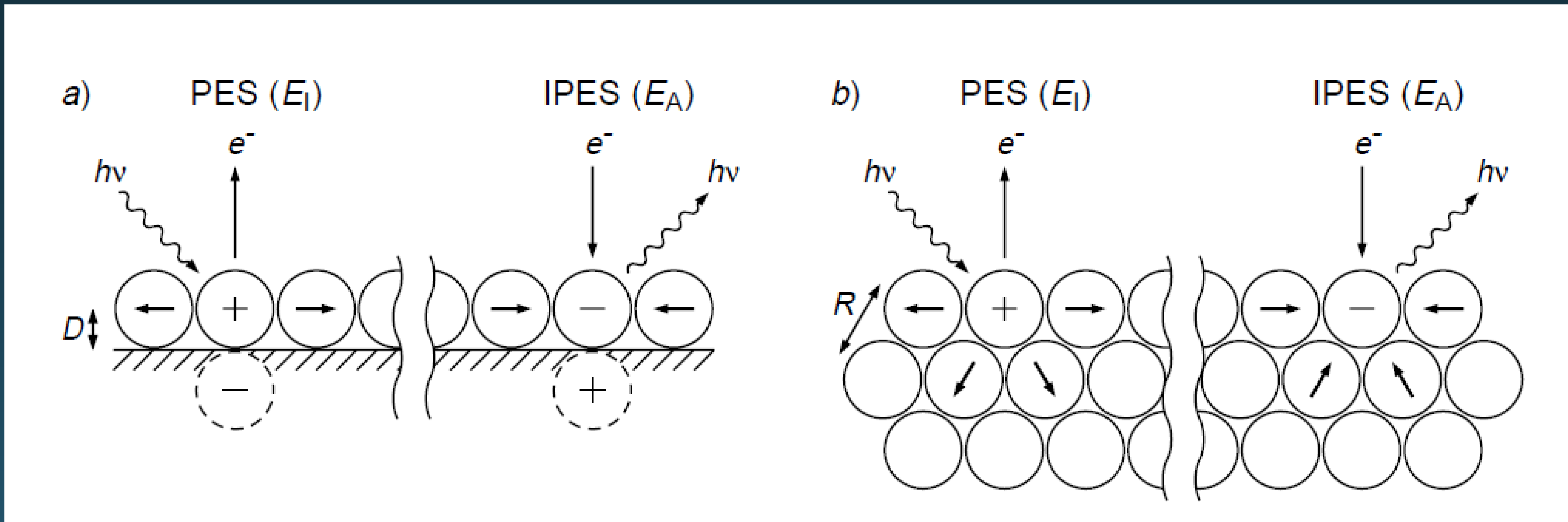
Bandgap is reduced! Rigidly!
Molecular orbital structure is conserved!



making K_6C_{60} on Ag(111)



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



$$E_g = E_g^{at} - 2E_p(C_{60}) - 2E_p(\text{metal})$$

E_g ↓ 2.2 eV; E_g^{at} ↓ 5.0 eV; $2E_p(C_{60})$ ↓ 1.2 eV → $2E_p(\text{metal})$ ⋮ 1.6 eV

(6 nearest neighbors)

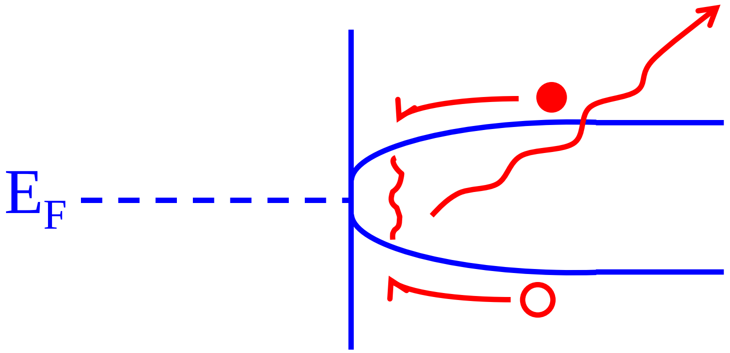
$$E_g = E_g^{at} - 2E_p(C_{60})$$

E_g ↓ 3.3 eV; E_g^{at} ↓ 5.0 eV → $2E_p(C_{60})$ ⋮ 1.7 eV

(9 nearest neighbors)

$$2E_p(\text{metal} = \text{image charge}) = \frac{e^2}{2D} = 1.44\ \text{eV} \qquad (D \approx 5\ \text{Å})$$

bandgap of semiconductor near interface



\+ Bending

G.A. Sawatzky

STM/STS: influence of the tip on the observed bandgap of semiconductors ?!

Electronic Structure of Oxide Thin Films on Metals

Salvatore Altieri

MgO(001) thin film on Ag(001) substrate

RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 59, NUMBER 4 15 JANUARY 1999-II

Phys. Rev. B 66 155432 (2002)

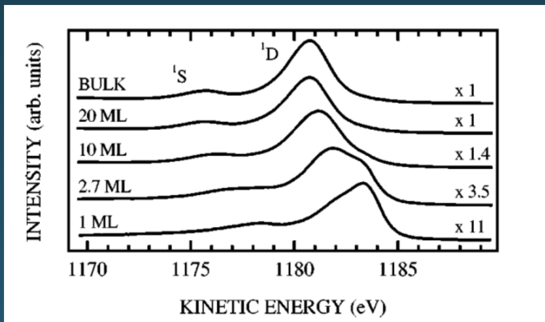
Reduction of Coulomb and charge-transfer energies in oxide films on metals

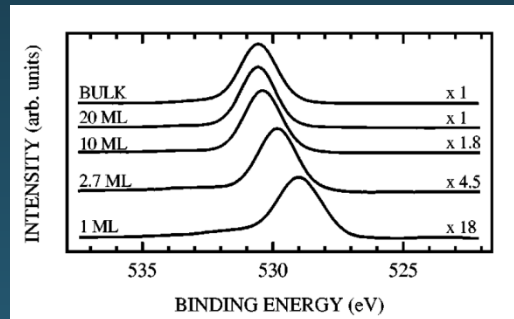
Thin Solid Films 400 (2001) 9-15

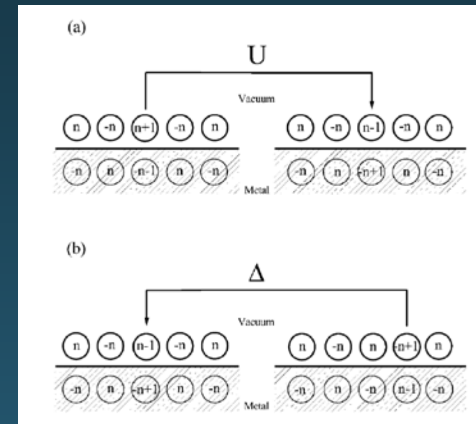
S. Altieri and L. H. Tjeng F. C. Voogt and T. Hibma G. A. Sawatzky

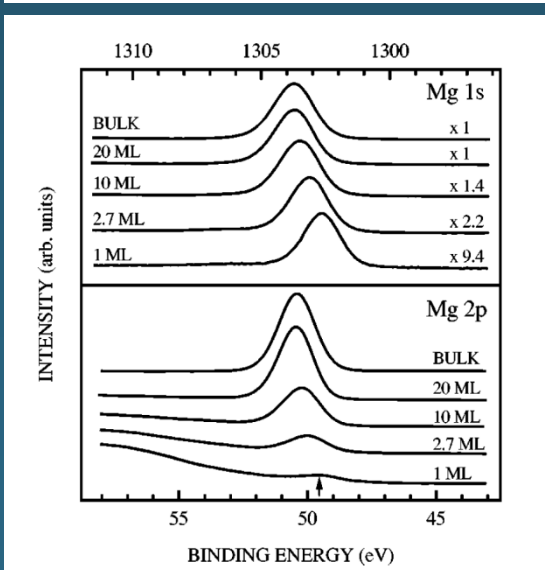
$$E_{kin}^{KLL} = E_b^{1s} - 2E_b^{2p} - U,$$

$$\delta\Delta = \delta E_b^{1s}(O) - \delta E_b^{1s}(Mg) + \delta U(Mg)$$









	1 ML	2.7 ML	10 ML	20 ML	Bulk
$U(\mathrm{Mg}\ 2p(^1D))$	20.3	21.3	21.7	22.1	22.1
$\delta U(\mathrm{Mg}\ 2p)$	−1.8	−0.8	−0.4	0	0
$\delta\Delta(\mathrm{O}\ 2p \rightarrow \mathrm{Mg}\ 3s)$	−2.5	−1.2	−0.5	0	0

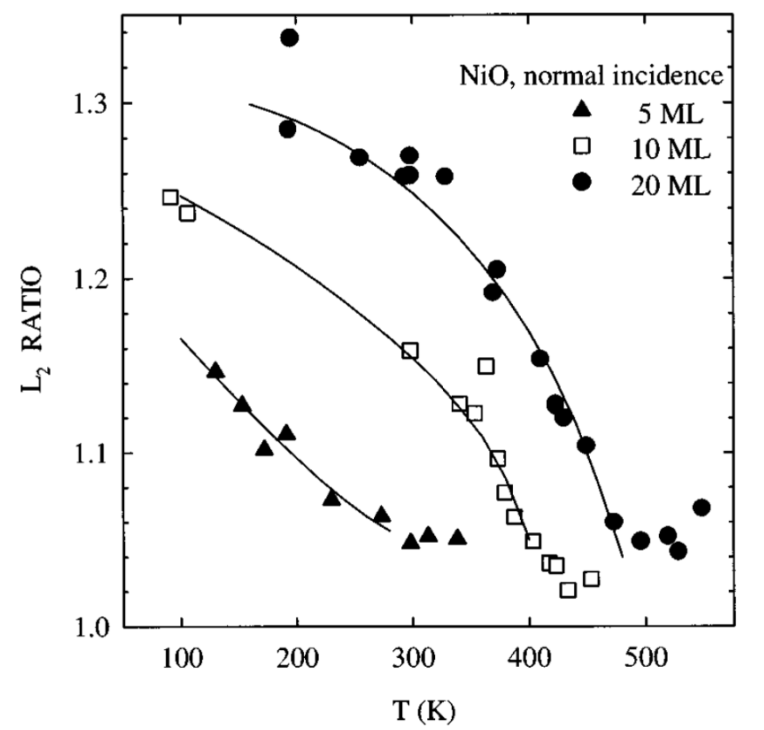
PHYSICAL REVIEW B **79**, 174431 (2009)

Image charge screening: A new approach to enhance magnetic ordering temperatures in ultrathin correlated oxide films

S. Altieri,[1] M. Finazzi,[2] H. H. Hsieh,[3] M. W. Haverkort,[4] H.-J. Lin,[5] C. T. Chen,[5] S. Frabboni,[1,6] G. C. Gazzadi,[1] A. Rota,[6] S. Valeri,[1,6] and L. H. Tjeng[4]

Thickness dependence of magnetic ordering temperature of oxide thin films

NiO on MgO(001)



20 ML: T_N = 500 K
10 ML: T_N = 400 K
5 ML: T_N = 250 K

PHYSICAL REVIEW B **79**, 174431 (2009)

Image charge screening: A new approach to enhance magnetic ordering temperatures in ultrathin correlated oxide films

S. Altieri,[1] M. Finazzi,[2] H. H. Hsieh,[3] M. W. Haverkort,[4] H.-J. Lin,[5] C. T. Chen,[5] S. Frabboni,[1,6] G. C. Gazzadi,[1] A. Rota,[6] S. Valeri,[1,6] and L. H. Tjeng[4]

Thickness dependence of magnetic ordering temperature of oxide thin films

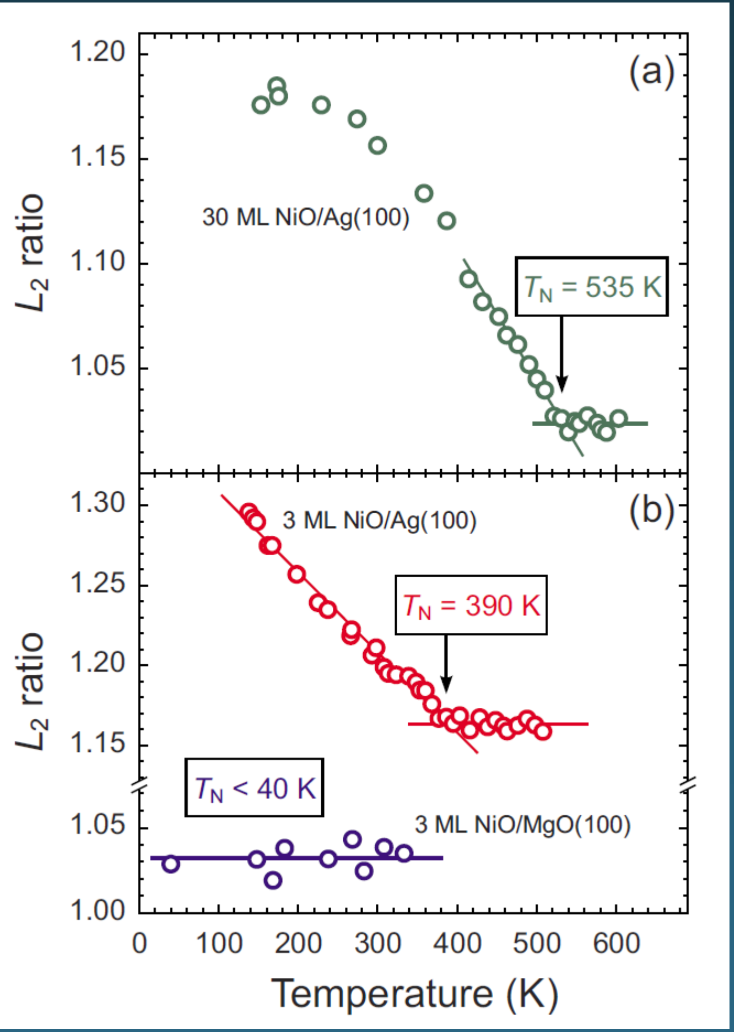
how about NiO on Ag(001) ?

$$J = -\frac{2t^4}{\Delta^2}\left(\frac{1}{\Delta}+\frac{1}{U}\right),$$

- Coulomb energy: $U = U_o - 2E_{image}$
- Charge transfer energy: $\Delta = \Delta_o - 2E_{image}$

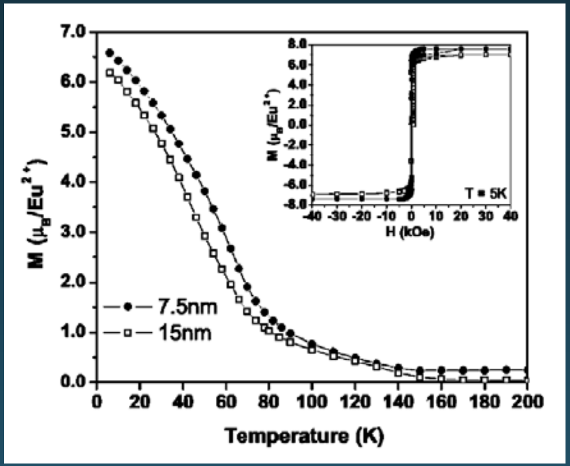
NiO on Ag(001) 3 ML: T_N = 390 K

NiO on MgO(001) 3 ML: T_N < 40 K



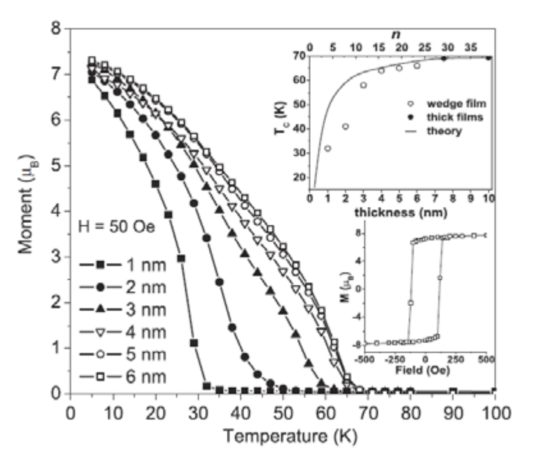
EuO thin films: thickness dependence of Curie temperature

Si – EuO – Al2O3



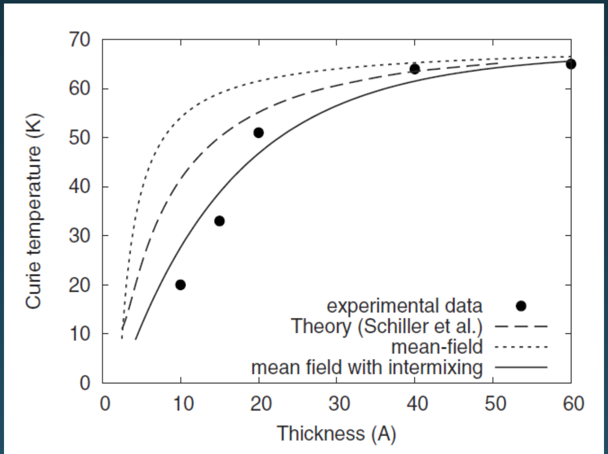
Santos/Moodera PRB 2004

Cr/Cu – EuO – Y/Al



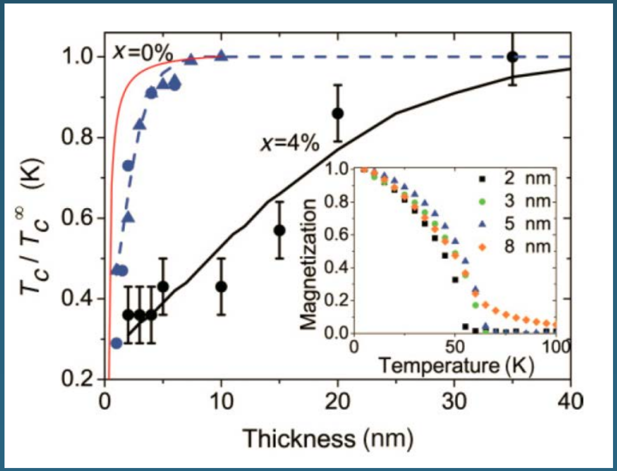
Santos et al. PRL 2008

Al – EuO – Y/Al



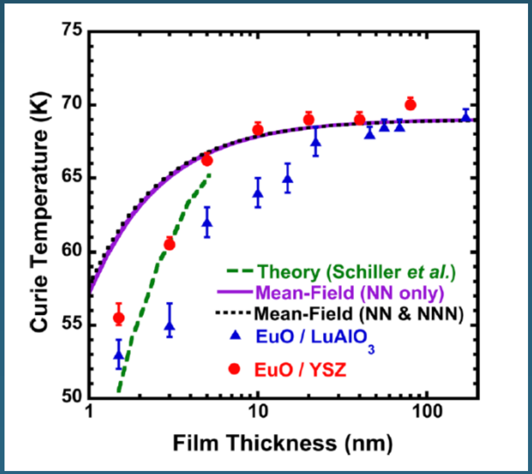
Müller et al. JAP 2009

Pt – EuO - Pt



Barbagallo et al. PRB 2011

YSZ/LuAO– EuO – Si/Al



Melville et al. APL 2013

influence of polarizability of buffer/capping layer ??

Intrinsic conduction through topological surface states of insulating Bi_2Te_3

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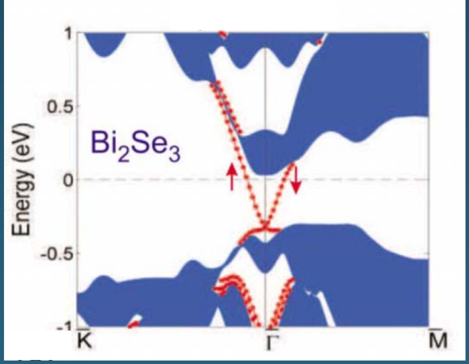
the ultimate surface science challenge ?!

control of doping at surface

minimize doping in bulk



FS volume:
0.1 x 0.1 BZ =
0.01 e/u.c. =
few 10^{12} e/cm^2

surface impurity concentration
must be much less than 1%.

10 μm thick sample = 10^4 layers
bulk impurity concentration
must be much less than 1 ppm

100 nm thin sample = 10^2 layers
bulk impurity concentration
must be much less than 100 ppm

topological surface states are protected against (non-magnetic) impurity scattering
but surface is not protected against impurity doping (surface band bending)

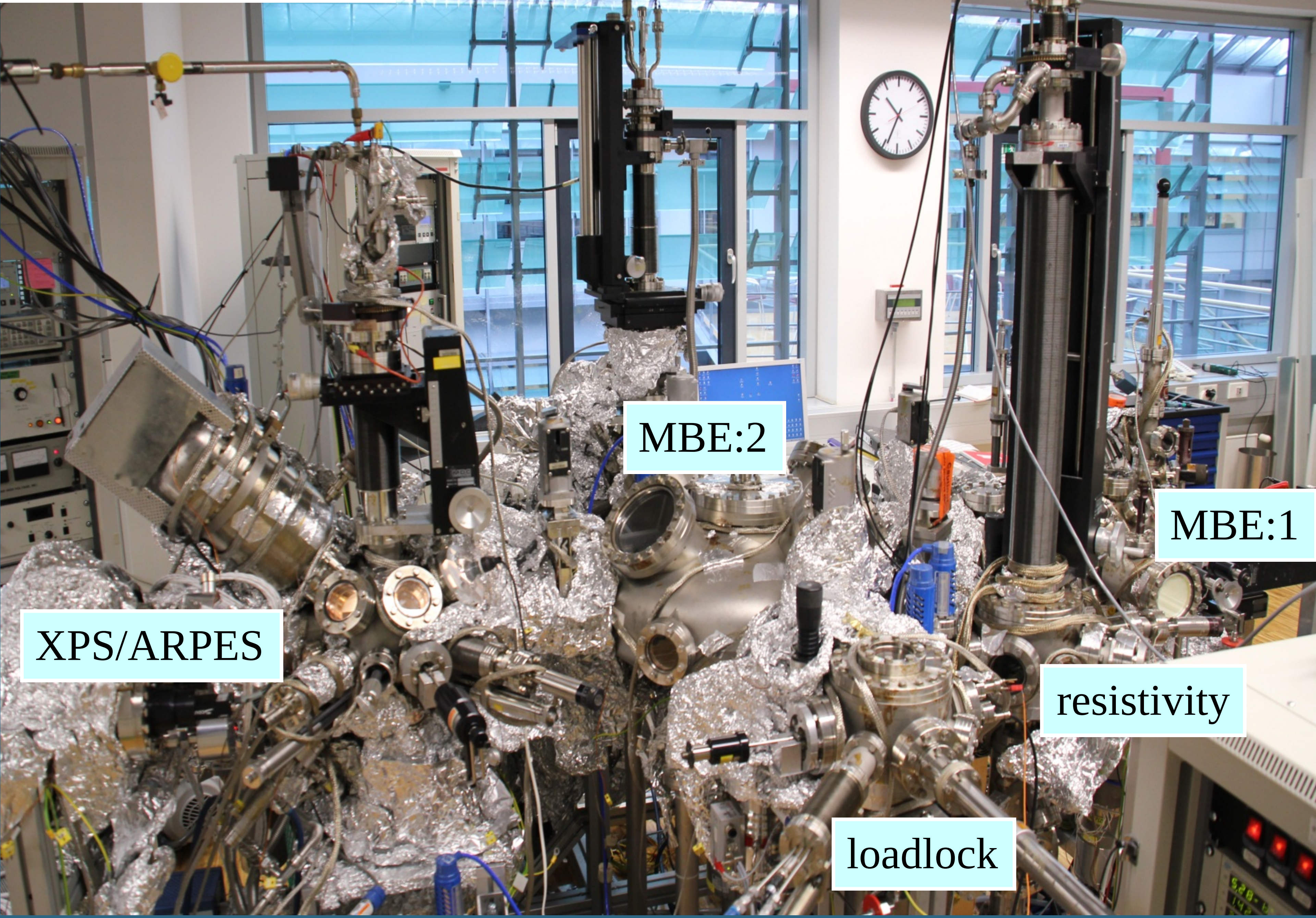
All *in-situ* ultra-high vacuum experiments

- preparation by true-MBE (10^{-10} mbar vacuum)
- *in-situ* structure characterization (RHEED, LEED)
- *in-situ* spectroscopy (XPS, ARPES)
- *in-situ* resistivity (four-point probe)

Katharina Höfer, Christoph Becker, Jesse Swanson, Diana Rata

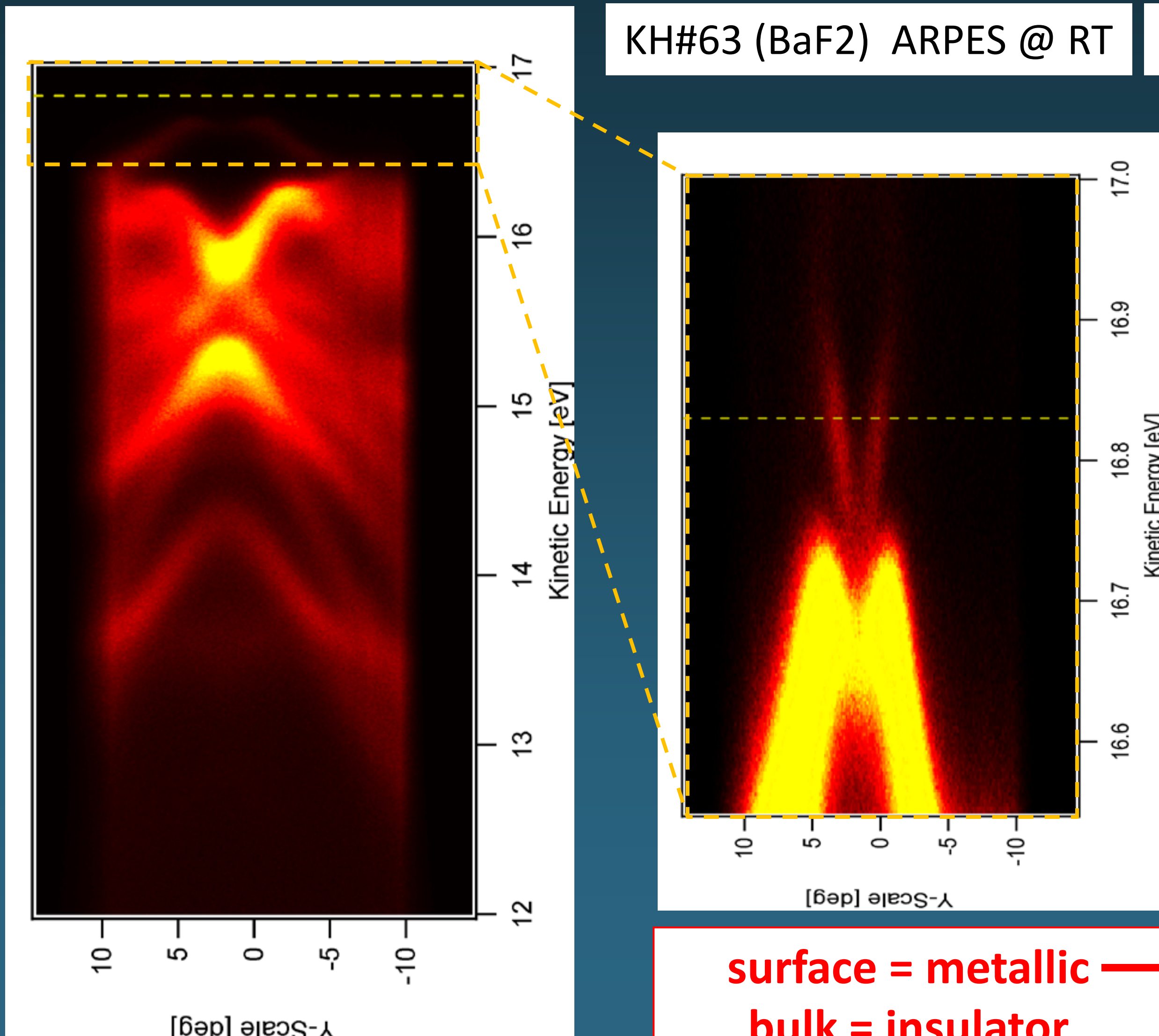
PhD thesis work

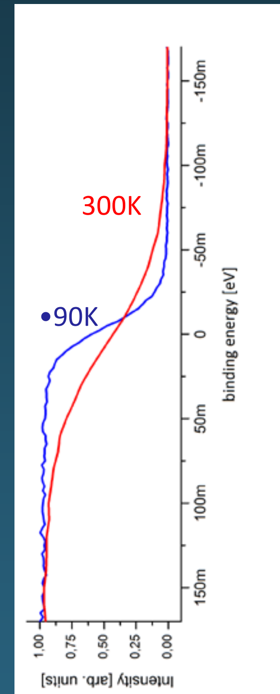
Our thin film system



ARPES – surface/bulk

KH#63 (BaF2) ARPES @ RT | 25 QL



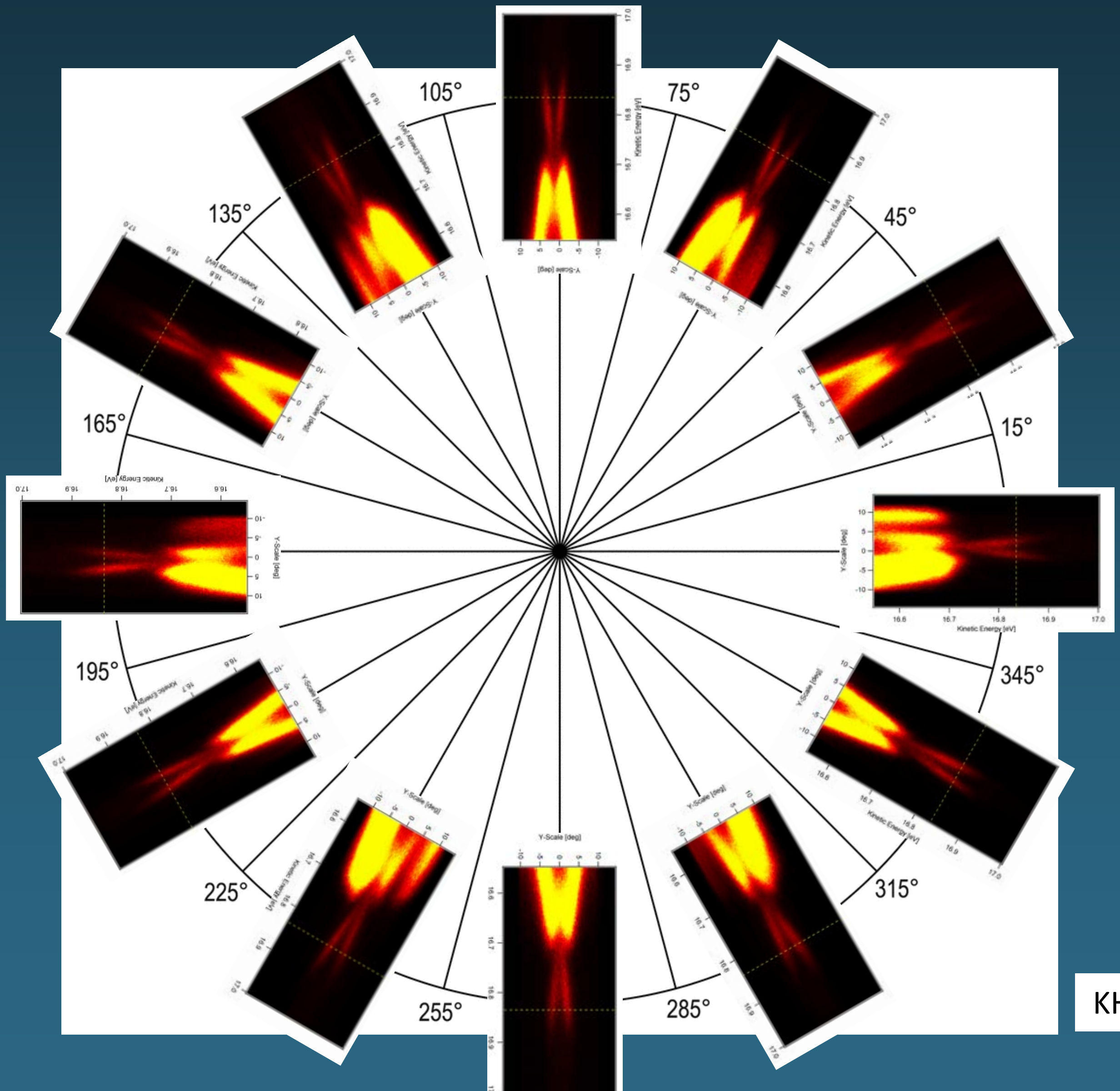


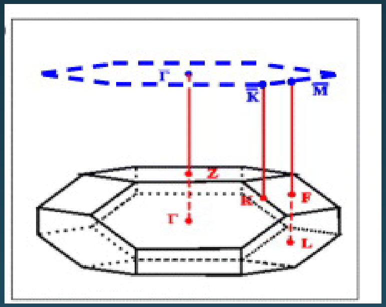
Ag fermi edge

surface = metallic
bulk = insulator

topological surface states
not surface band bending

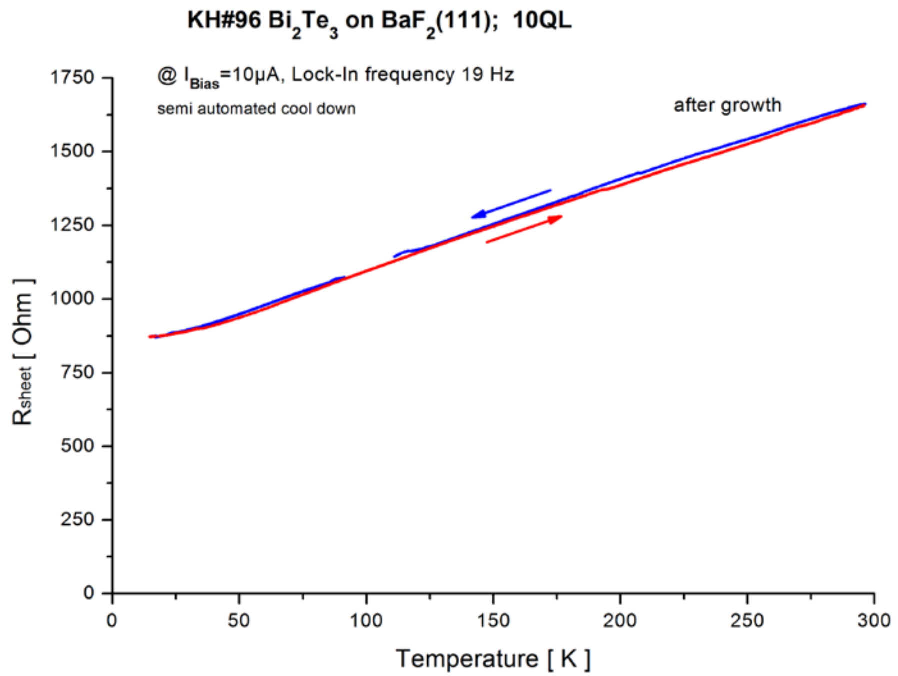
ARPES : 3-fold symmetry





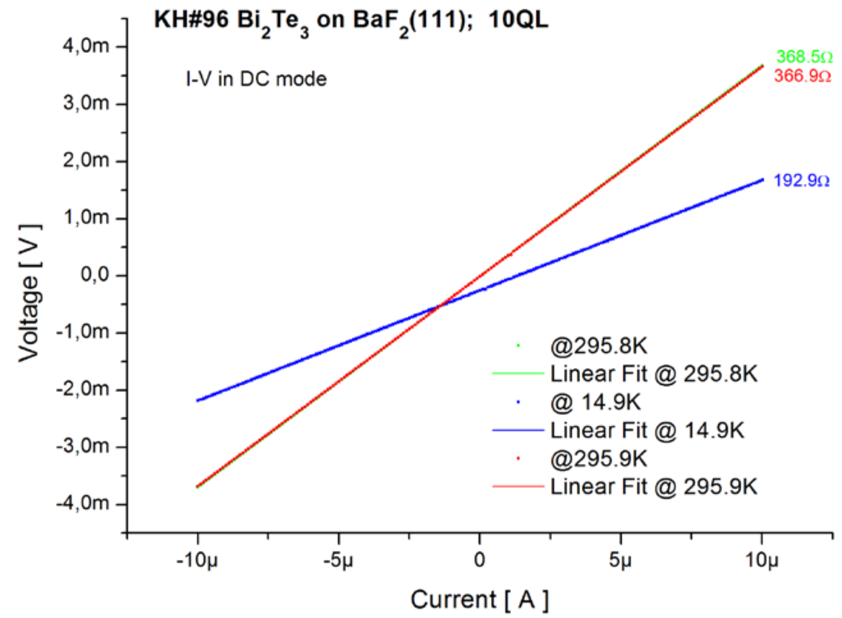
KH#81 (BaF2) 11QL

in-situ electrical resistivity



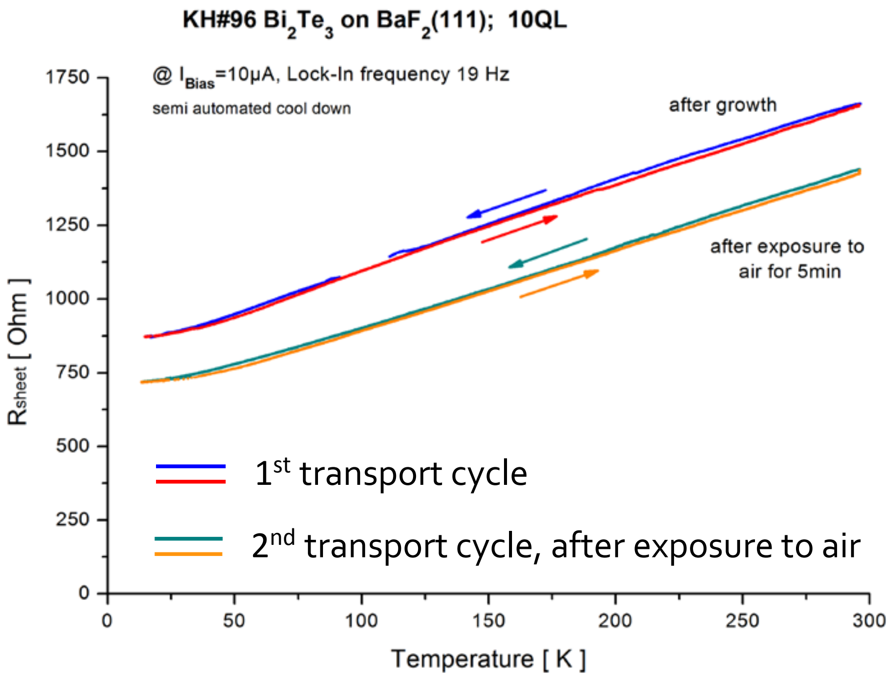
metallic- like behaviour

in-situ electrical resistivity

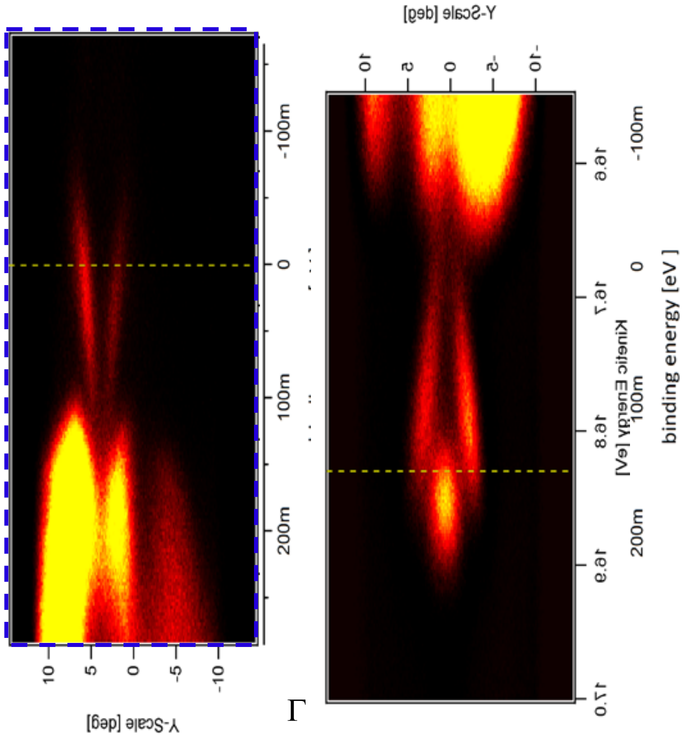


ohmic contacts

electrical resistivity : contaminations



ARPES @ RT

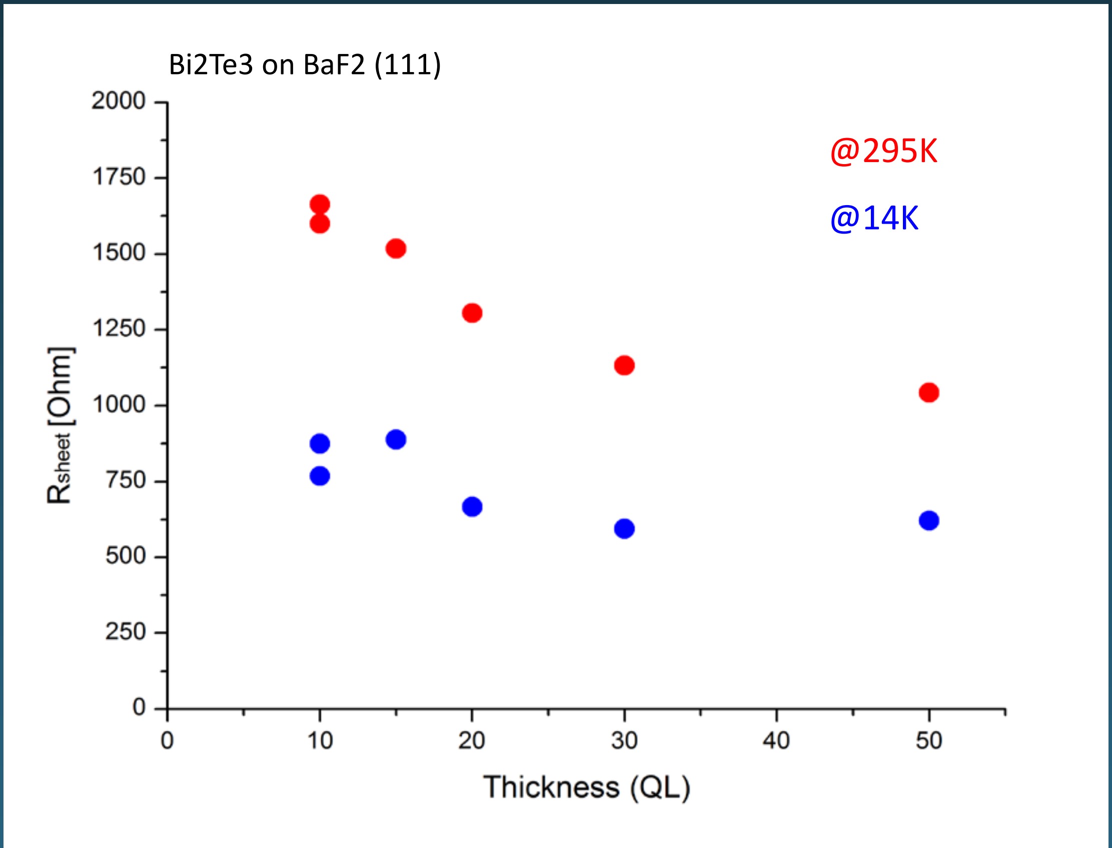


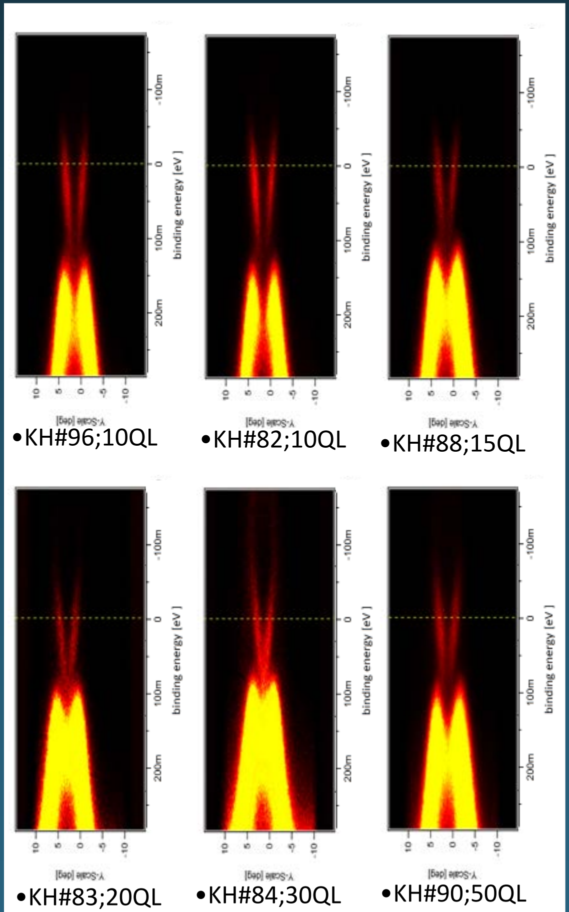
as grown

exposure to air for 5min

KH#96 (BaF2) 10QL

in-situ electrical resistivity: thickness dependence

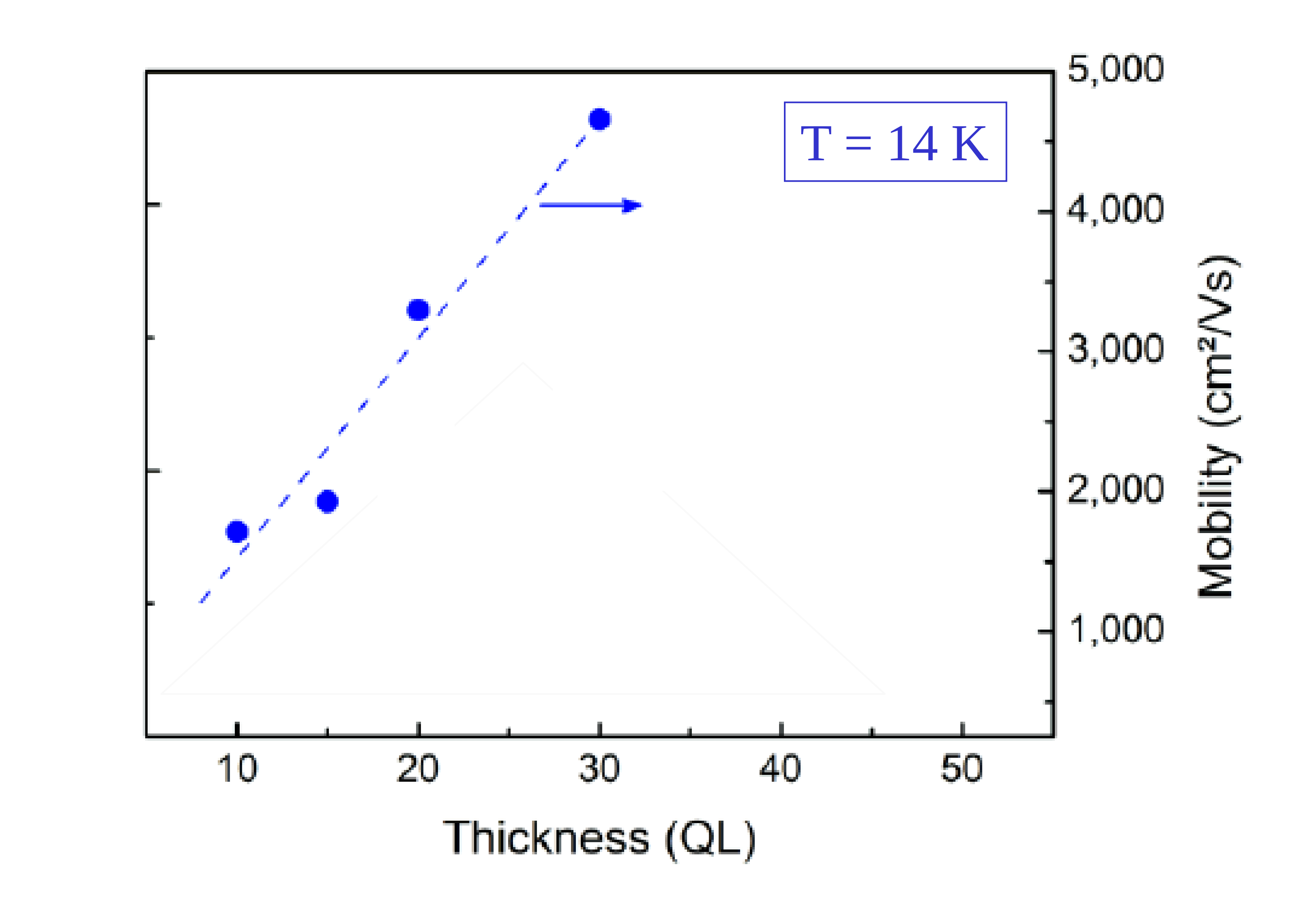




variation in resistivity by factor 1.6, while varying thickness by factor 5

⇒Resistivity dominated by surface

very high mobilities



Conclusions

- good epitaxial films of Bi_2Te_3
- ARPES: films are insulating in the bulk, metallic at the surface
- in-situ resistivity: - good ohmic contacts
- - metallic behaviour > dominated by surface states
- resistivity and chemical potential extremely sensitive

  to adsorption of contaminants, especially water

PNAS 2014

PNAS

Intrinsic conduction through topological surface states of insulating Bi_2Te_3 epitaxial thin films

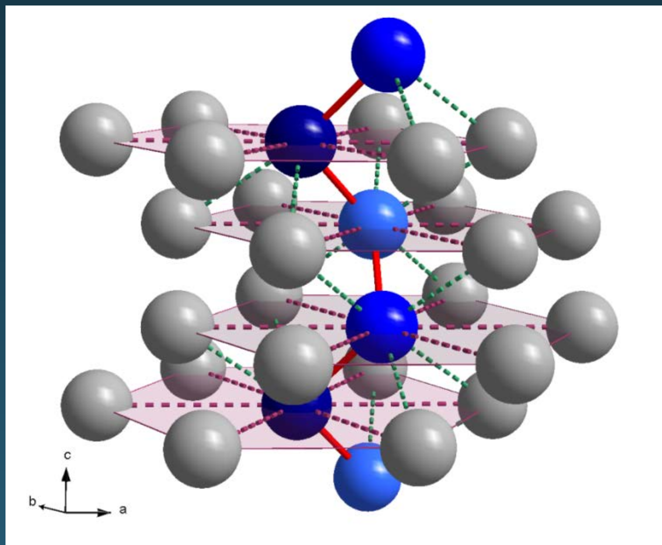
Katharina Hoefer[a,1], Christoph Becker[a], Diana Rata[a], Jesse Swanson[a,b], Peter Thalmeier[a], and L. H. Tjeng[a]

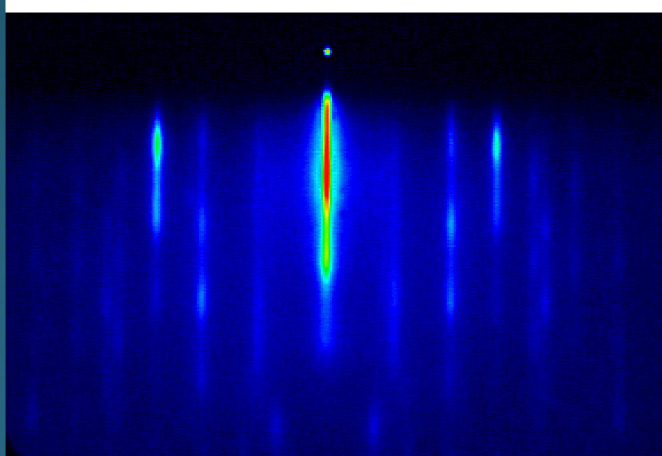
[a]Max Planck Institute for Chemical Physics of Solids, Dresden 01187, Germany; and [b]University of British Columbia, Vancouver, BC, Canada V6T 1Z4

Edited by Zachary Fisk, University of California, Irvine, CA, and approved September 18, 2014 (received for review June 6, 2014)

Protective capping of topological surface states of Bi2Te3

Capping with Tellurium



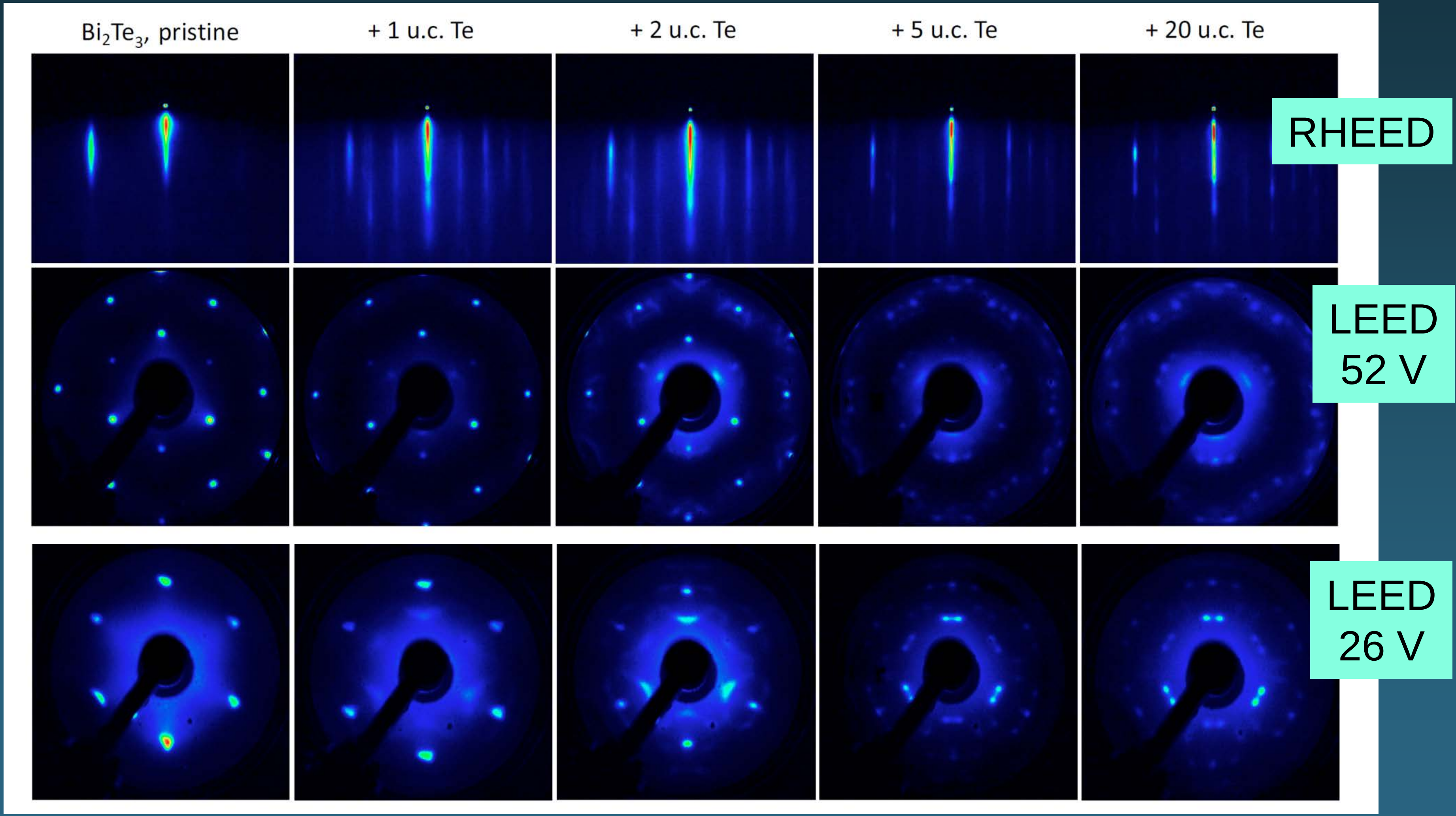


Bi2Te3 20QL + 10ML Te

- trigonal crystal structure
    - a= 4.456Å
    - c= 5.927Å (≙ 1ML)
- 1.6% mismatch to Bi_2Te_3
- half metal
    - ρ_{Te} = 5 mΩm (|| to c axis @ 20°C)
    - ρ_{Te} = 1.5 mΩm (⊥ to c axis @ 20°C)
    - e.g. 10ML Te ⇒ $R_{\square}$(@RT)= 250 kΩ
- Te is top layer of Bi_2Te_3

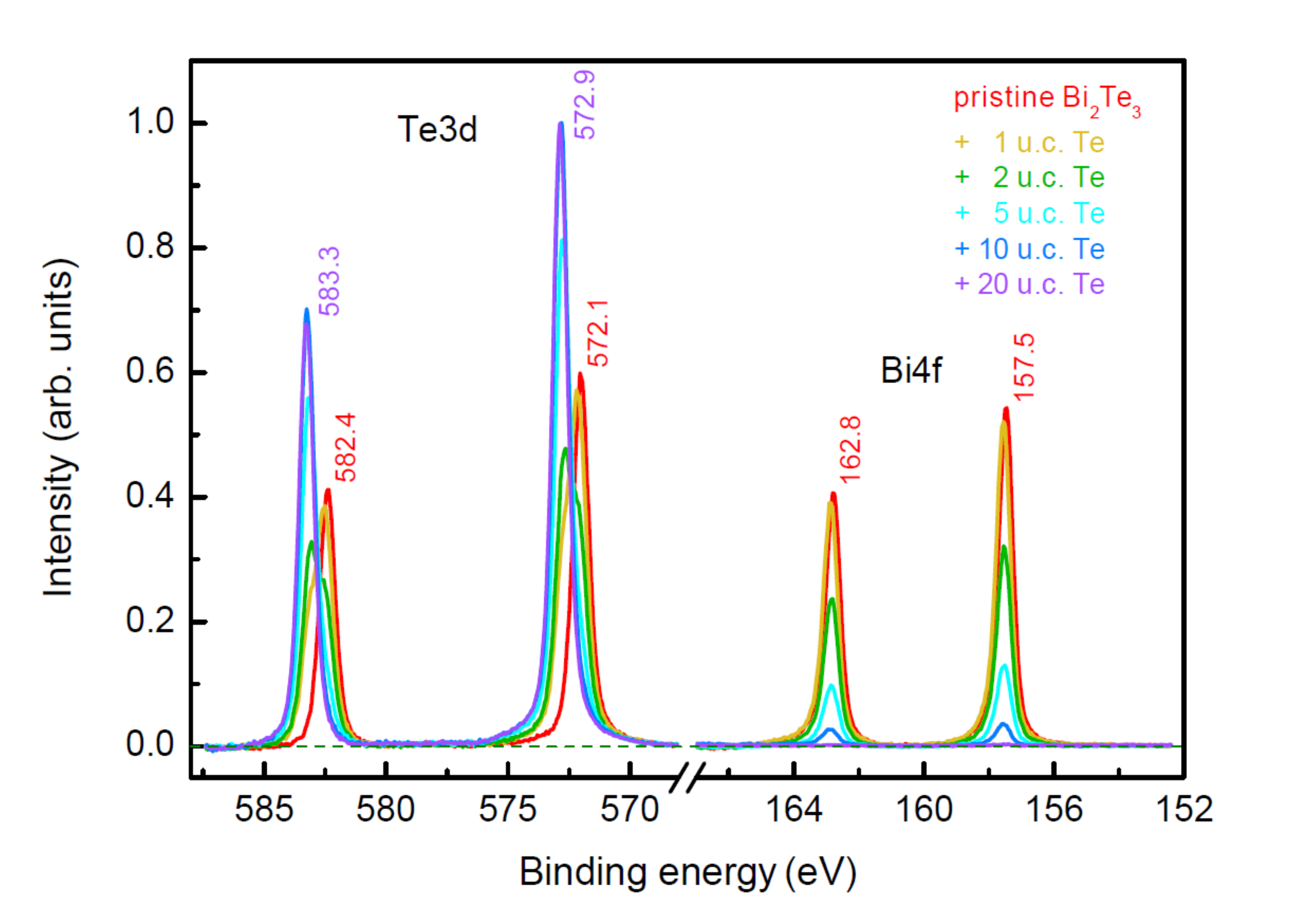
- MBE growth:
    - T_{Te} = 185°C (1 Å/min)
    - epitaxial growth on Bi_2Te_3 @ RT
    - multi-domain

Capping with Tellurium



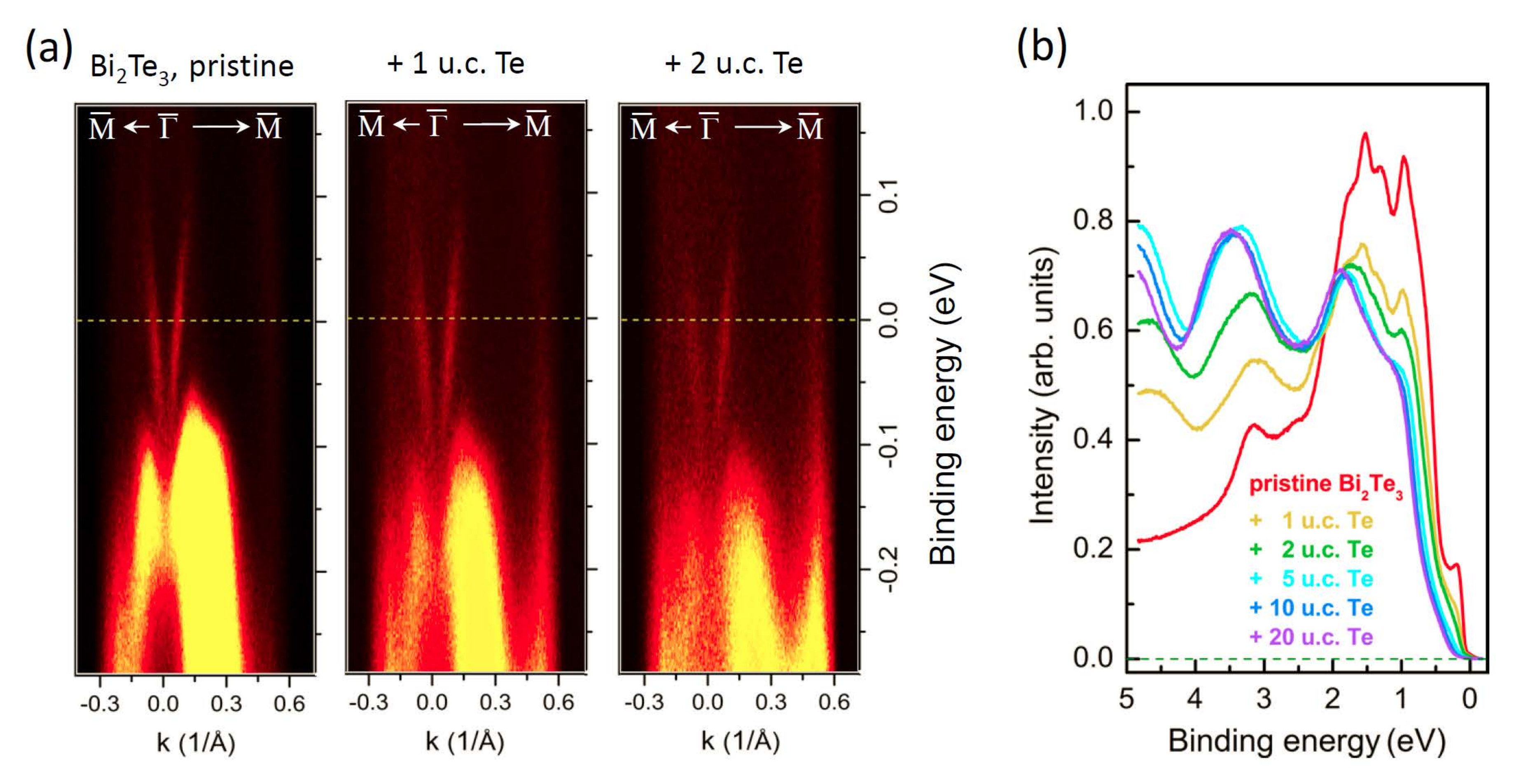
epitaxial growth -- domains due 1.6% misfit

Capping with Tellurium



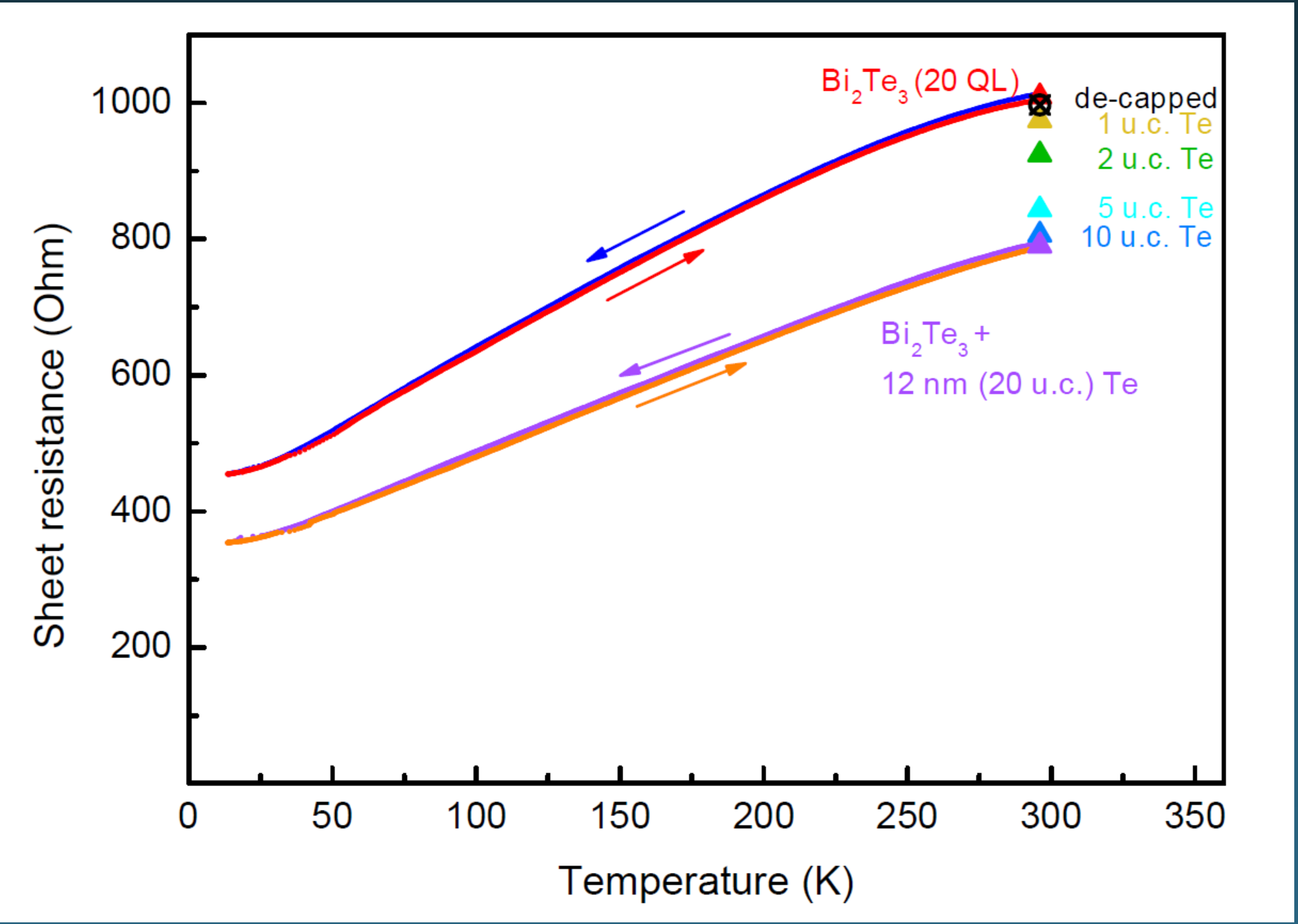
capping films are closed (no pinholes)

Capping with Tellurium



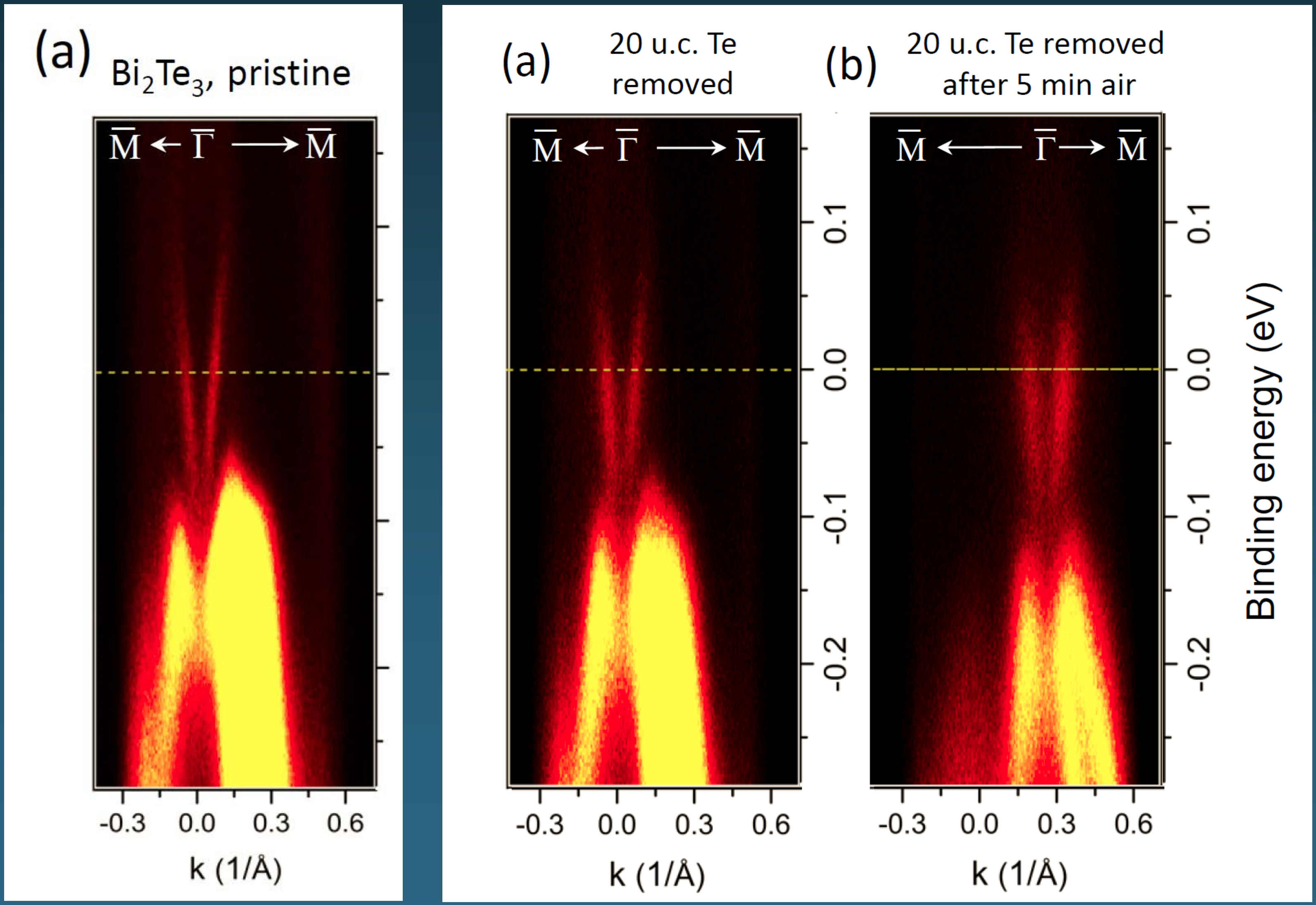
Te capping leaves surface states bands intact + no doping !

Capping with Tellurium



Te capping gives only small parallel conductivity

Removing Tellurium capping



Pristine state can be restored, also after air-exposure !

capping of Bi_2Te_3 films with Te

- Capping by Te leaves the topological surface states intact (ARPES)
- No doping (ARPES), minor influence on conductivity (4 point)
- Epitaxy can be achieved (RHEED, LEED), no pinholes (XPS)
- Protective against air
- Capping can be removed, pristine state recovered (ARPES, 4 point)

AIP Advances

AIP ADVANCES **5**, 097139 (2015)

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Protective capping of topological surface states of intrinsically insulating Bi_2Te_3

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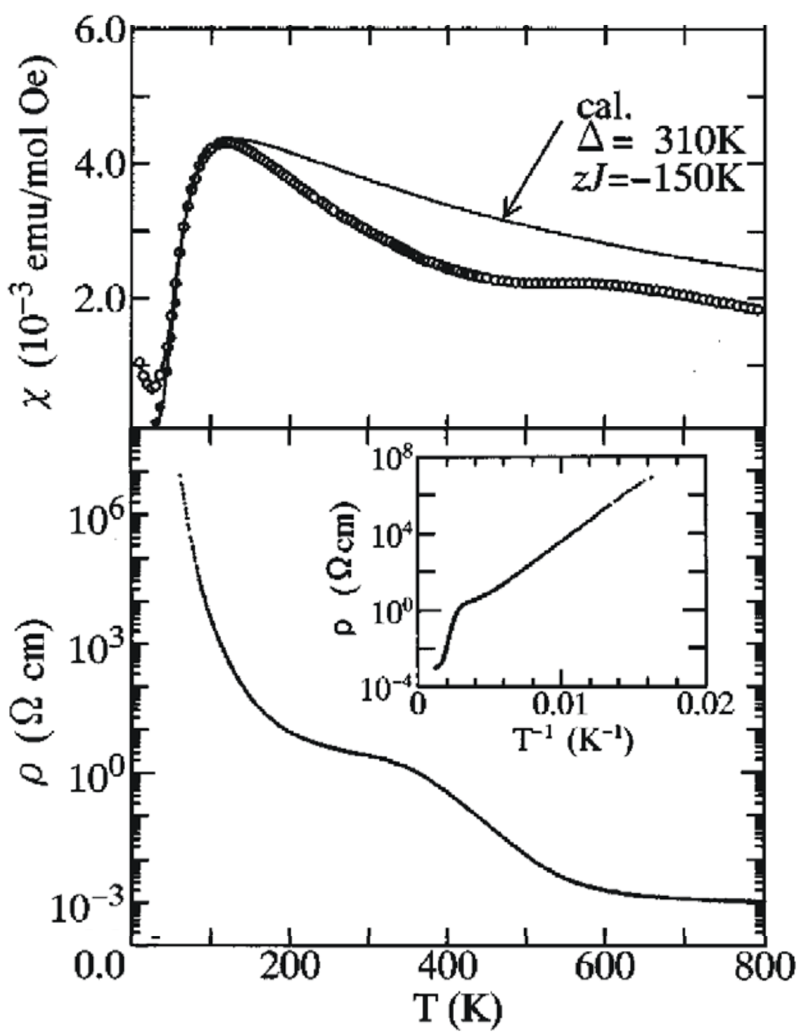
(Received 23 June 2015; accepted 1 September 2015; published online 11 September 2015)

$LaCoO_3$: a benchmark system Co^{3+}: $3d^6$

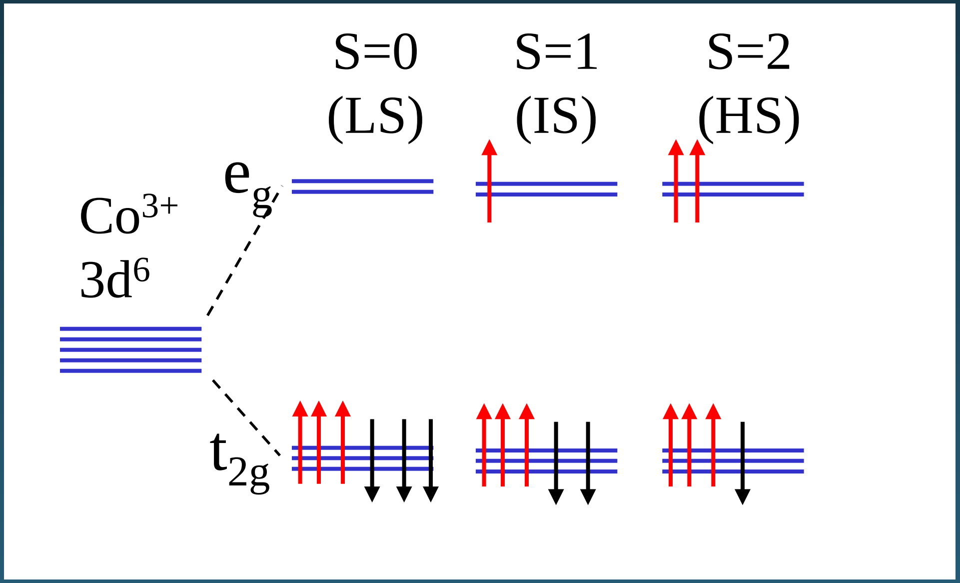


S. Yamaguchi *et al.*, PRB **53**, 2926 (1996)

- non-magnetic insulator at low T
- non-magnetic to paramagnetic transition for T>25K, with max. in magn. susceptibility at 100K
- resistivity drop T = 350K -550K, "metal-insulator transition"

Spin-state transitions ?
Low – Intermediate – High spin ?

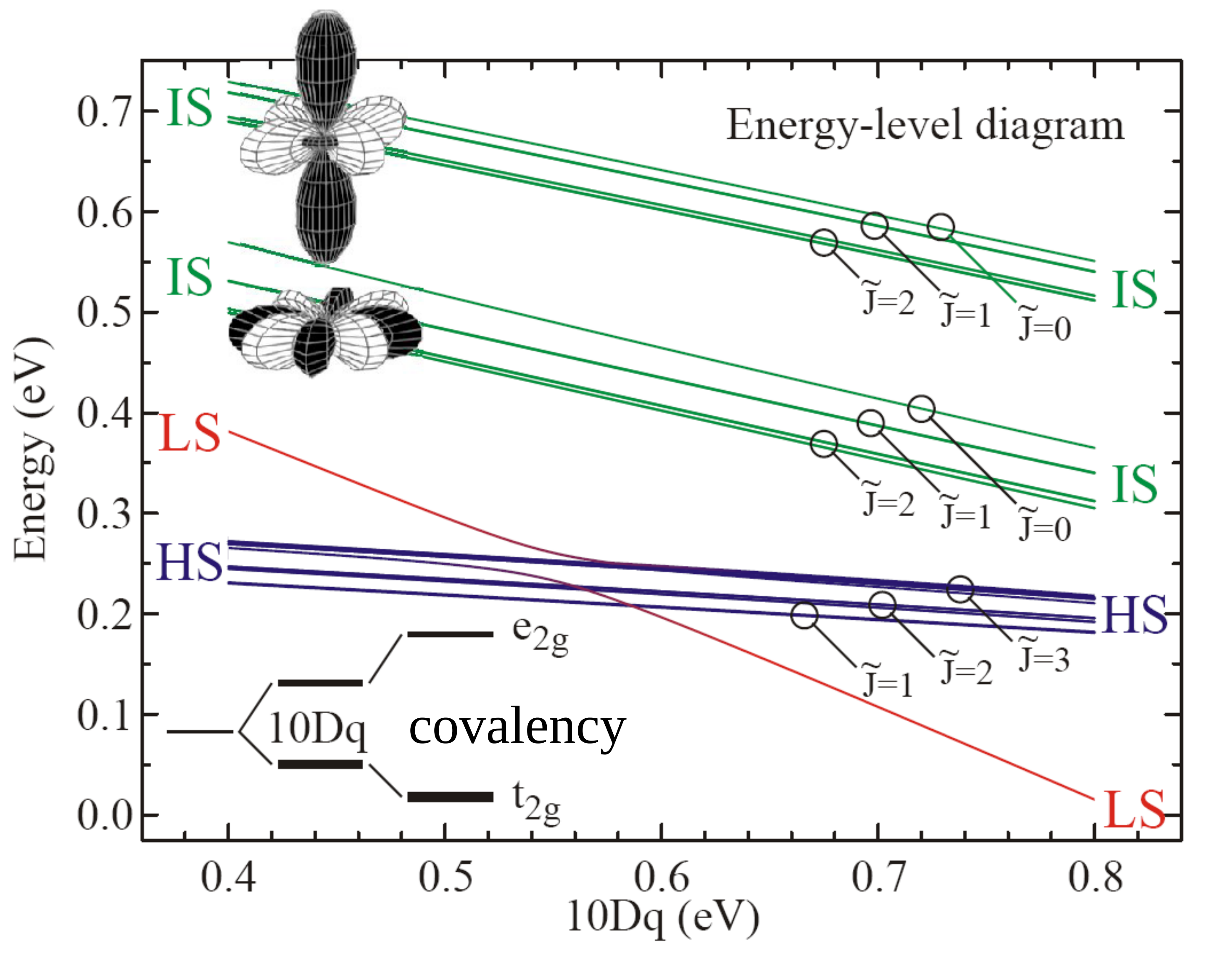
Puzzle: what is the spin state of Co^{3+} ??



competition:
crystal field - band formation - Hund‘s exchange

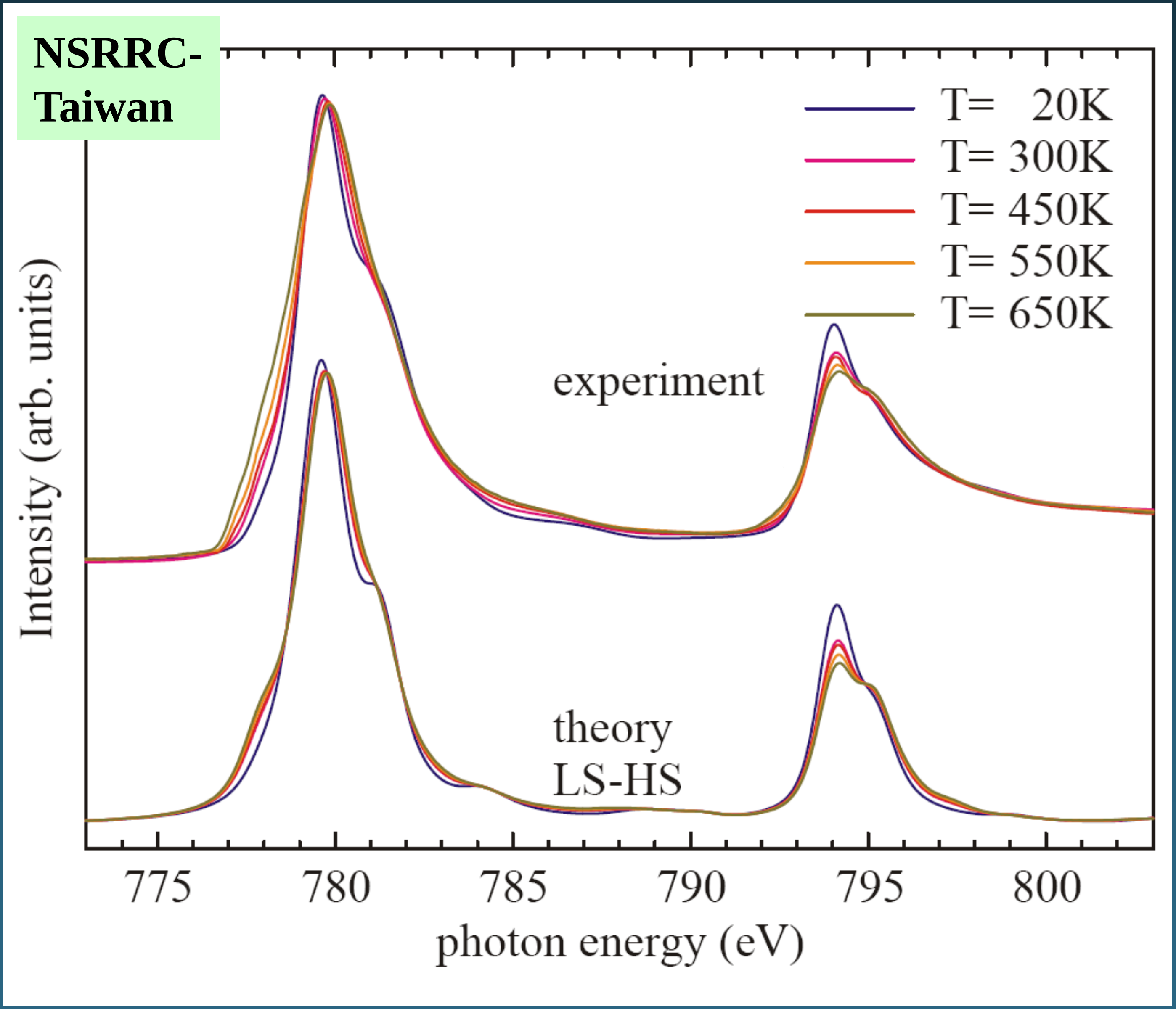
Haverkort, Hu, Tjeng - PRL **94,** 056401 (2005)

Energy level diagram: CoO_6 cluster incl. covalency



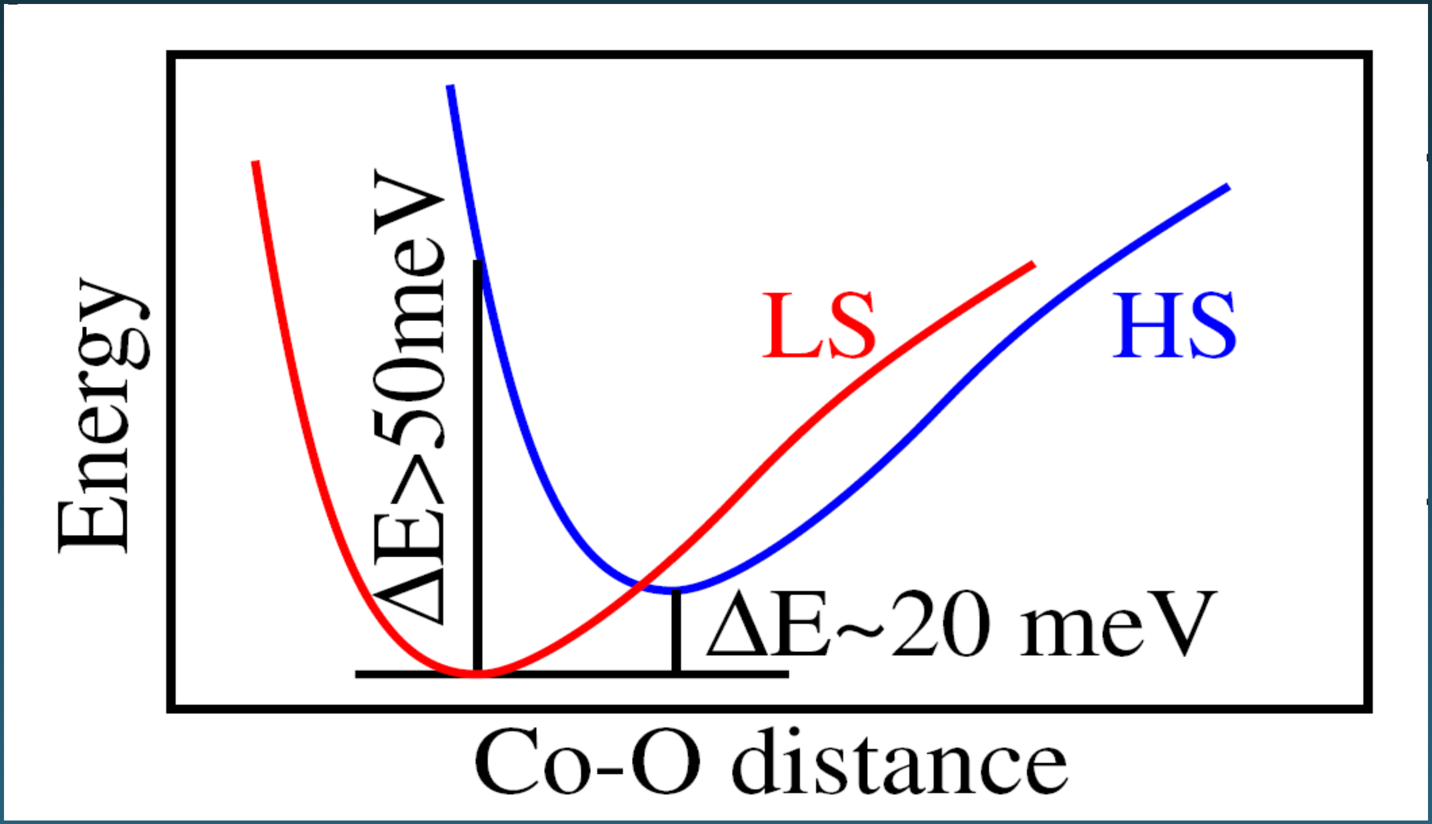
Haverkort, Hu, Tjeng - PRL **94,** 056401 (2005)

XAS study on the spin state of Co^{3+} ion in $LaCoO_3$



Haverkort, Hu, Tjeng - PRL **94,** 056401 (2005)

Spin state transition: local lattice relaxation



- frozen lattice: $\Delta E >> k_B T$

  otherwise too much Van Vleck and incorrect XAS spectra
- inhomogeneous mixed spin-state system

H2-molecule: photoemission and vibrational levels

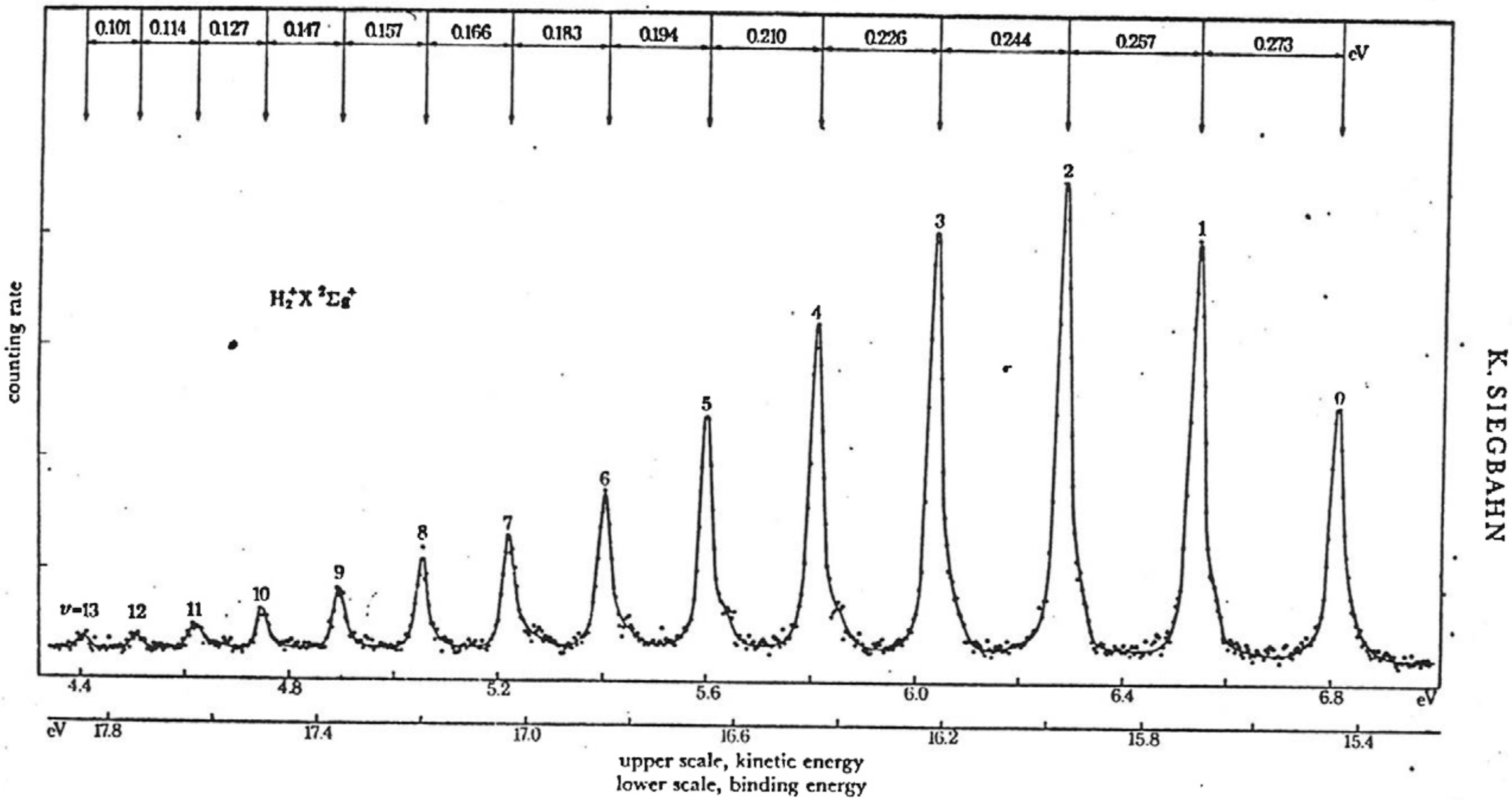
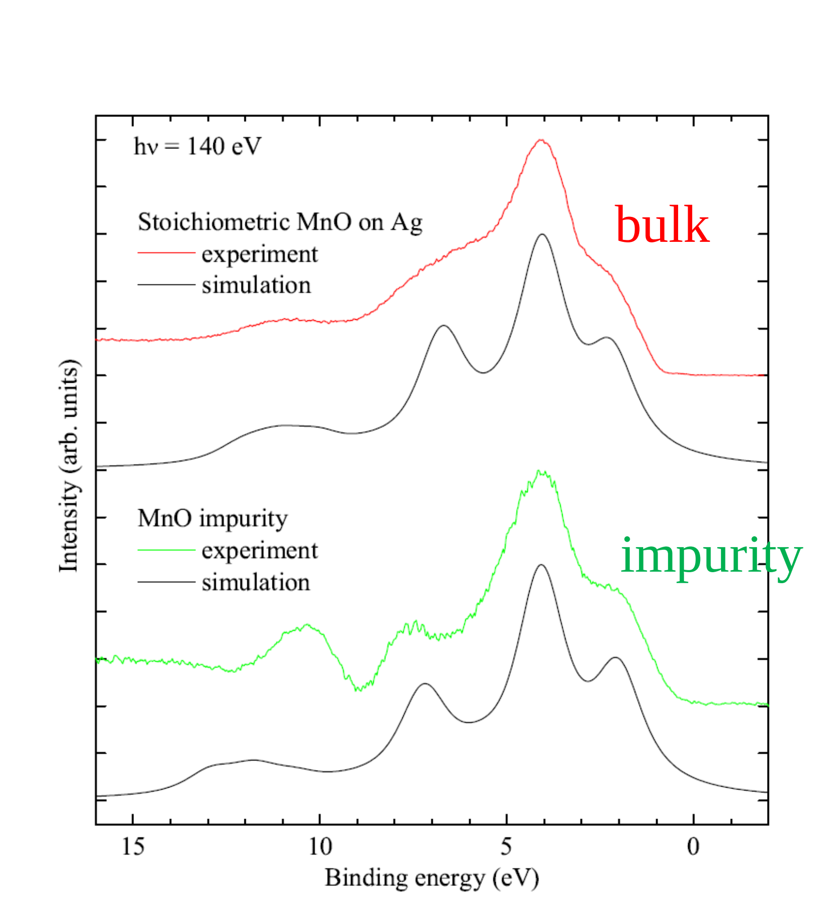


FIGURE 27*a*. Electron spectrum from molecular hydrogen, excited by helium resonance radiation. Fourteen peaks are seen which correspond to vibrational levels of the molecule ion.

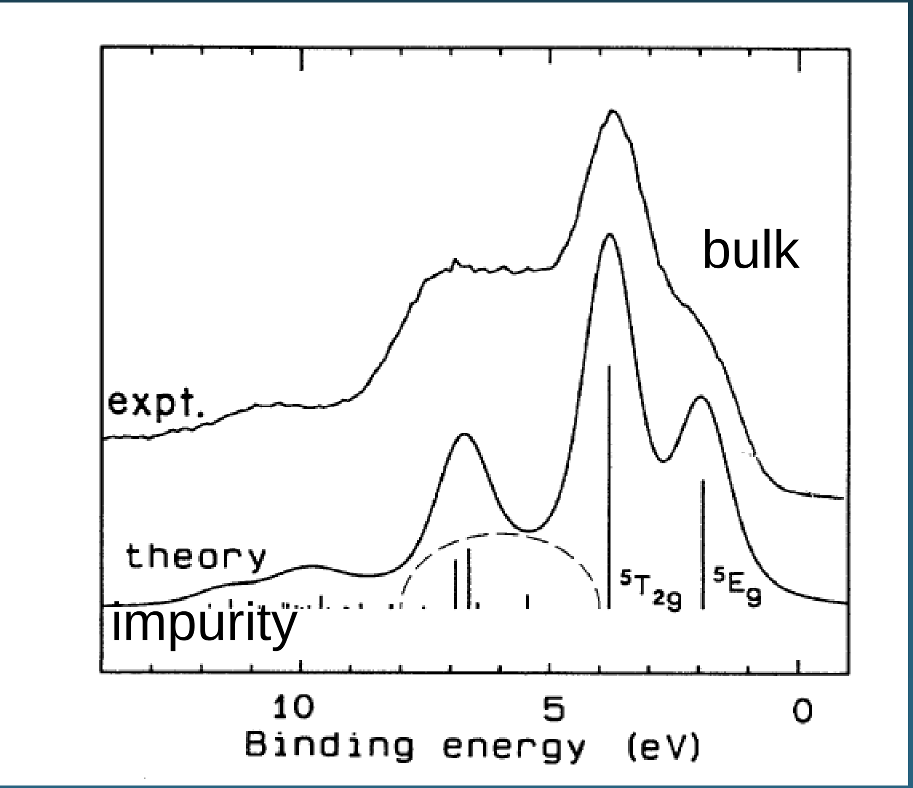
MnO bulk vs Mn in MgO

propagation of an extra hole in MnO

Haupricht thesis 2010

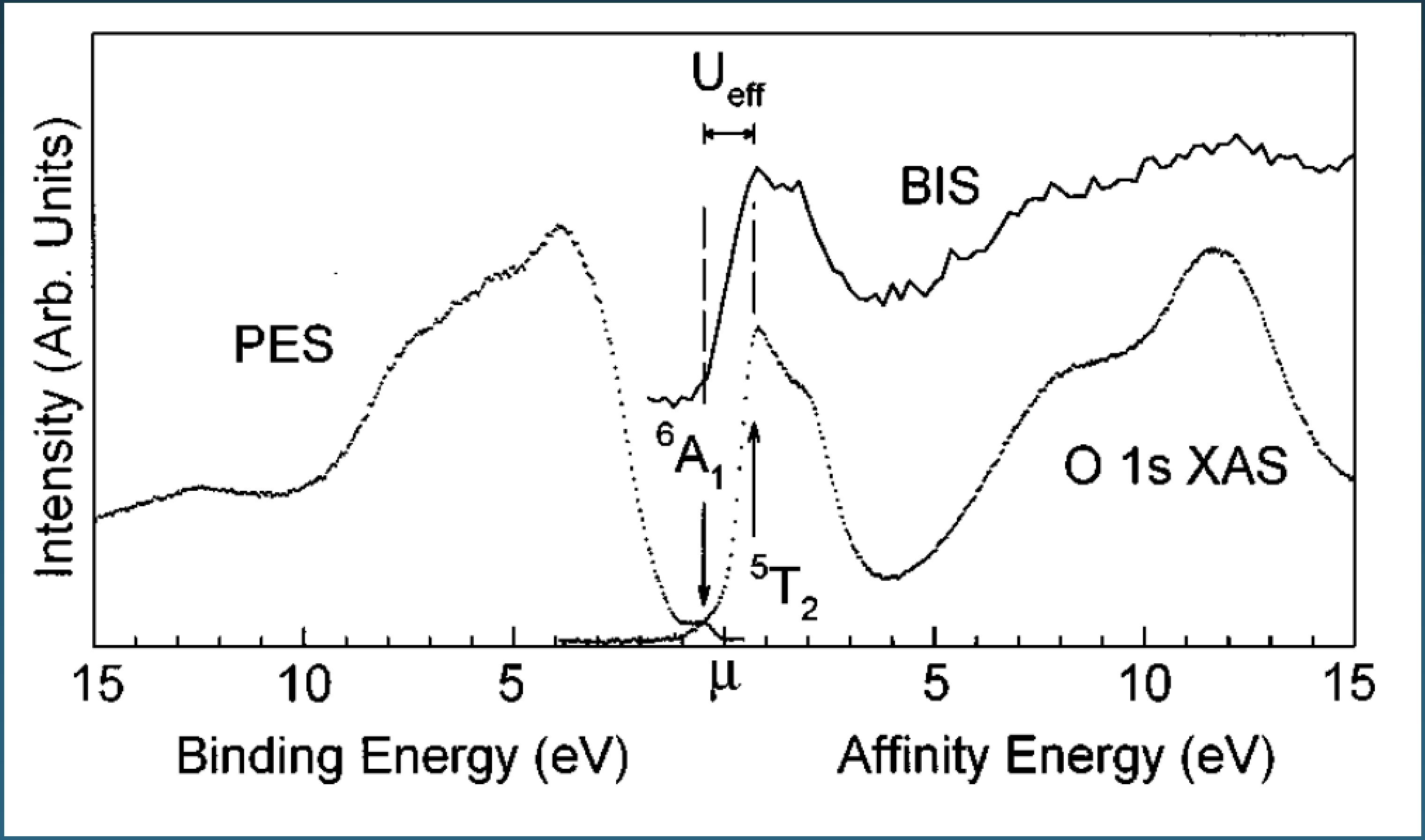


van Elp et al. PRB 1991



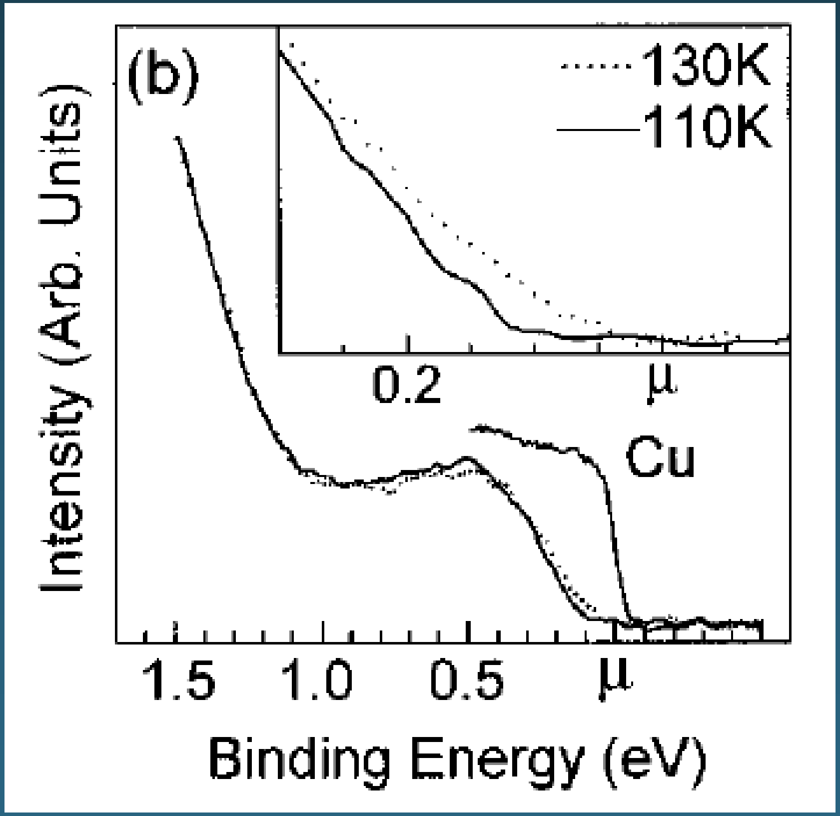
Fe_3O_4: an insulator at low temperatures

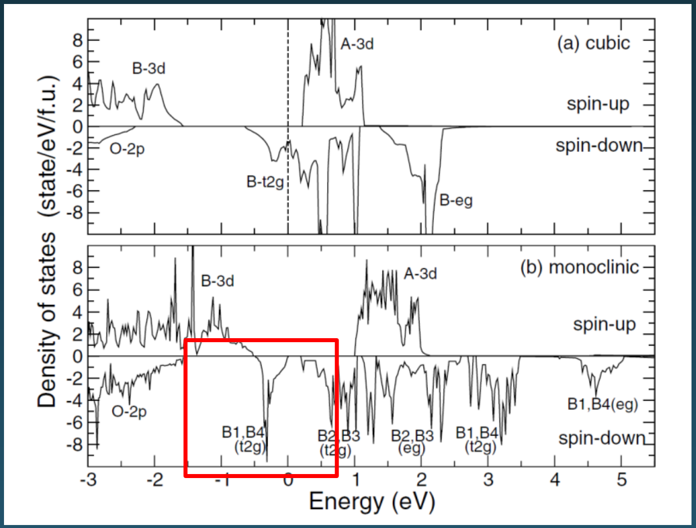
Park, Tjeng, Allen et al. PRB 1997

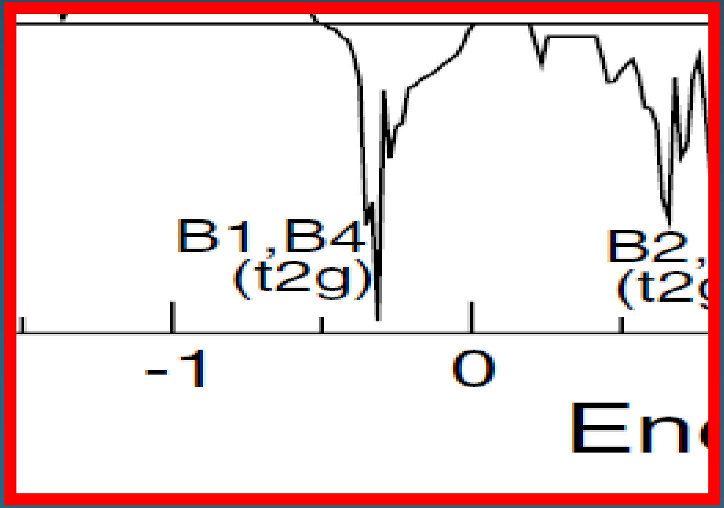


Fe_3O_4: an insulator at low temperatures

Park, Tjeng, Allen et al. PRB 1997







Fe_3O_4: Polarons and Verwey transition ?

Europhys. Lett., **70** (6), pp. 789–795 (2005)
DOI: 10.1209/epl/i2005-10045-y

High-energy photoemission on Fe_3O_4: Small polaron physics and the Verwey transition

D. Schrupp[1], M. Sing[1,2], M. Tsunekawa[2], H. Fujiwara[2], S. Kasai[2], A. Sekiyama[2], S. Suga[2], T. Muro[3], V. A. M. Brabers[4] and R. Claessen[1]

Polaronic Behavior of Photoelectron Spectra of Fe_3O_4 Revealed by Both Hard X-ray and Extremely Low Energy Photons

Masato Kimura[1], Hidenori Fujiwara[1], Akira Sekiyama[1,2], Junichi Yamaguchi[1], Kazumasa Kishimoto[1], Hiroshi Sugiyama[1], Gen Funabashi[1], Shin Imada[3], Satoshi Iguchi[4], Yoshinori Tokura[4], Atsushi Higashiya[2,5], Makina Yabashi[2,6], Kenji Tamasaku[2], Tetsuya Ishikawa[2], Takahiro Ito[7*], Shin-ichi Kimura[7], and Shigemasa Suga[1,2]

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Modification of material properties using image charge screening

Reduction of charge excitation energies:

- Coulomb energy: $U = U_o - 2E_{image}$
- Charge transfer energy: $\Delta = \Delta_o - 2E_{image}$
- Bandgap: $E_g = E_{go} - 2E_{image}$

Examples from experiments:

- Monolayer C_{60} on Ag : U and E_g reduced by 1 eV
- MgO film on Ag : U and Δ reduced by 2 eV
- NiO on Ag vs on MgO : influence on Neel temperature
- Te film on Bi_2Te_3 : more conducting due to polarization ?

Small polarons: energy lowering

- Spin state transition in $LaCoO_3$
- Propagation of extra hole in MnO, Fe_3O_4