Finding Happiness and Saving the World through Electronic-Structure Calculations

Nicola Spaldin
Materials Theory
ETH Zürich


SUSTAINABLE DEVELOPMENT GOALS
1 NO POVERTY
2 ZERO HUNGER
3 GOOD HEALTH AND WELL-BEING
4 QUALITY EDUCATION
5 GENDER EQUALITY
6 CLEAN WATER AND SANITATION
7 AFFORDABLE AND CLEAN ENERGY
8 DECENT WORK AND ECONOMIC GROWTH
9 INDUSTRY, INNOVATION AND INFRASTRUCTURE
10 REDUCED INEQUALITIES
11 SUSTAINABLE CITIES AND COMMUNITIES
12 RESPONSIBLE CONSUMPTION AND PRODUCTION
13 CLIMATE ACTION
14 LIFE BELOW WATER
15 LIFE ON LAND
16 PEACE, JUSTICE AND STRONG INSTITUTIONS
17 PARTNERSHIPS FOR THE GOALS
SUSTAINABLE DEVELOPMENT GOALS

1990s:
A huge breakthrough in electronic-structure theory

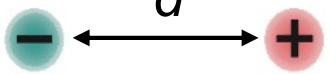
Resta, *Macroscopic electric polarization as a geometric quantum phase* (1993)

King-Smith and Vanderbilt, *Theory of polarization of crystalline solids* (1993)

The problem that was solved

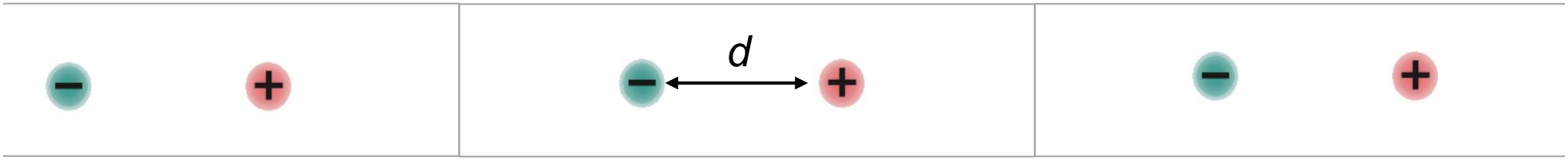
Is the polarization of a periodic solid a *bulk* quantity, and how should it be defined?

"Polarization" in a molecule: No problem



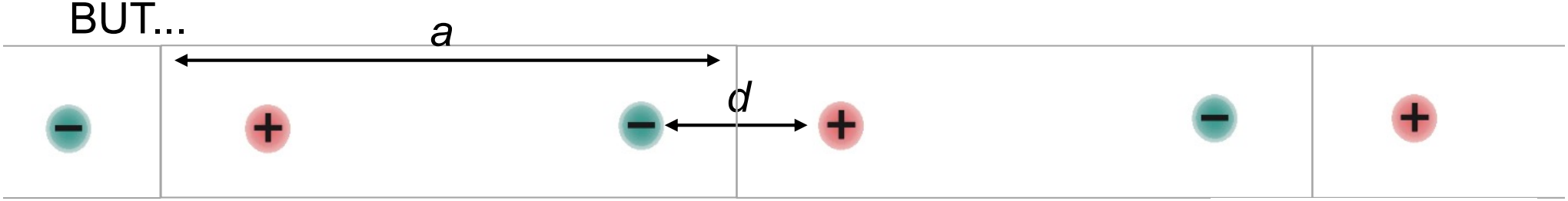
dipole = Σ(charge x position) = e *d* ⟶

Polarization in a periodic solid: dipole per unit volume, *V* ?



Polarization = e *d* /*V* ⟶

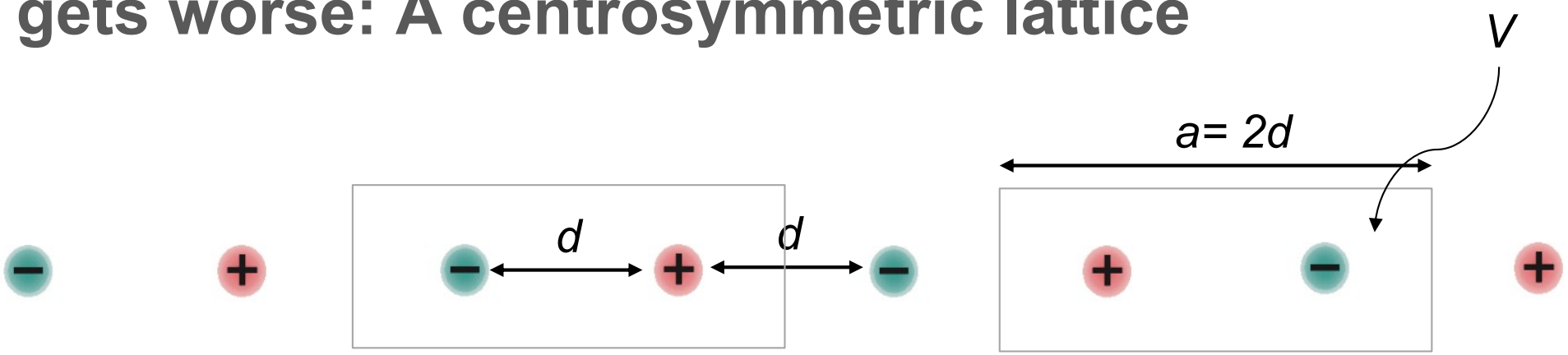
BUT...



⟵ Polarization = e *d* /*V* – e *a* /*V*

Polarization Quantum, P_q

It gets worse: A centrosymmetric lattice



Polarization = $-\,e\,d\,/V, +\,e\,d\,/V \quad \ldots \quad = e\,d\,/\,V + n\,e\,a\,/\,V$

NO ZERO!

x	x	x	x	x	x
$-5P_q/2$	$-3P_q/2$	$-P_q/2$	$P_q/2$	$3P_q/2$	$5P_q/2$

$$P_q = e\,a\,/\,V$$

Modern Theory of Polarization: Key Results

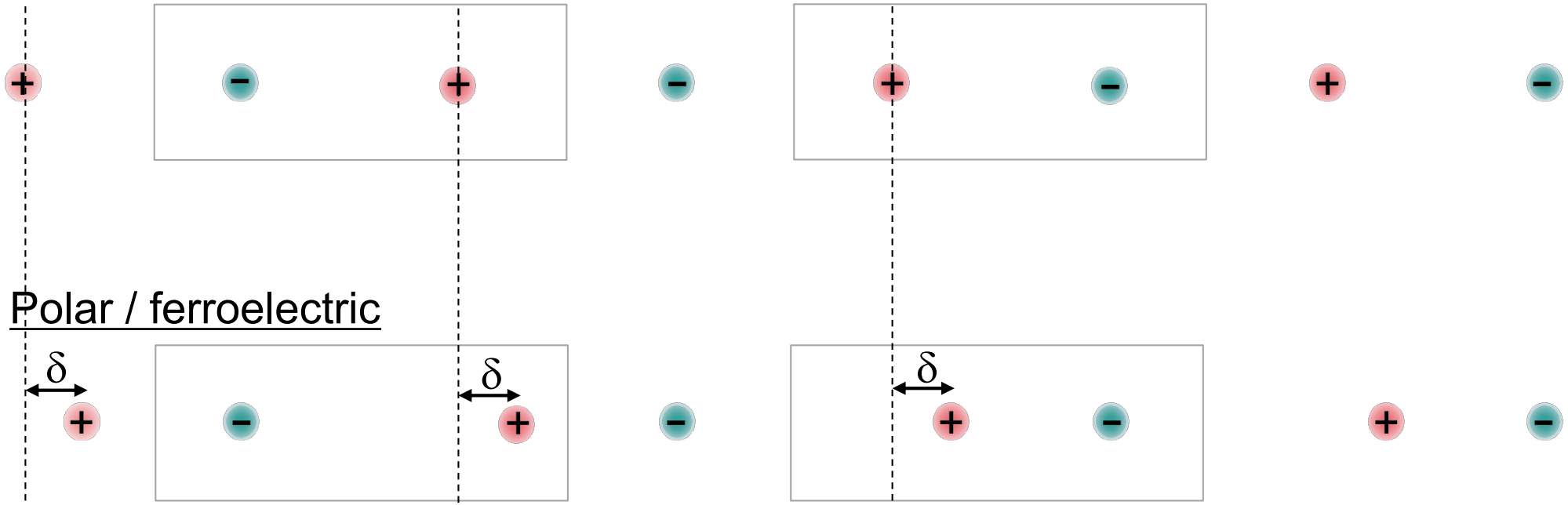
1) The polarization of a periodic insulating solid is a bulk property and is multivalued,

$P = P_0 + nP_q$; $P_q = eR/V$

2) Centrosymmetric insulating periodic solids have centrosymmetric polarization lattices that either contain zero or $P_q / 2$

How can we connect this to experimental reality?

Centrosymmetric / paraelectric



Polar / ferroelectric

Change in polarization = + e δ / *V* for any choice of unit cell

Modern Theory of Polarization: Key Results

1) The polarization of a periodic insulating solid is a bulk property and is multivalued,

$P = P_0 + nP_q$; $P_q = eR/V$

2) Centrosymmetric insulating periodic solids have centrosymmetric polarization lattices that either contain zero or $P_q / 2$

3) *Differences* between polarizations (e.g. the "spontaneous polarization" between the para- and ferroelectric states) are singlevalued

The Beginner's Guide to the Modern Theory of Polarization

14 videos • 1,142 views • Last updated on Dec 31, 2020

Public

The Beginners' Guide to the Modern Theory of Polarization. A series of modules to help you understand how the electric polarization is defined, calculated and measured in bulk periodic solids.

A beginner's guide to the modern theory of polarization

Nicola A. Spaldin Journal of Solid State Chemistry 195 (2012) 2–10

How can we calculate polarization using Quantum Espresso?

0) Calculate the positions of the ions and make sure your system is insulating! Then:

Option 1: Sum over the ionic positions multiplied by their formal charges (not bad).

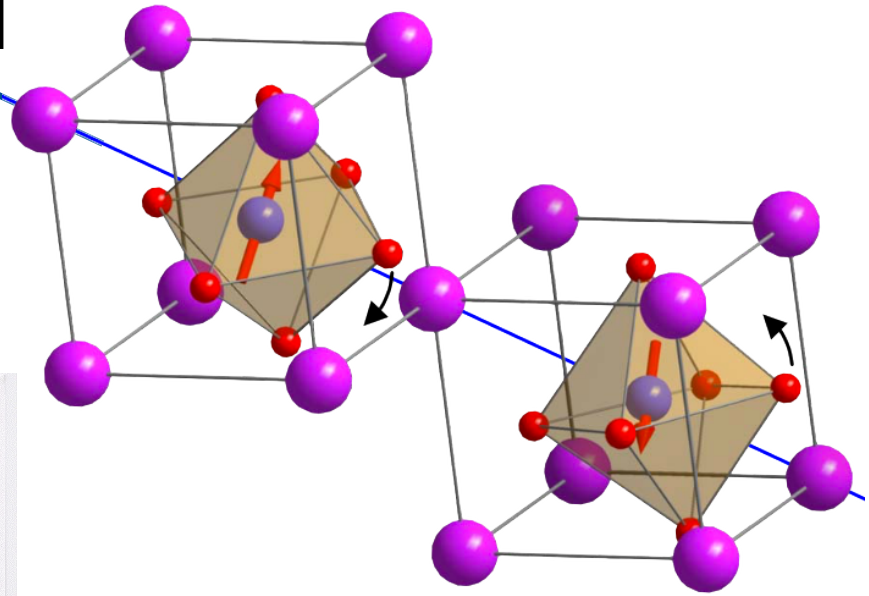
Option 2: Sum over the ionic positions multiplied by their pseudo charges. Add to this the sum over the Wannier centers multiplied by the number of electrons per Wannier function (formally correct).

Option 3: Sum over the ionic positions multiplied by their pseudo charges. Make a Berry phase calculation of the electronic contribution and add it to the ionic contribution (also formally correct).

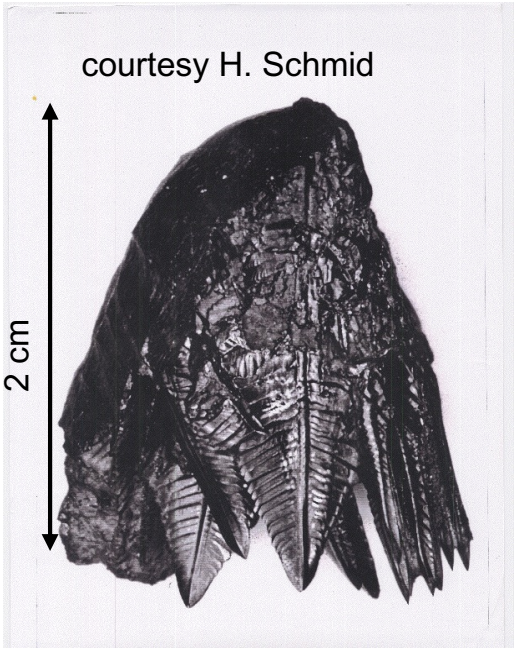
For every option your answer will be multi-valued!

A real material: Multiferroic bismuth ferrite, $BiFeO_3$

P_{spont} [111]

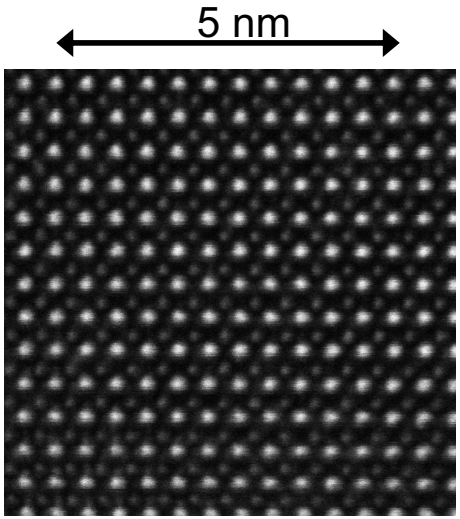


courtesy H. Schmid



P_{spont} [001]

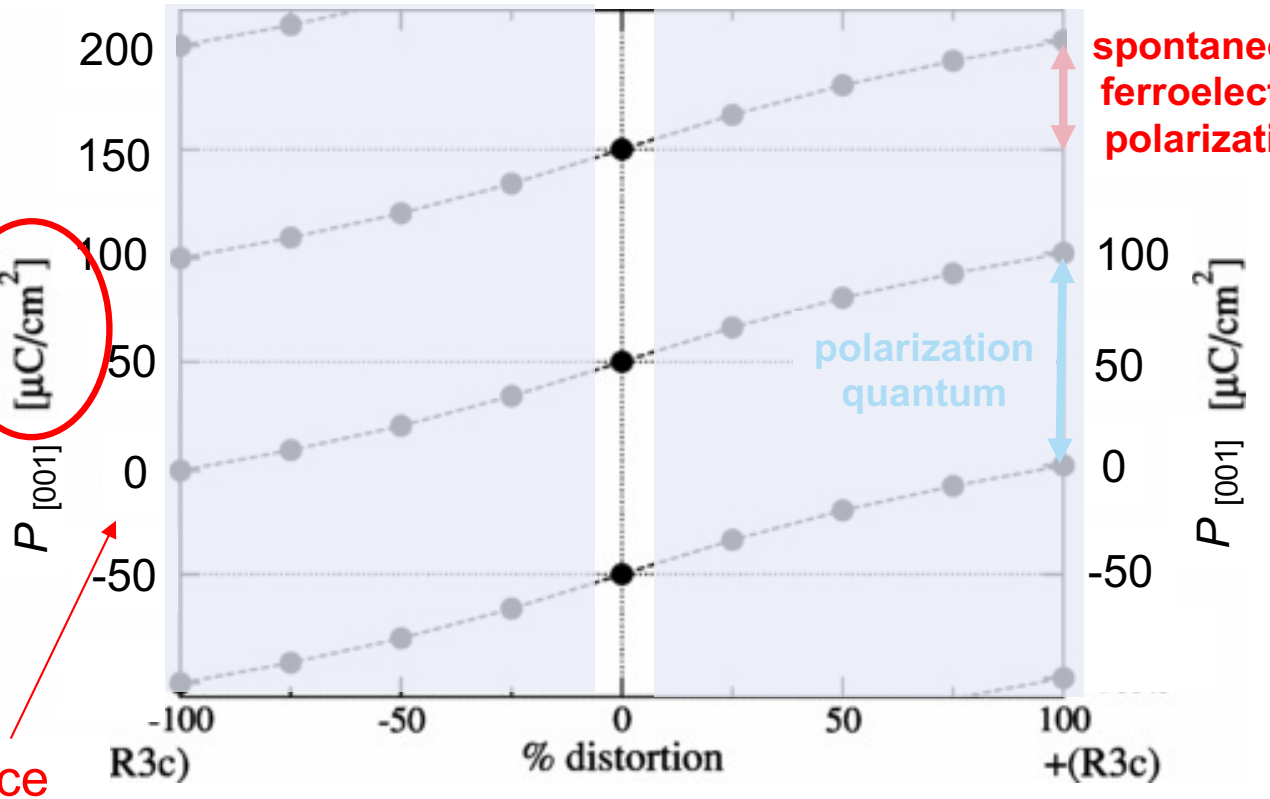
$50\mu C/cm^2$



courtesy R: Ramesh and M. Rossell

Calculation of polarization in $BiFeO_3$

Notice the units!



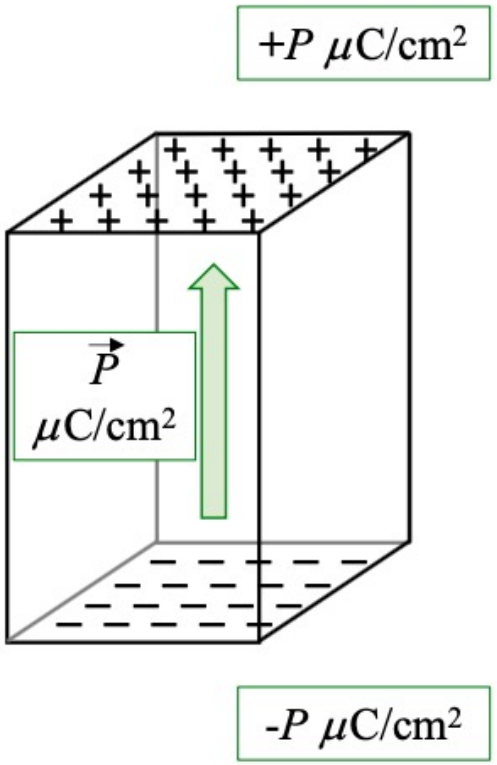
Notice the zero!

PHYSICAL REVIEW B **71**, 014113 (2005)

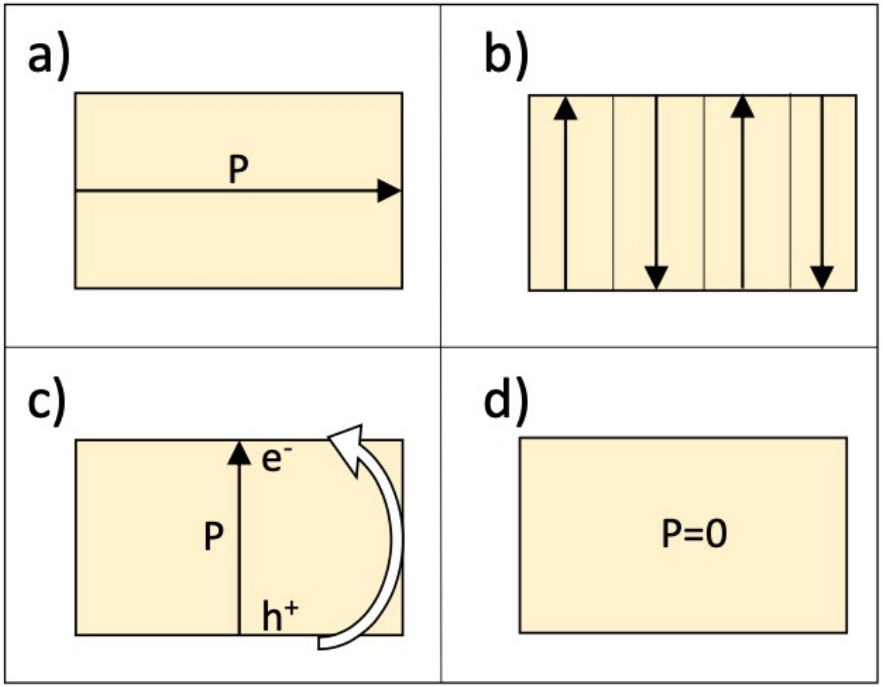
First-principles study of spontaneous polarization in multiferroic $BiFeO_3$

J. B. Neaton,[1,*] C. Ederer,[2] U. V. Waghmare,[3] N. A. Spaldin,[2] and K. M. Rabe[1]

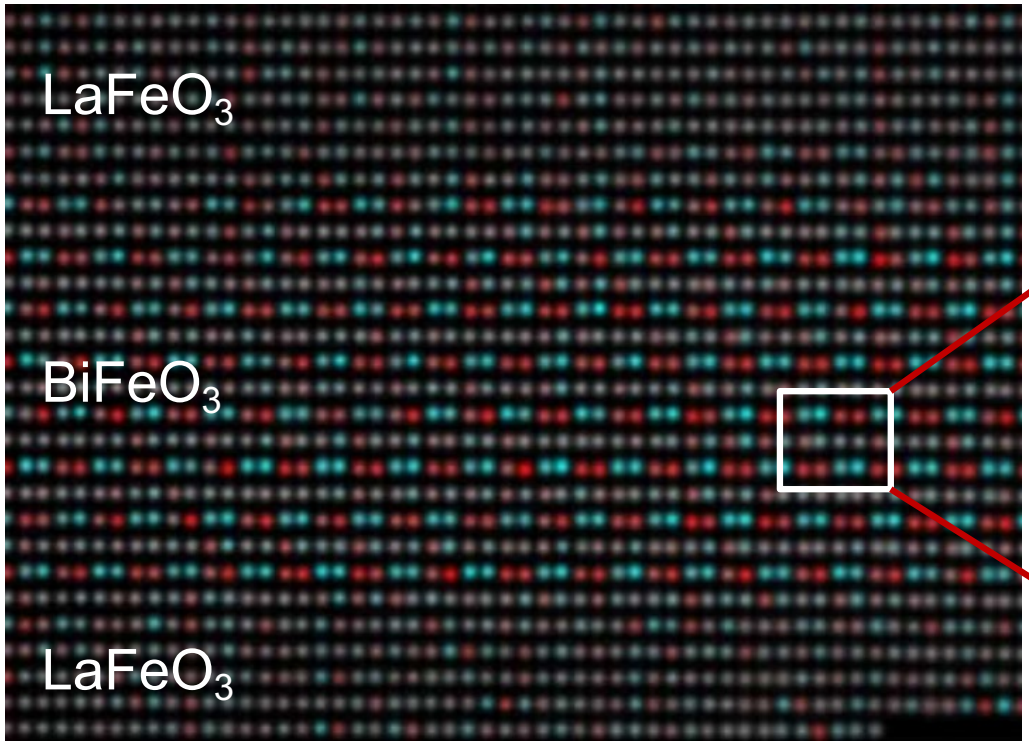
Surface charge associated with ferroelectricity

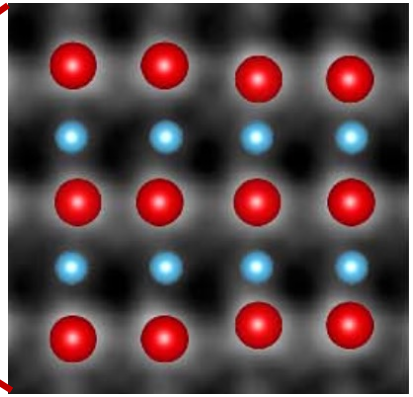


Usually BAD NEWS – leads to suppression of polarization



Stabilization of a meta-stable antiferroelectric phase



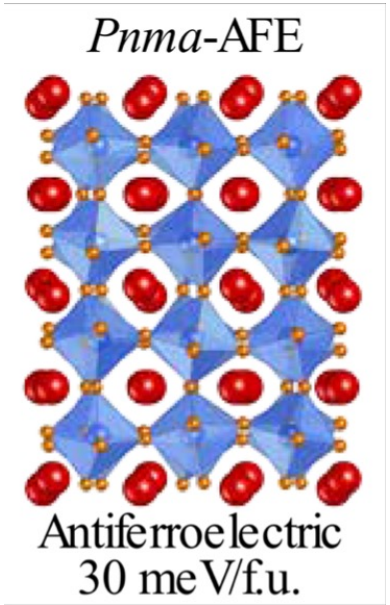


arXiv.org > cond-mat > arXiv:1812.09615

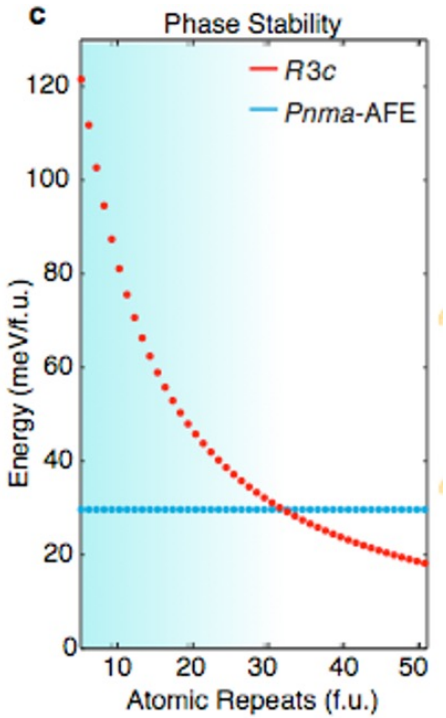
A high-energy density antiferroelectric made by interfacial electrostatic engineering Julia A. Mundy, Bastien F. Grosso ...

Stabilization of a meta-stable antiferroelectric phase

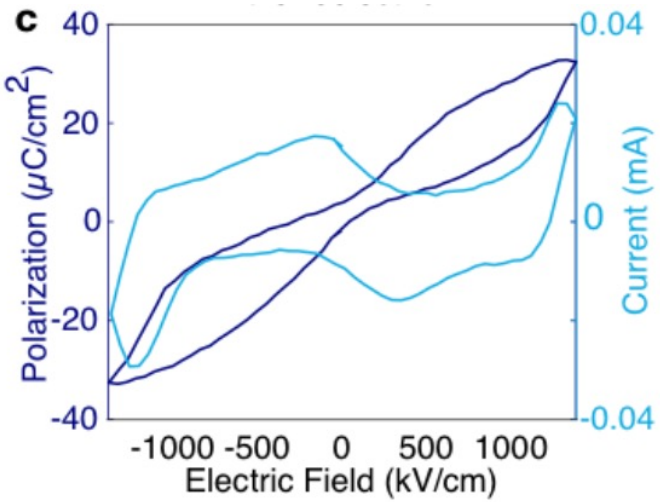
New phase identified using DFT, and shown to be close in energy to *R3c* ground state:



New phase is stabilized in thin films relative to polar *R3c* ground state:



Measurement of antiferroelectric hysteresis:

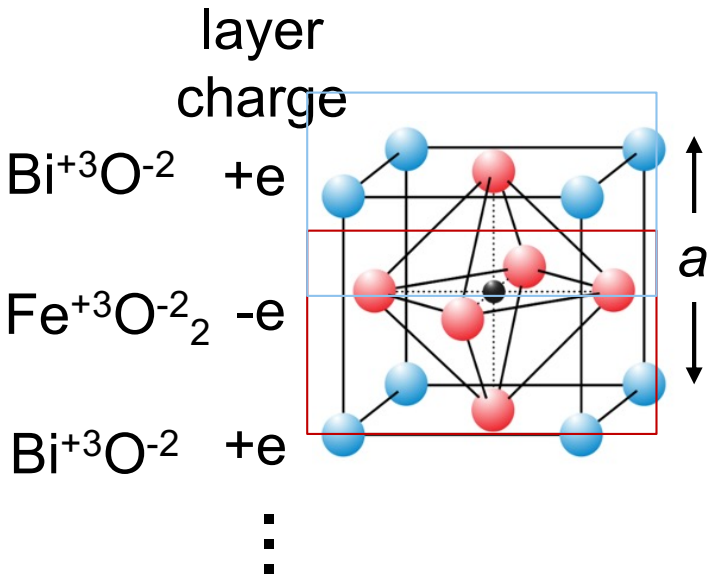


arXiv.org > cond-mat > arXiv:1812.09615

A high-energy density antiferroelectric made by interfacial electrostatic engineering Julia A. Mundy, Bastien F. Grosso ...

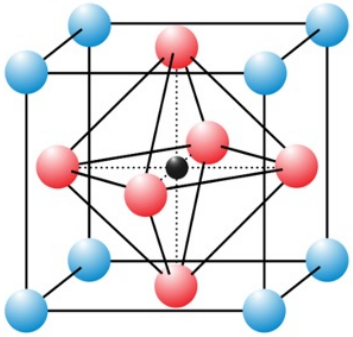
Saving the World I: Energy-storage materials

In its centrosymmetric form, the polarization lattice of $Bi^{3+}Fe^{3+}O_3$ contains the half quantum...



$P_{[001]} = \ldots \boxed{-ea/2V,} \boxed{+ea/2V} \ldots = \ldots -P_q/2, +P_q/2 \ldots$

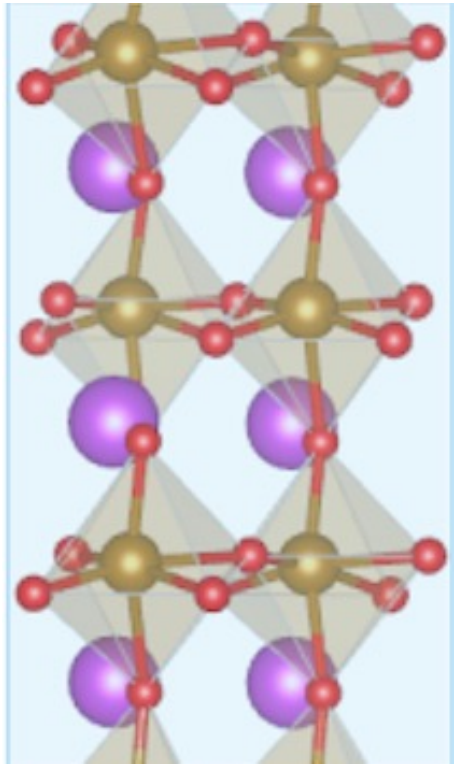
... therefore there is a surface charge associated with the charged ionic layers *even in the centrosymmetric paraelectric phase*

		Charge (electrons per unit cell)		Charge ($\mu C/cm^2$)
$Bi^{+3}O^{-2}$		+1	BiO positive surface charge	$+50\mu C/cm^2$
$Fe^{+3}O^{-2}_2$		-1	FeO_2 negative surface charge	$-50\mu C/cm^2$
$Bi^{+3}O^{-2}$		+1		
⋮				

Notice that the size of the surface charge is by coincidence equal to the size of the spontaneous polarization!

Surface charge compensation in $Bi^{3+}Fe^{3+}O_3$

[001]



FeO_2 -

Surface charge from charged layers
= –50μC/cm²

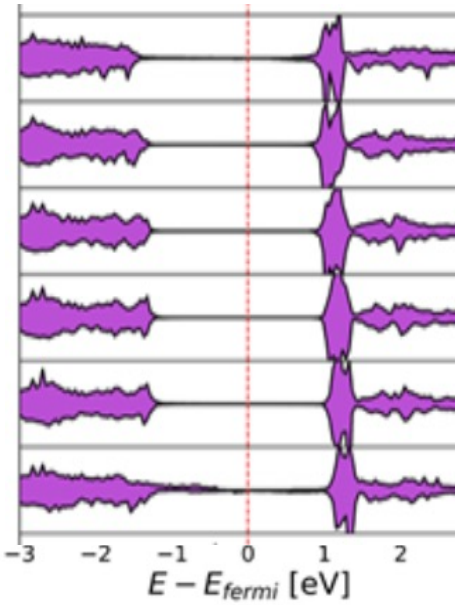
|Spontaneous polarization$_{[001]}$| = 50μC/cm² !

BiO +

Surface charge from charged layers
= +50μC/cm²

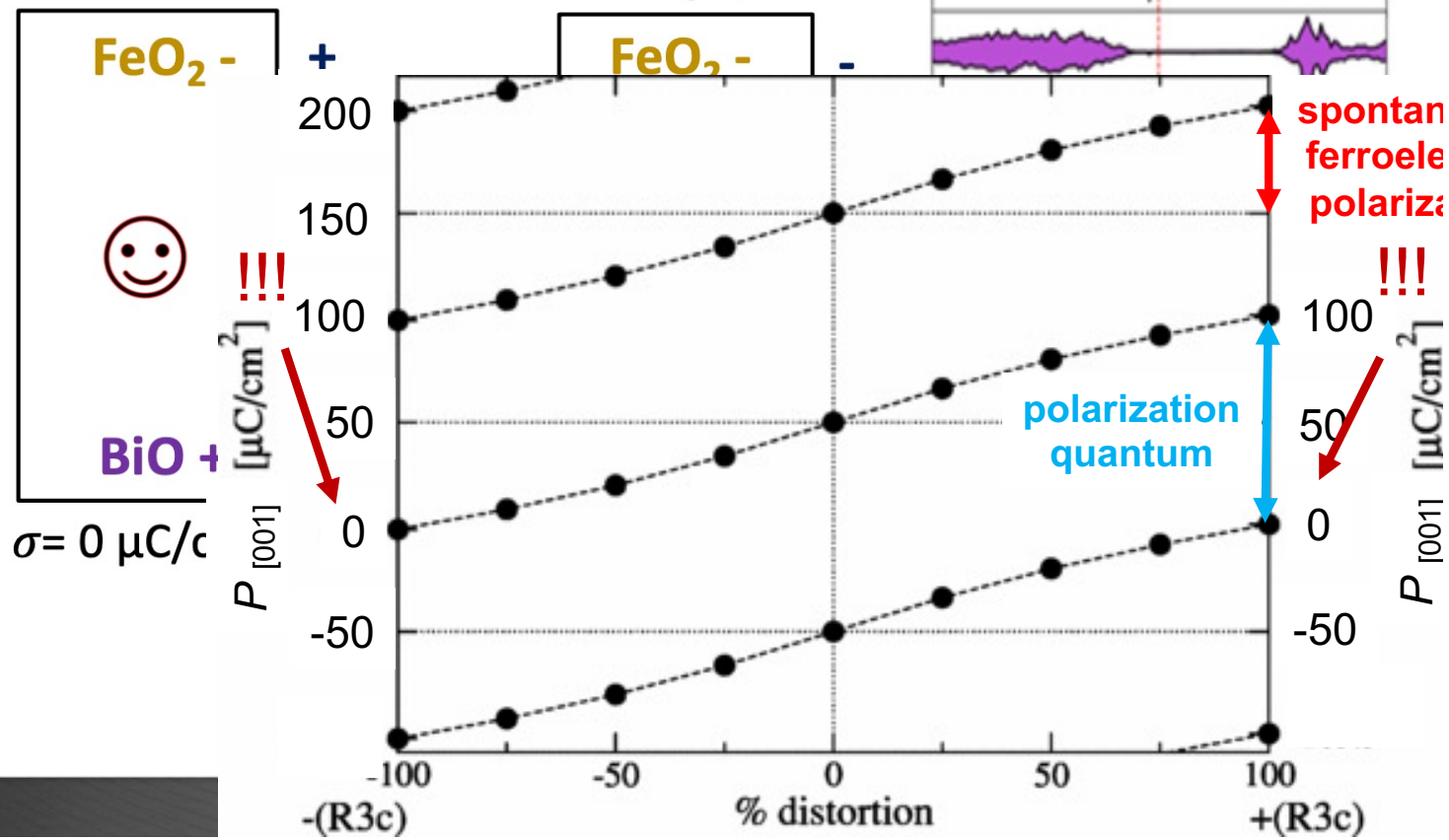
Surface charge compensation in $Bi^{3+}Fe^{3+}O_3$

For two combinations of polarization orientation and surface termination, the surface charge from the spontaneous polarization along [001] exactly compensates the surface charge from the half quantum of polarization



HAPPY SURFACES
σ= 0 µC/cm²

VERY UNHAPPY SURFACES
σ= -100 µC/cm²



On the happiness of ferroelectric surfaces and its role in water dissociation: The example of bismuth ferrite

Ipek Efe

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Submitted: 20 October 2020 . Accepted: 16 December 2020 .

Ipek Efe, Nicola A. Spaldin, and Chiara Gattinoni

Chiara Gattinoni

Layer and spontaneous polarizations in perovskite oxides and their interplay in multiferroic bismuth ferrite

Marta Rossell

Cite as: J. Chem. Phys. **154**, 154702 (2021); https://doi.org/10.1063/5.0046061
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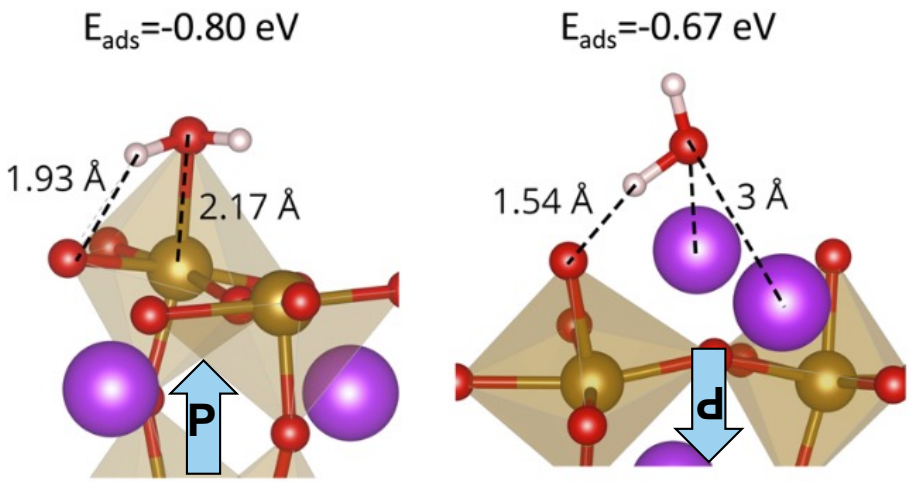
Nicola A. Spaldin, Ipek Efe, Marta D. Rossell, and Chiara Gattinoni

Saving the World II – Water Splitting

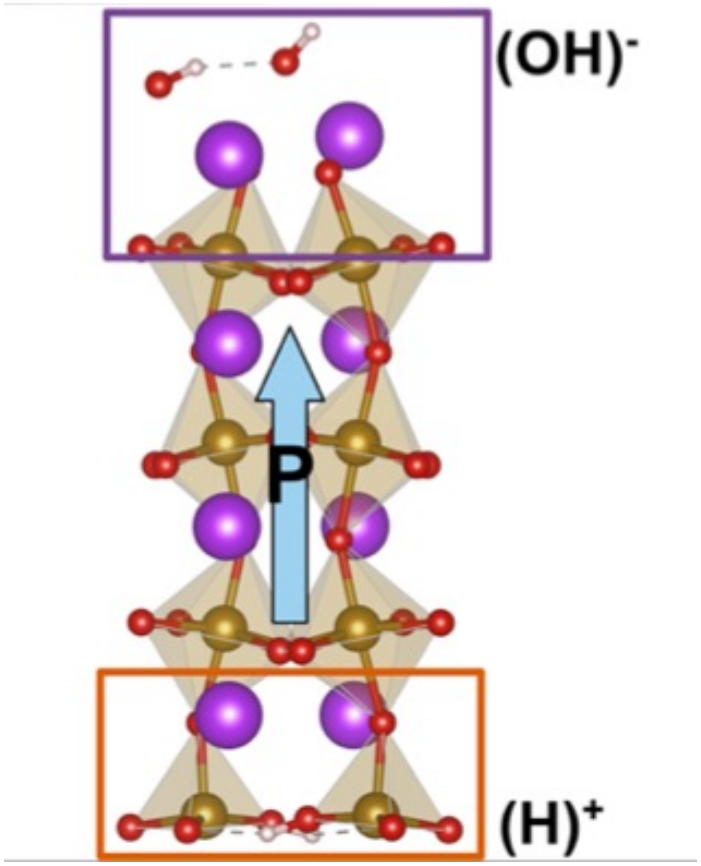
Happy Surfaces

Molecular adsorption of H_2O stable

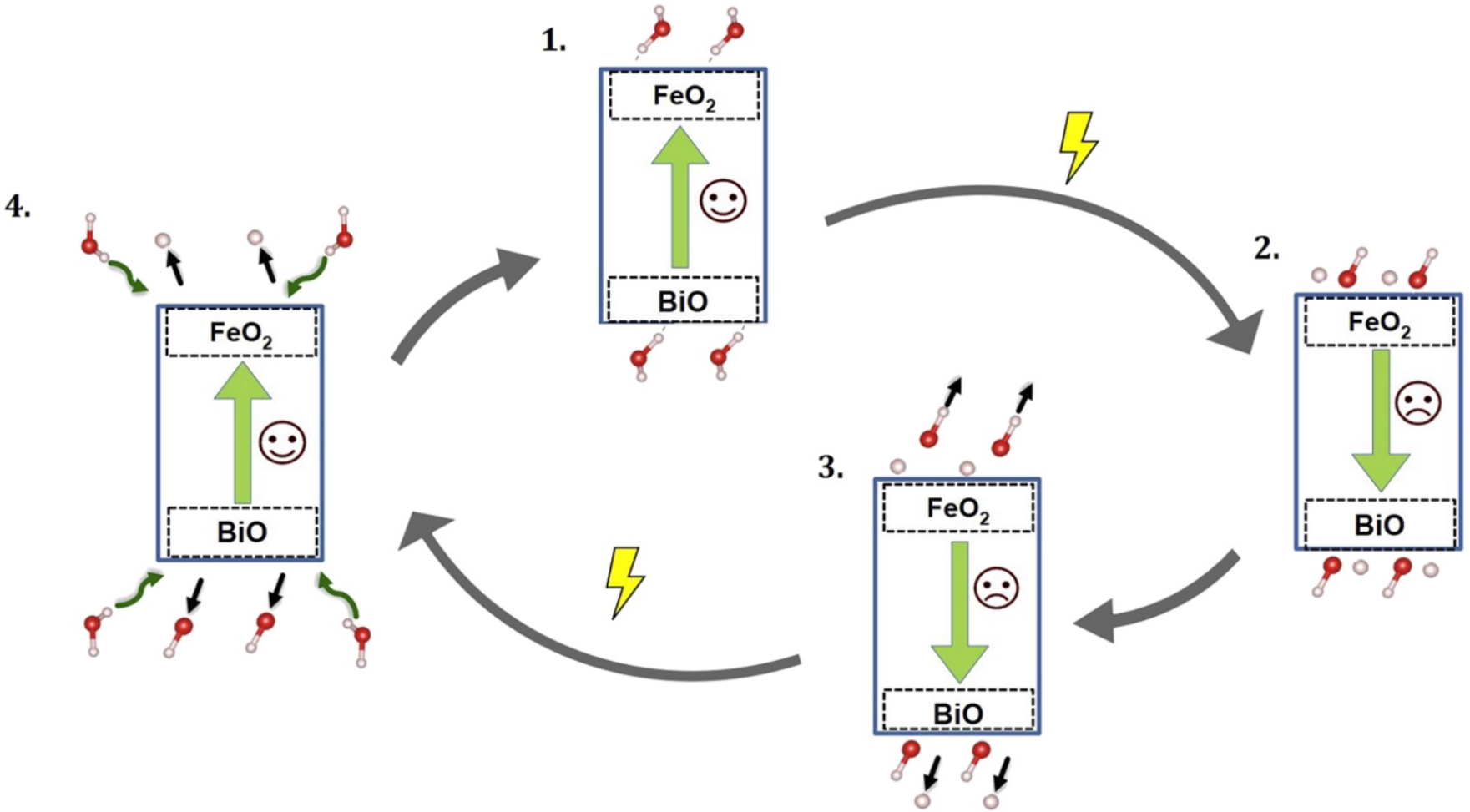


Unhappy Surfaces

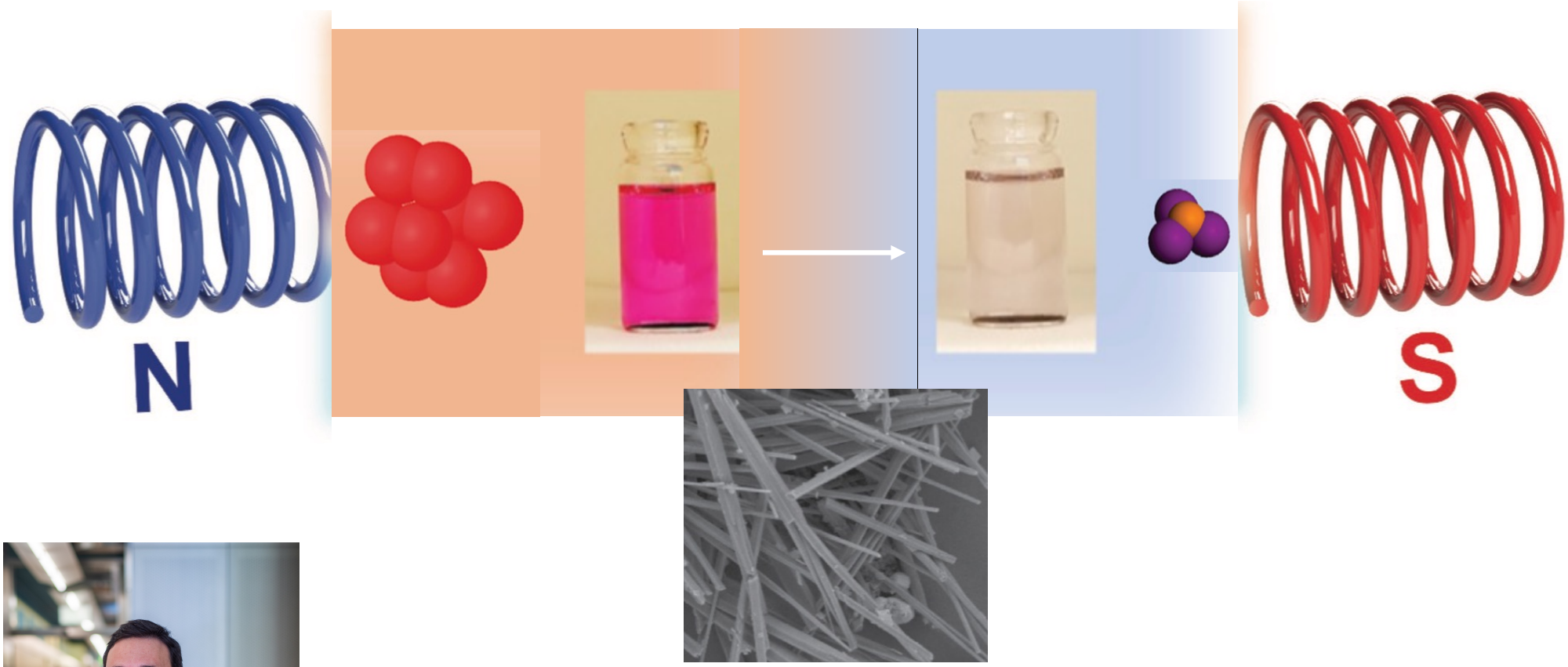
Dissociative adsorption preferred



Saving the World II – Water Splitting



Saving the World II' – Water Remediation



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Magnetoelectrically Driven Catalytic Degradation of Organics

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Homework Deadline: Summer 2065