Chemical Gating of a Weak Topological Insulator: $Bi_{14}Rh_3I_9$

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1. Introduction: the story of a new Bismuth compound
2. How the surface polarity of $Bi_{14}Rh_3I_9$ can be compensated
3. Does the polarity hinder cleavage?
4. Summary

1. Introduction: a new Bismuth compound

Collaboration:

B. Rasche, A. Isaeva, M. Ruck (synthesis and characterization, TU Dresden)

S. Borisenko, V. Zabolotnyy, B. Büchner (ARPES, IFW Dresden)

K. Koepernik, C. Ortix (now Uni Eindhoven), J. van den Brink (theory, IFW Dresden)

C. Pauly, M. Liebmann, M. Pratzer, J. Kellner, B. Kaufmann, M. Morgenstern (STM, RWTH Aachen)

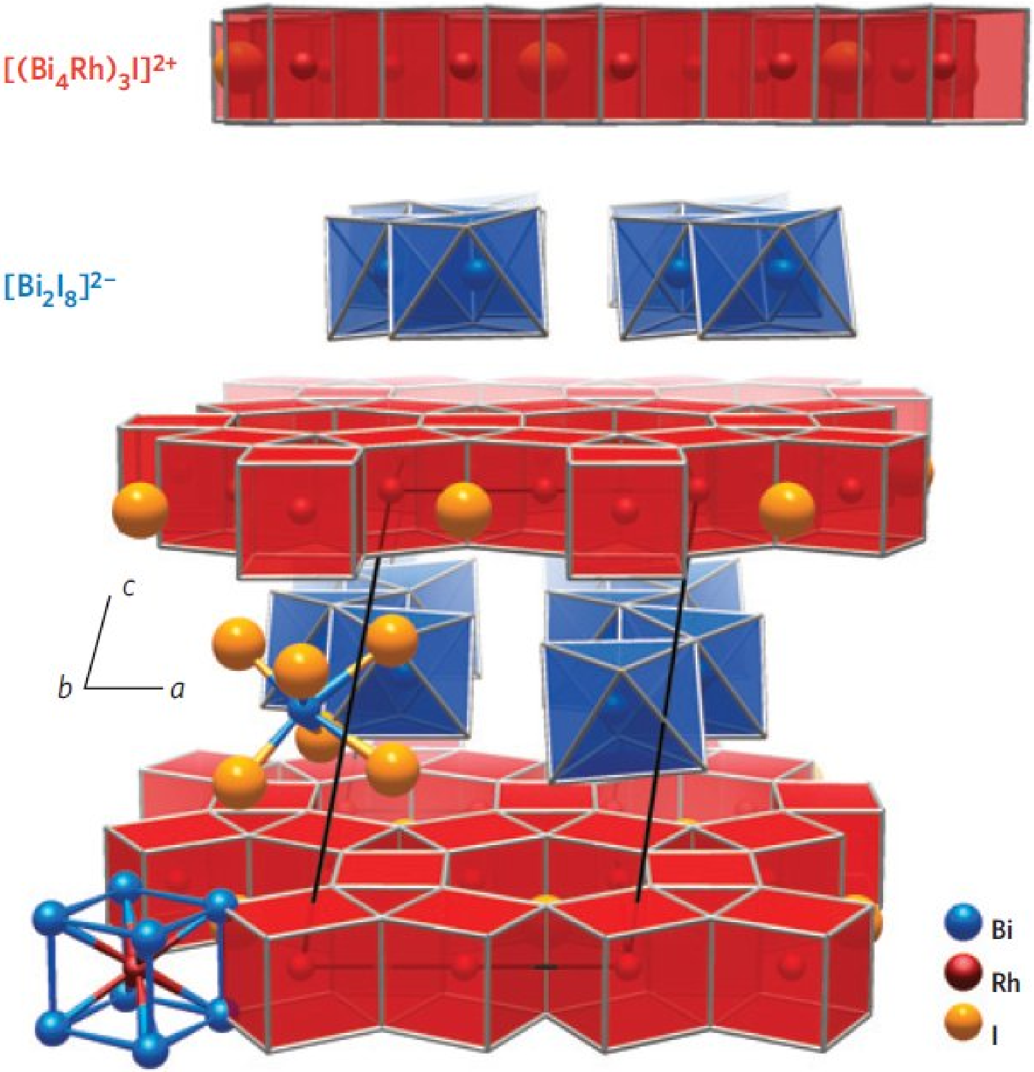
M. Eschenbach, L. Plucinski, C. M. Schneider (ARPES, FZ Jülich)

1. Introduction: a new Bismuth compound

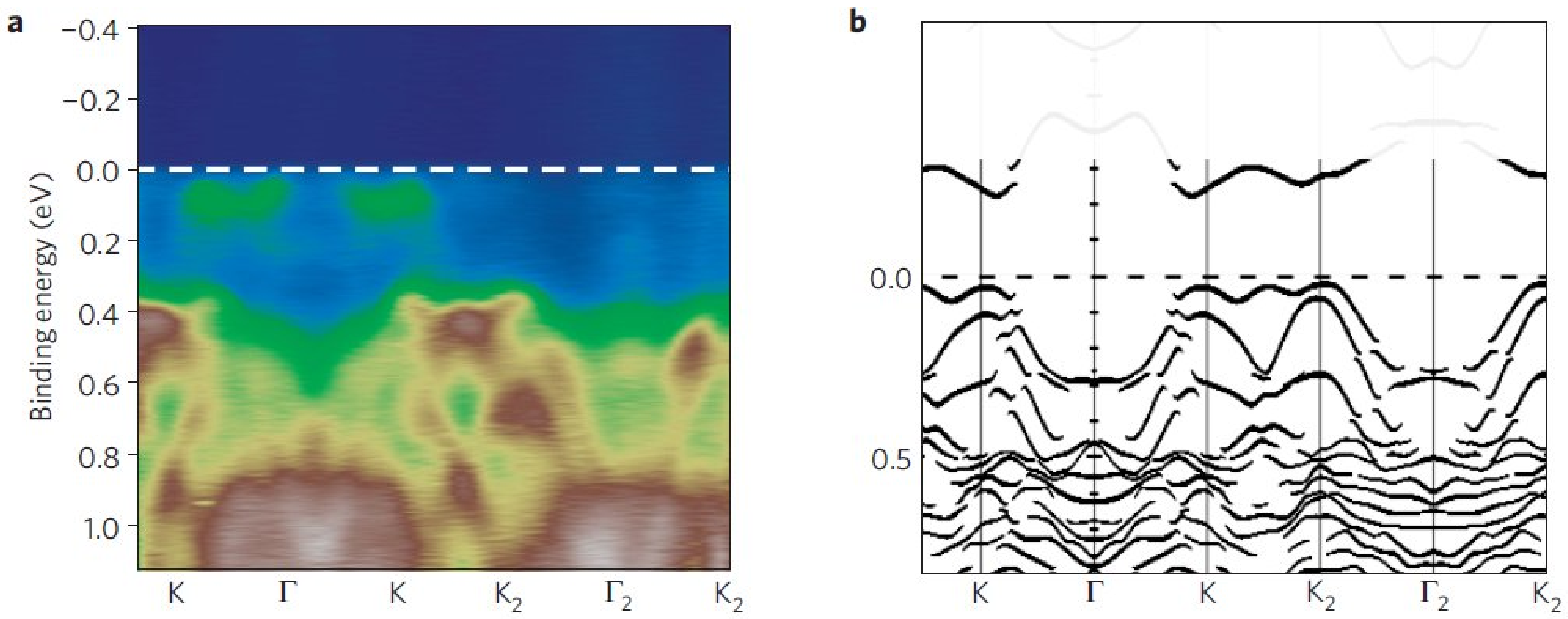
$Bi_{14}Rh_3I_9$:

a new compound composed of alternating $[(Bi_4Rh)_3I]^{2+}$ and $[Bi_2I_8]^{2-}$ layers

Does this material show any peculiar topological property?



1. Introduction: a new Bismuth compound

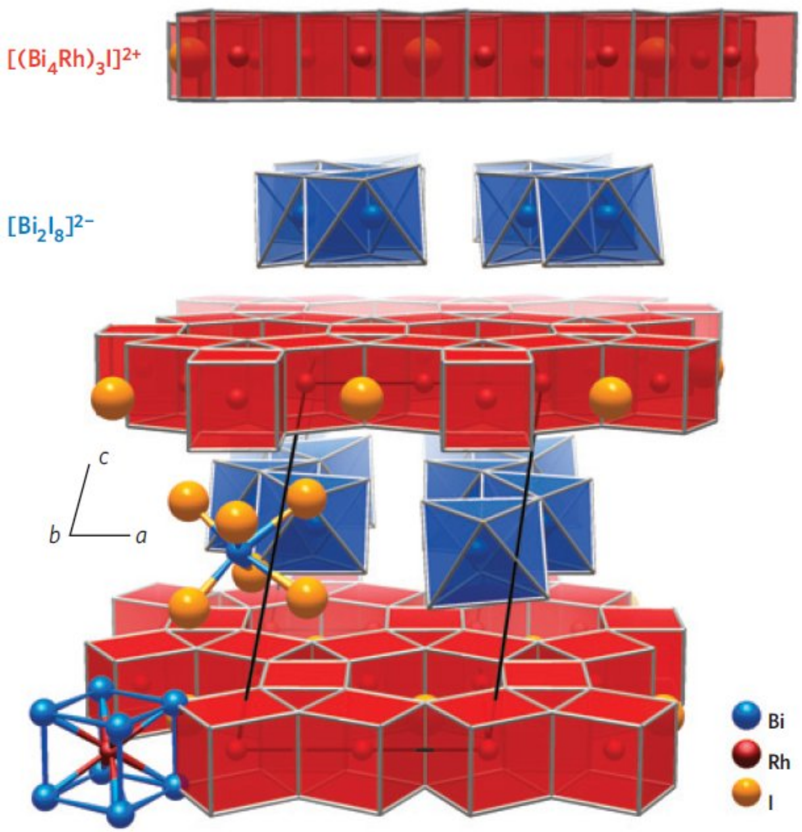


LDA yields Z_2 invariants (0;0,0,1): $Bi_{14}Rh_3I_9$ is a weak 3D TI.

This prediction is supported by the good agreement between ARPES data and unfolded LDA band structure, but this is of course only an indirect evidence. The sample seems to be n-doped. Why?

B. Rasche *et al*., Nat. Mat. **12**, 422 (2013)

1. Introduction: a new Bismuth compound



Nominal charges:

$(Bi_4Rh)_3I$: 2+

Bi_2I_8: 2-

$(Bi_4Rh)_3I$: 2+

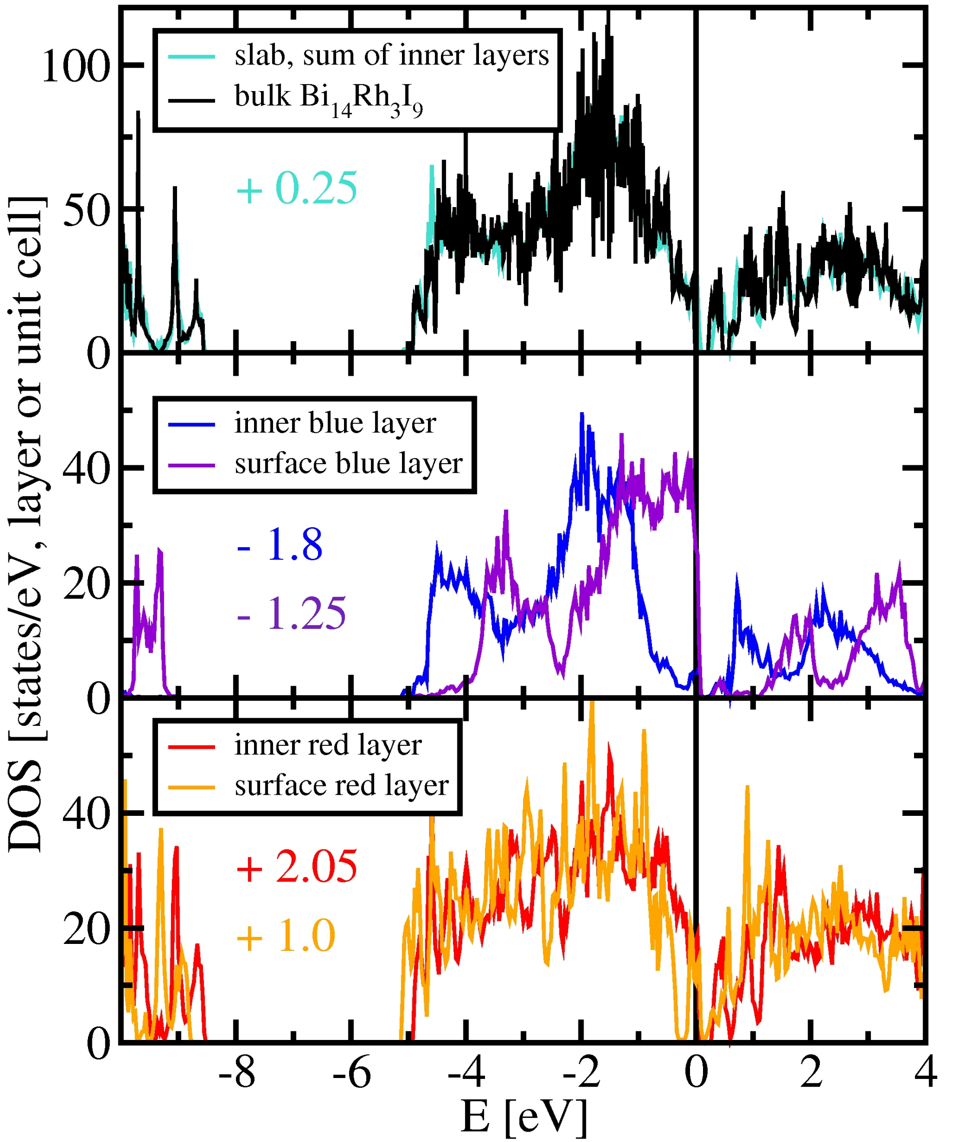
Bi_2I_8: 2-

$(Bi_4Rh)_3I$: 2+

…

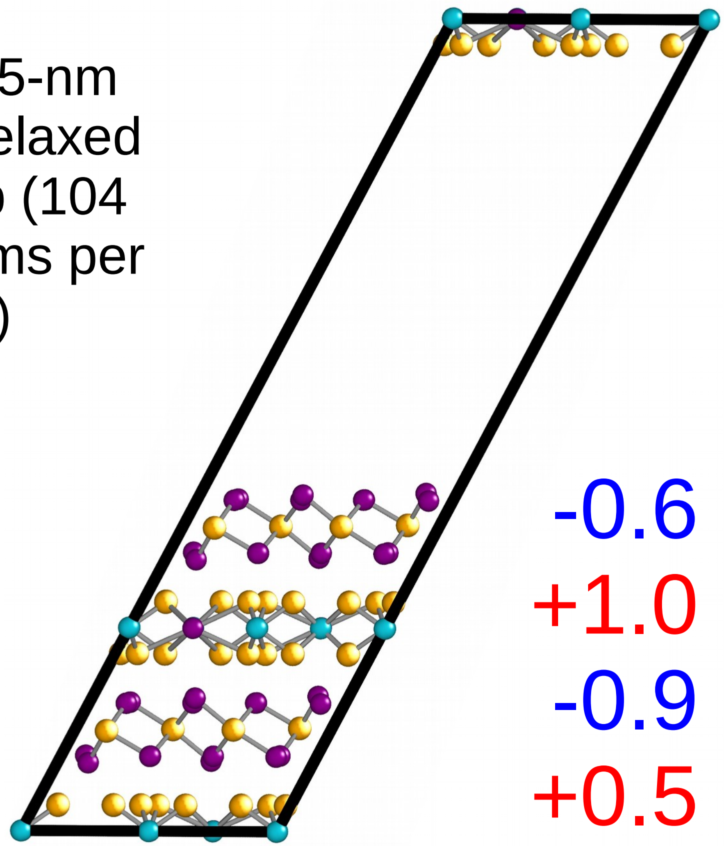
Polar surfaces are expected: the n-doping is probably intrinsic.

Intrinsic surface charge of $Bi_{14}Rh_3I_9$



Model:

a 2.5-nm unrelaxed slab (104 atoms per u.c.)

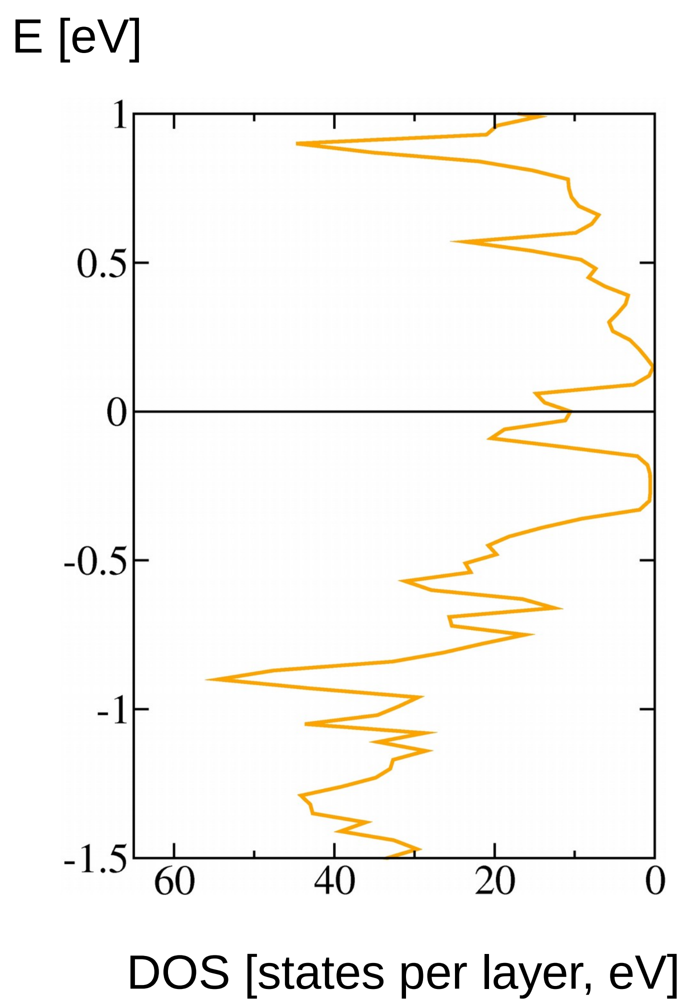


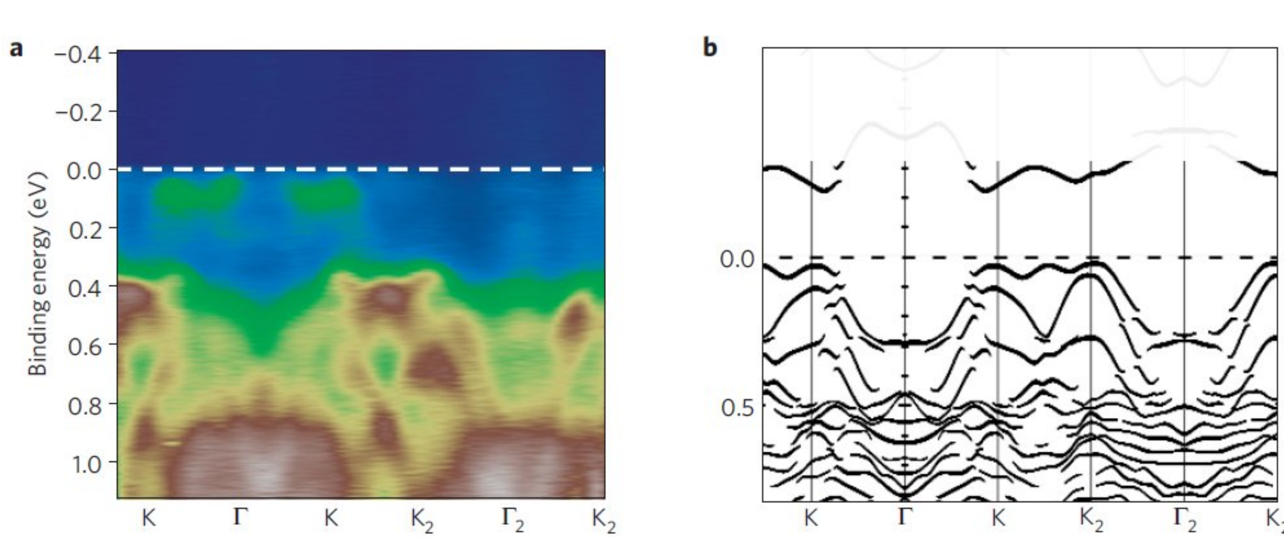
-0.6
+1.0
-0.9
+0.5

(Mulliken charge per chem. unit)

Intrinsic surface charge of $Bi_{14}Rh_3I_9$

LDA-DOS of a surface $(Bi_4Rh)_3I$ layer vs. ARPES vs. shifted bulk bands

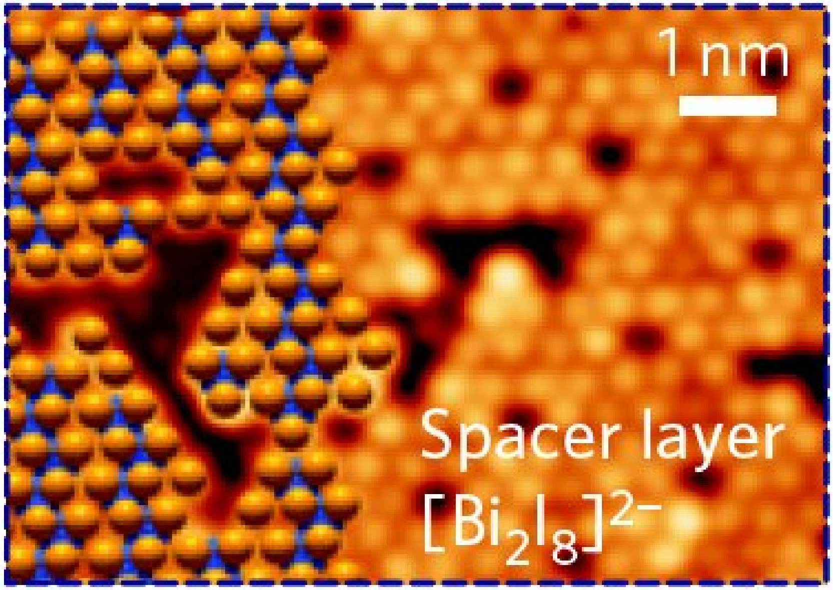


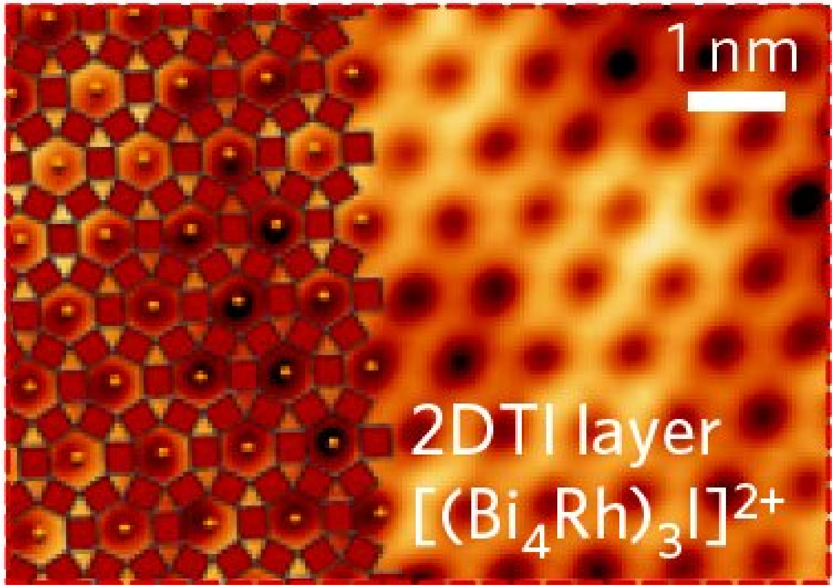


Intrinsic surface charge of $Bi_{14}Rh_3I_9$

The origin of the n-doping is plausible; But, why does ARPES receive only a signal from the $(Bi_4Rh)_3I$ layer?

(1) The surface consists of both anionic and cationic layers:

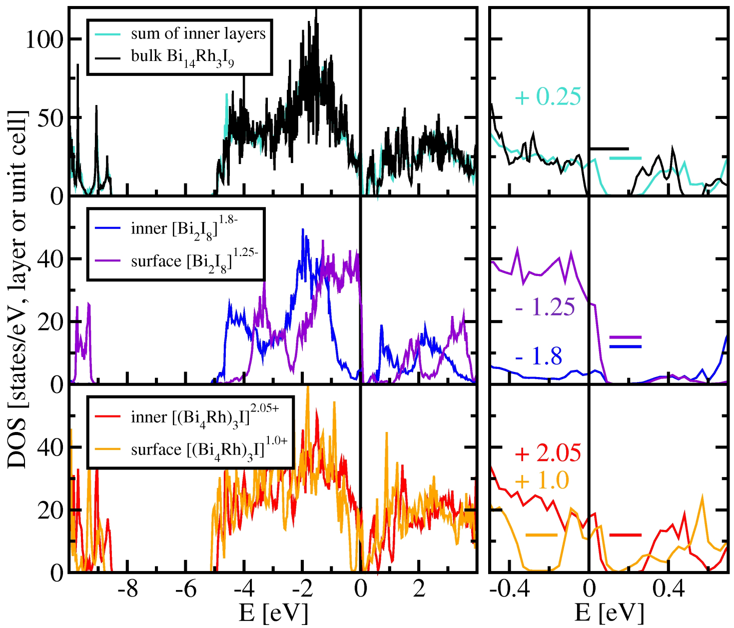




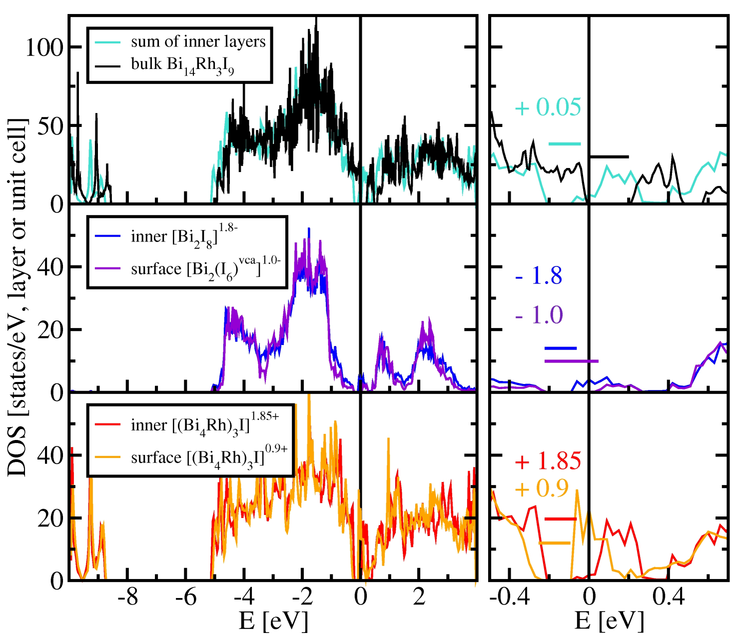
(2) STM on the spacer Bi_2I_8 layer shows „holes“ in this layer, which could be understood as about 1/8 iodine-vacancies. There is no trace of adatoms visible on the $(Bi_4Rh)_3I$ layer.

C. Pauly *et al.*, Nat. Phys. **11** (2015) 338

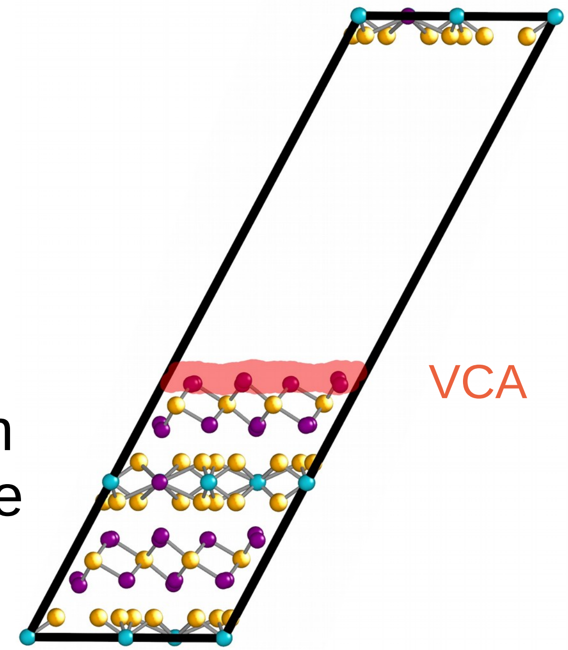
Intrinsic surface charge of $Bi_{14}Rh_3I_9$

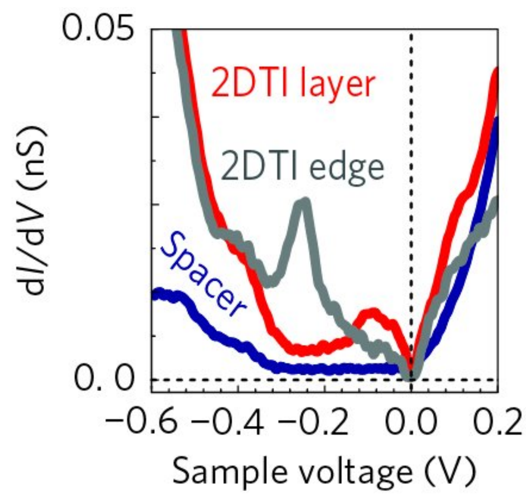


Upper DOS:
original structure



Lower DOS:
simulation of 12.5% iodine evaporation = partial compensation of the surface charge





STM signal from different regions

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Intrinsic surface charge of $Bi_{14}Rh_3I_9$

Results so far:

The surface $(Bi_4Rh)_3I$ layer is intrinsically n-doped with about 0.5 electrons per chemical unit cell. This explains why ARPES finds the gap between 0.37 and 0.17 eV binding energy.

If we assume evaporation of 12.5% Iodine from the outermost Bi_2I_8 layer, this spacer layer shows a gap between 0.25 eV binding energy and the Fermi level, in agreement with STM. The low DOS of this layer at binding energies up to about 1 eV explains why it is not visible in the ARPES data.

The band bending of the Bi_2I_8 layer is „cured“ by partial Iodine-evaporation. Iodine-decoration of the $(Bi_4Rh)_3I$ layer might shift the gap toward the Fermi level. This would be a necessary condition to measure the quantum spin Hall effect as a final confirmation of the suggested toplogical state.

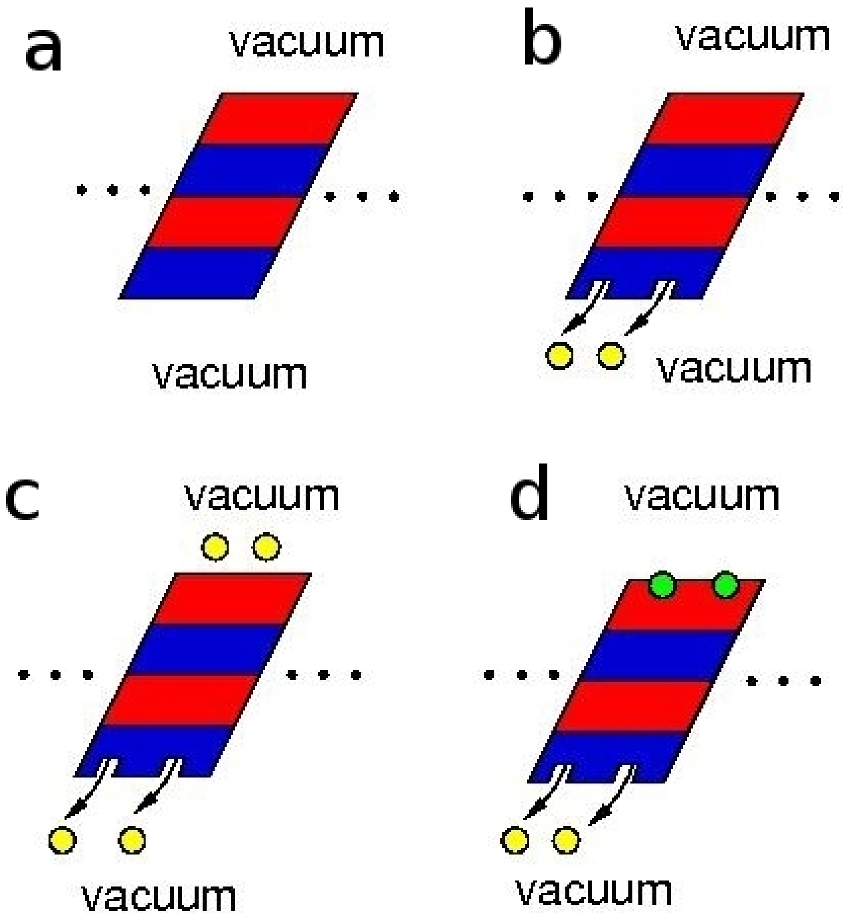
2. How the surface polarity of $Bi_{14}Rh_3I_9$ can be compensated

a: Unreconstructed surfaces with full polarity

b: Observed Iodine evaporation upon cleaving

c: Suggested doping by Iodine deposition at the 2D-TI surface

d: Suggested Sn-doping of the 2D-TI surface



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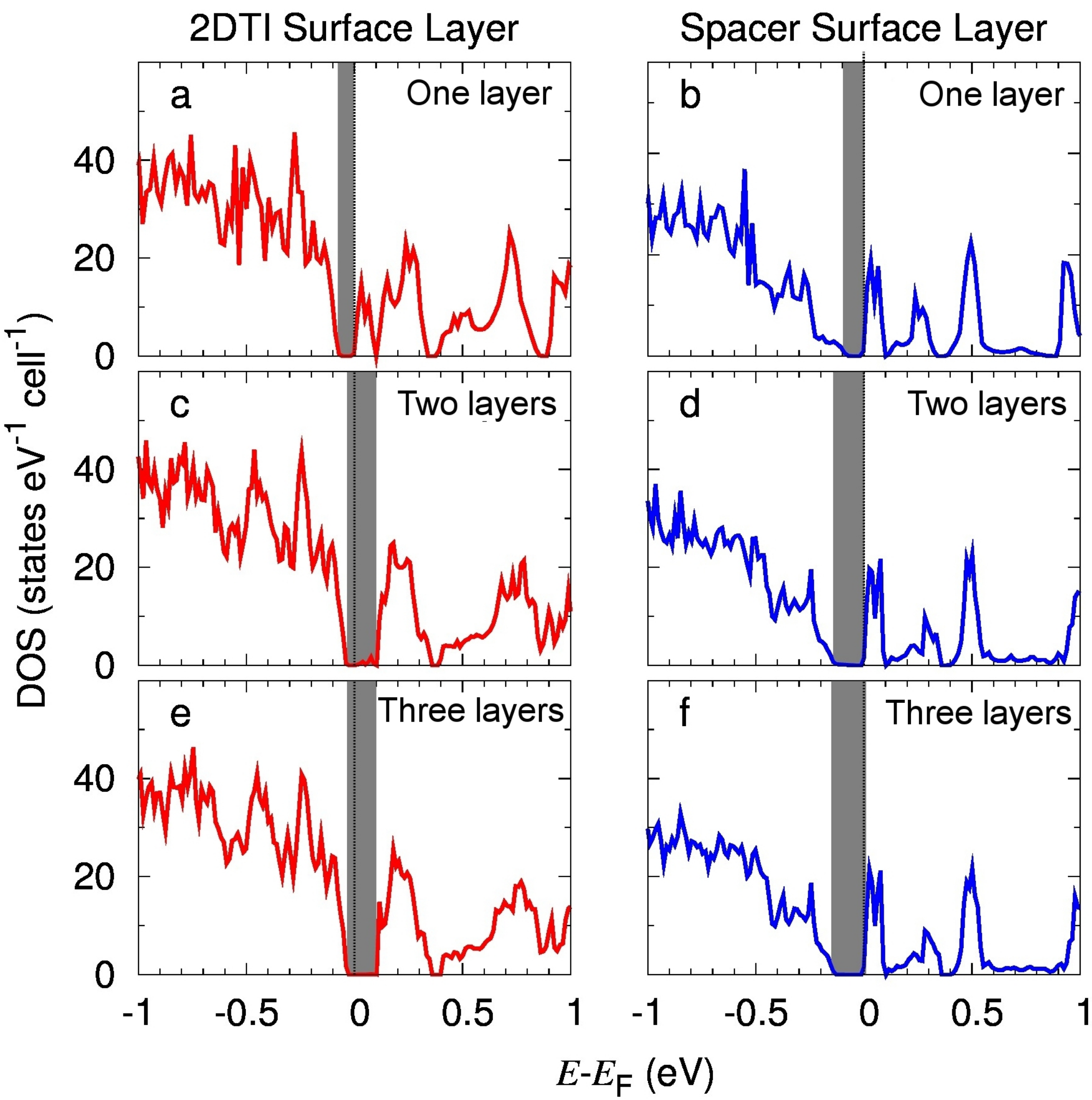


Deposition of one Iodine atom per surface chemical unit compensates the intrinsic polarity = chemical gating.

The topological gap is not closed by chemical gating but is reduced for sample thickness below 4 nm. Thus, transport experiments would not need ultimately thin samples.

M.P. Ghimire and M.R., Nano Letters **17**, 6303 (2017).

3. Does the polarity hinder cleavage?

Cleavage energies calculated with GGA + Grimme corrections:

Surface	quasi-2D		3D
Non-polar	graphite	0.48 J/m^2	FeAl {110} 5.6 J/m^2
	MoS_2	0.55 J/m^2	
	Bi_2TeI	0.45 J/m^2	
Polar	$Bi_{14}Rh_3I_9$	0.75 J/m^2	FeAl {100} 6.7 J/m^2

Many thanks to Bertold Rasche, Thomas Mühl, and Joseph Dufouleur with his group for many discussions and for their courage to try a new way to determine experimental cleavage energies.

4. Summary

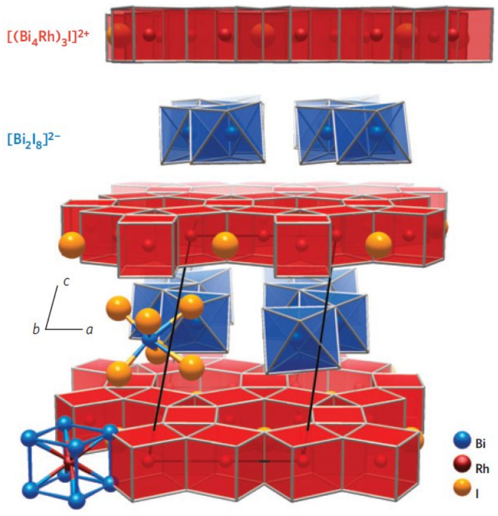
2011: Synthesis of $Bi_{14}Rh_9I_3$

2013: ARPES and LDA suggests a weak 3D topological state

2015: Edge states are detected and characterized by STM

2017: The surface polarity can be compensated

2019: Quantum spin-Hall state measured?



4. Summary

2012: Synthesis of Bi14Rh9I3

2013: ARPES and LDA suggests a weak 3D topological state

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Thanks for your attention!