



# Tailoring oxide thin films by ion beam

**Shengqiang Zhou**  
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**Department Head, Semiconductor Materials**  
**Helmholtz-Zentrum Dresden-Rossendorf (HZDR)**

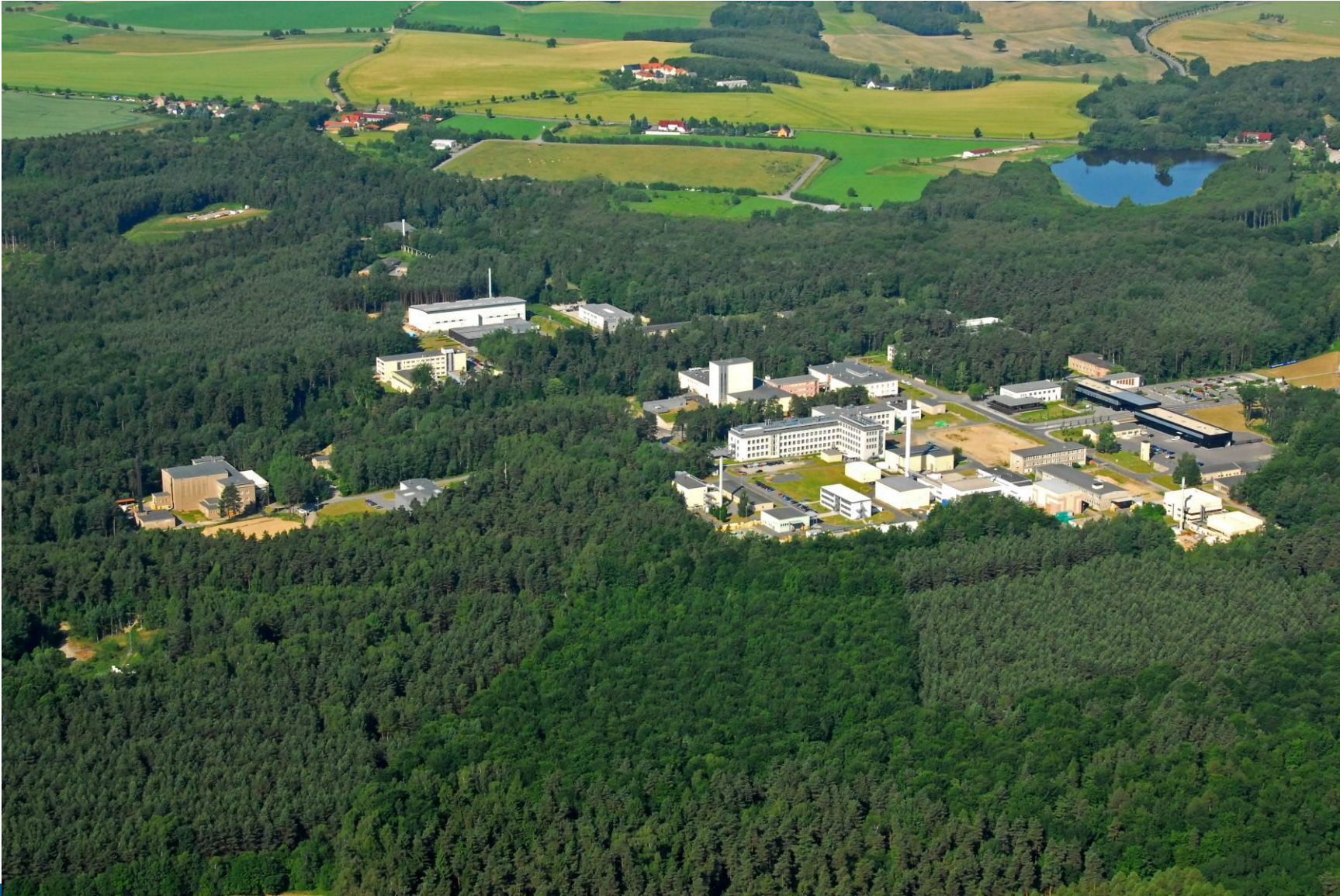
# Always along a river



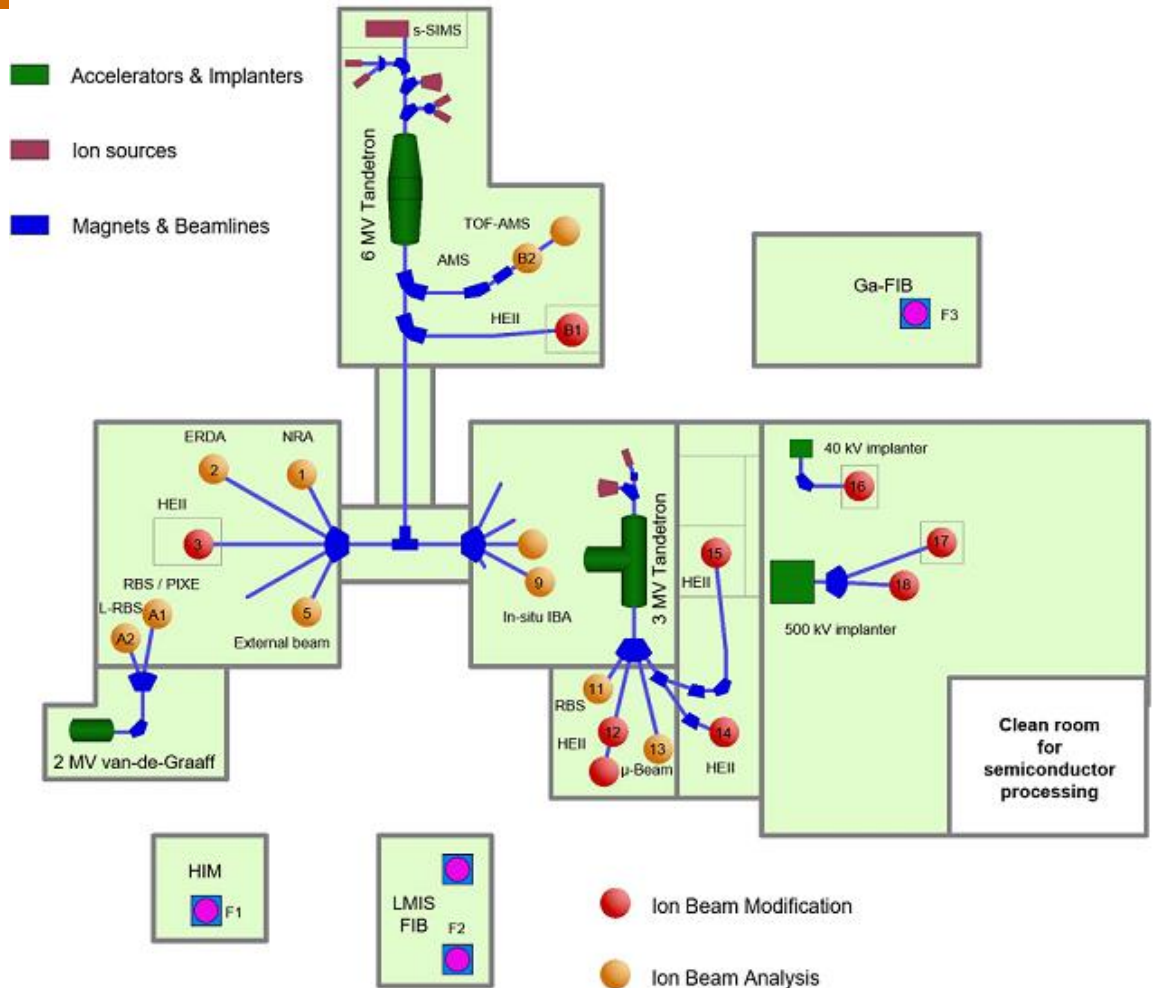
Dresden



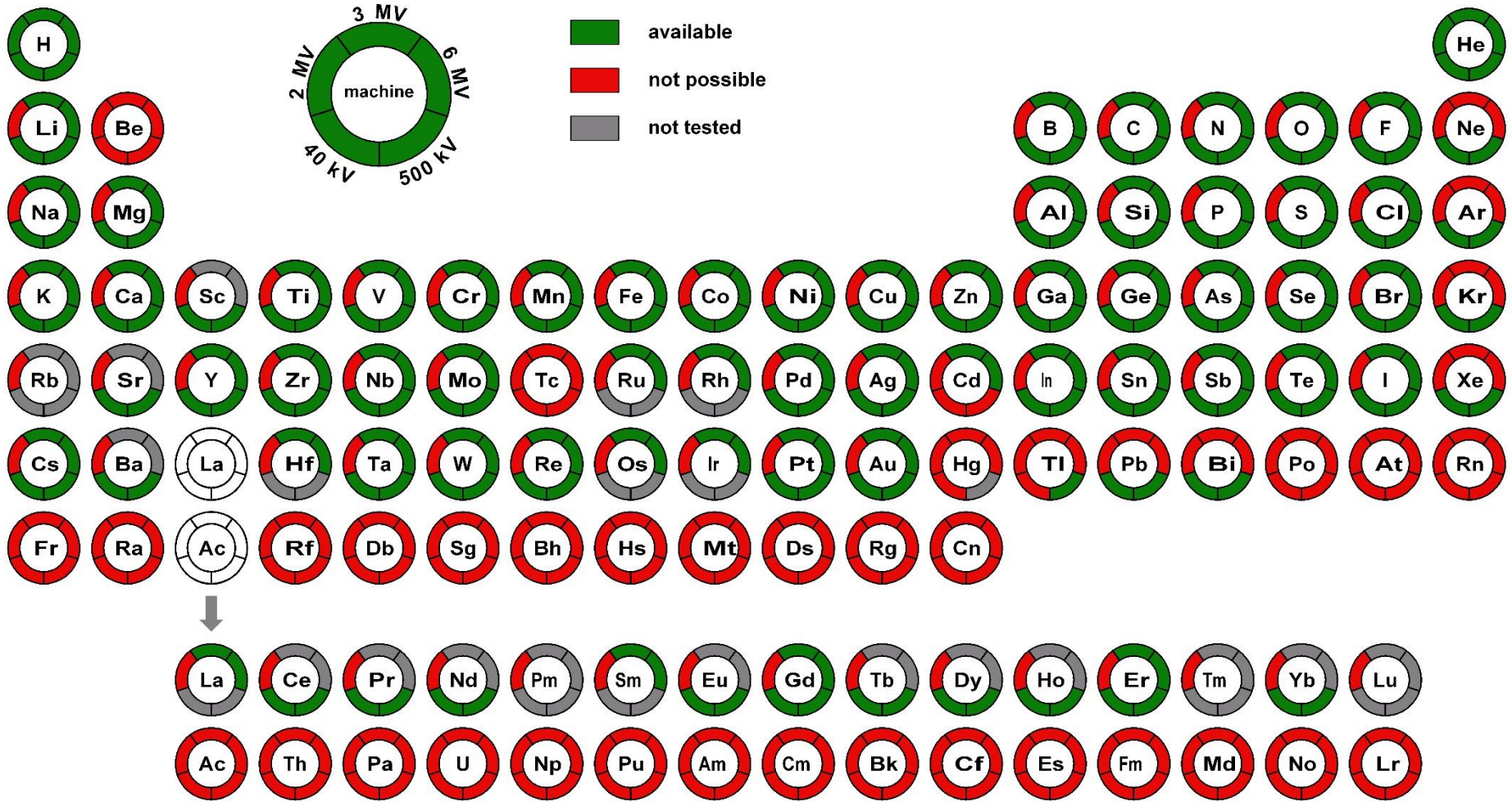
# Aerial View



# Ion Beam Center



# Ion Beam Center

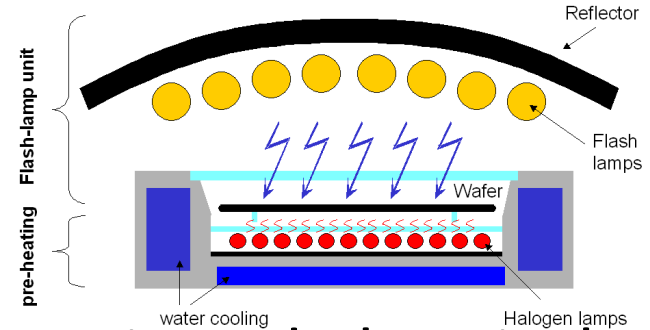


# Department of Semiconductor Materials



# Resources: Semiconductor materials

## Material processing: laser and flash lamp annealing



## Material characterization: magnetic and electrical



SQUID-VSM  
SQUID-MPMS  
Lakeshore Hall Measurement system  
1.8-400 K  
up to 7 T

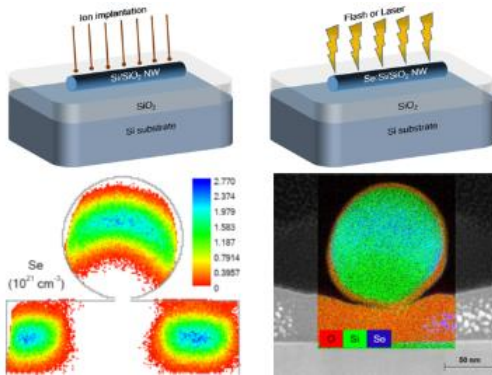


## Material characterization: optics Raman, PL and attoCube-dry

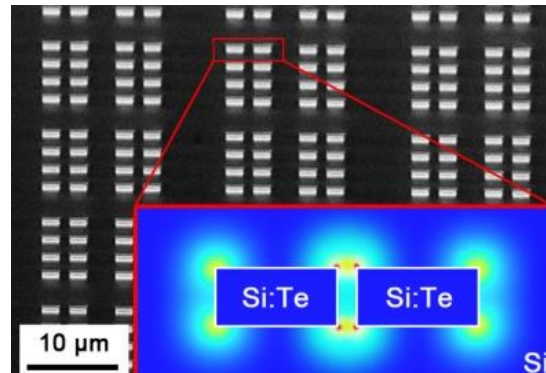
And the user facilities: ion beam center

# Department of Semiconductor Materials

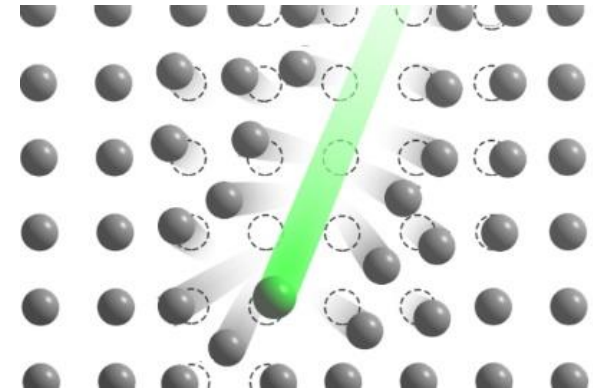
## Hyperdoped semiconductors



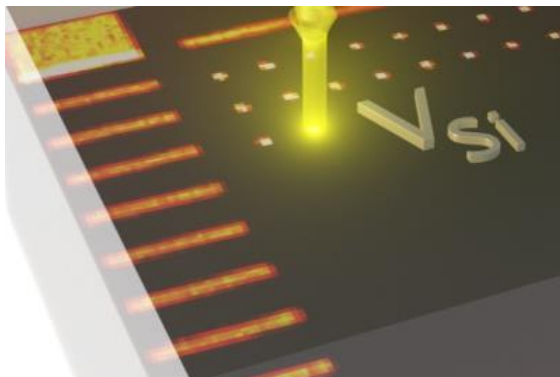
## Optoelectronics



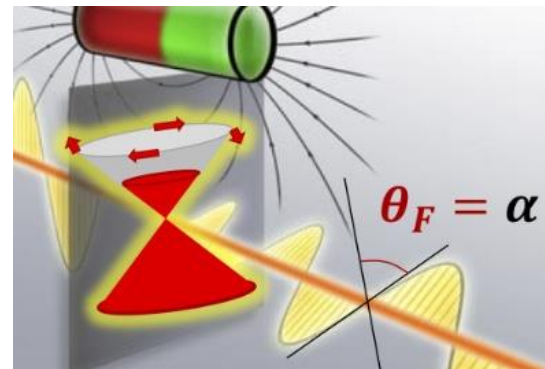
## Defect engineering by ions



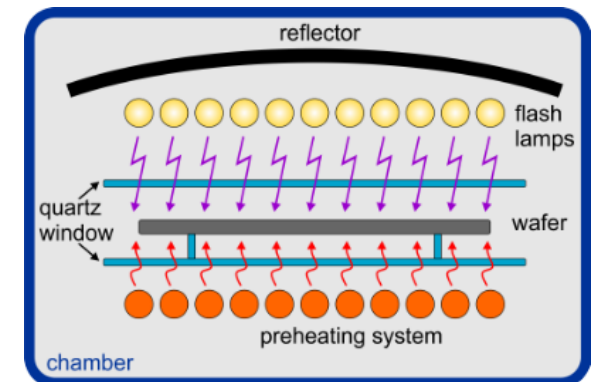
## Quantum technology



## Quantum metrology

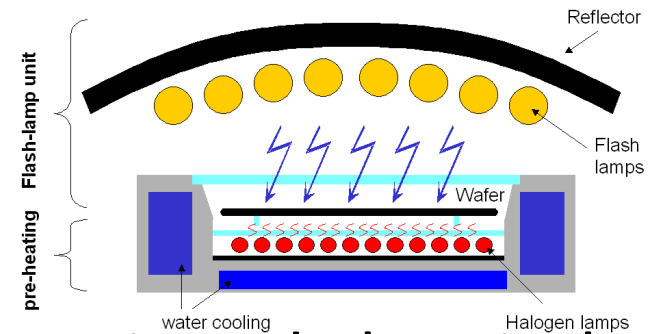


## Flash lamp and pulsed laser





## Material processing: laser and flash lamp annealing



## Material characterization: magnetic and electrical



SQUID-VSM  
SQUID-MPMS  
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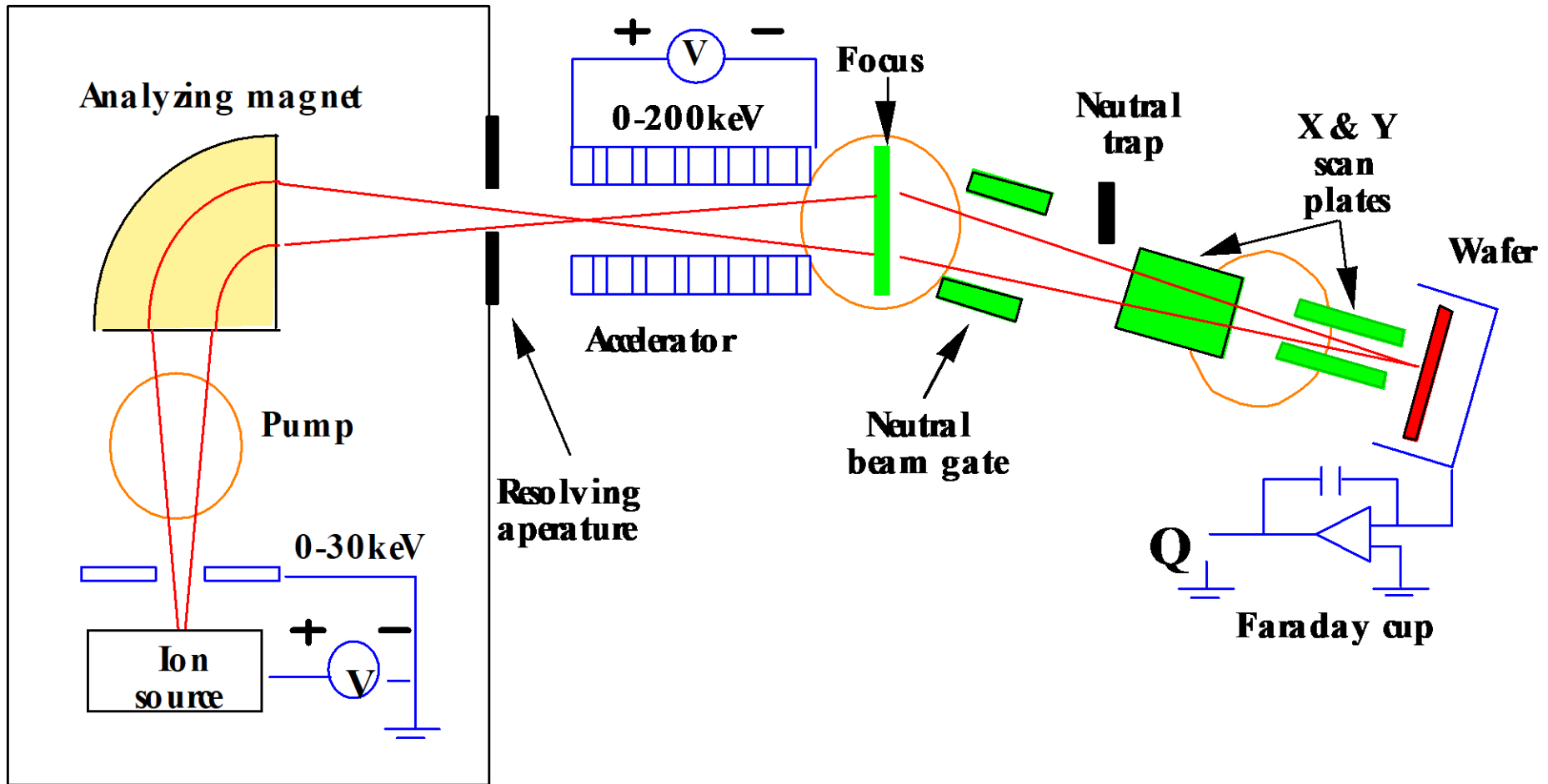


## Material characterization: optics Raman, PL and attoCube-dry

And the user facilities: ion beam center

# Ion irradiation effect in matter

# Ion implantation: basic layout



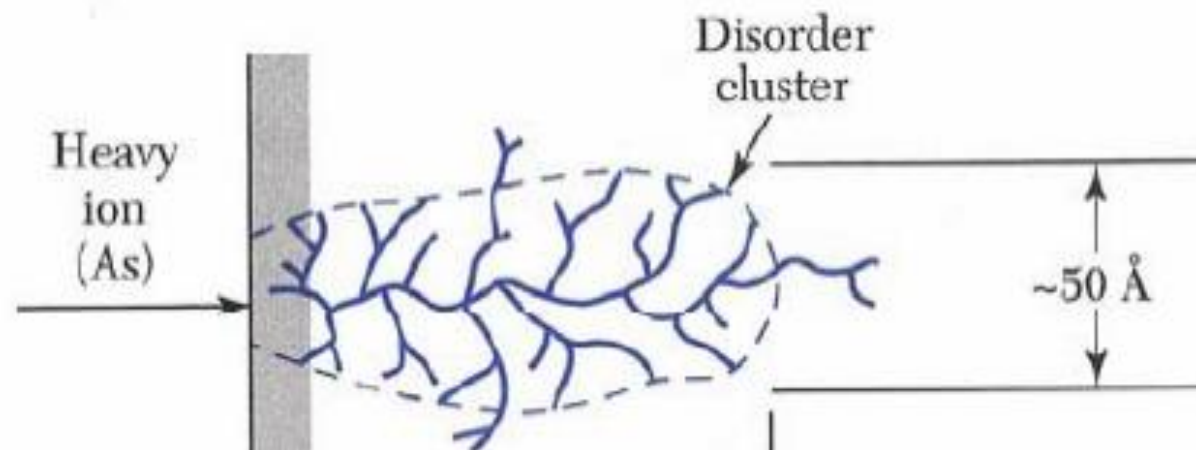
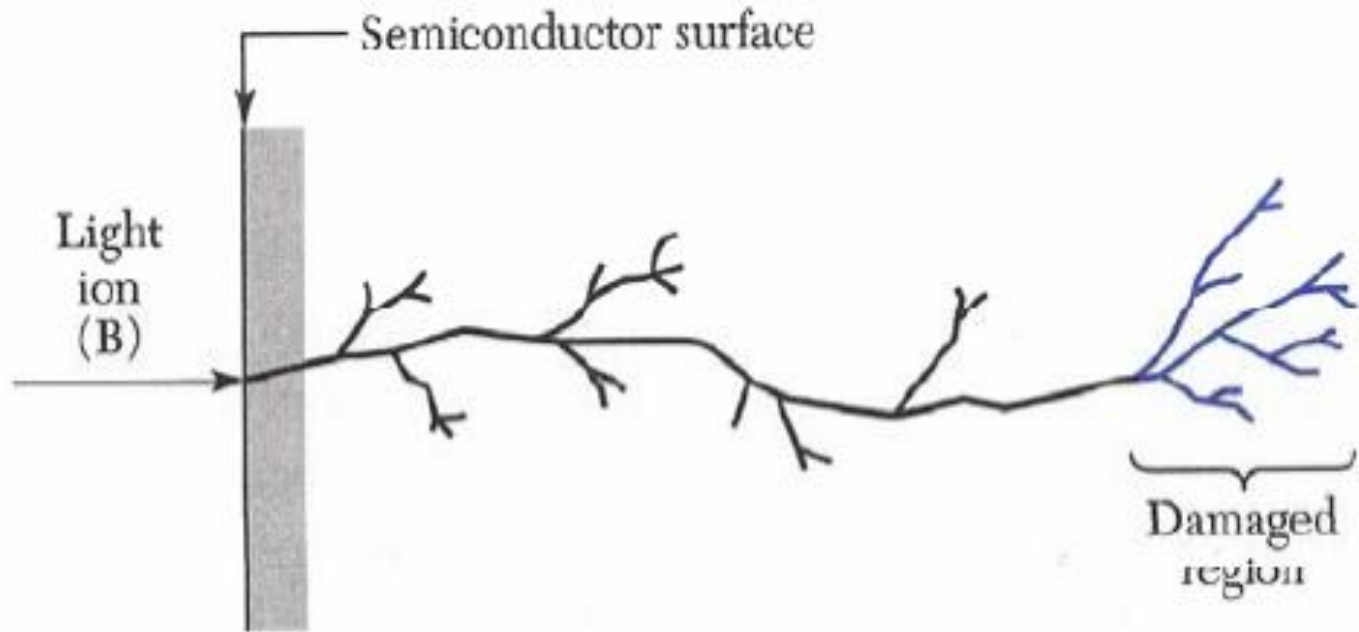
# Ion Implanter



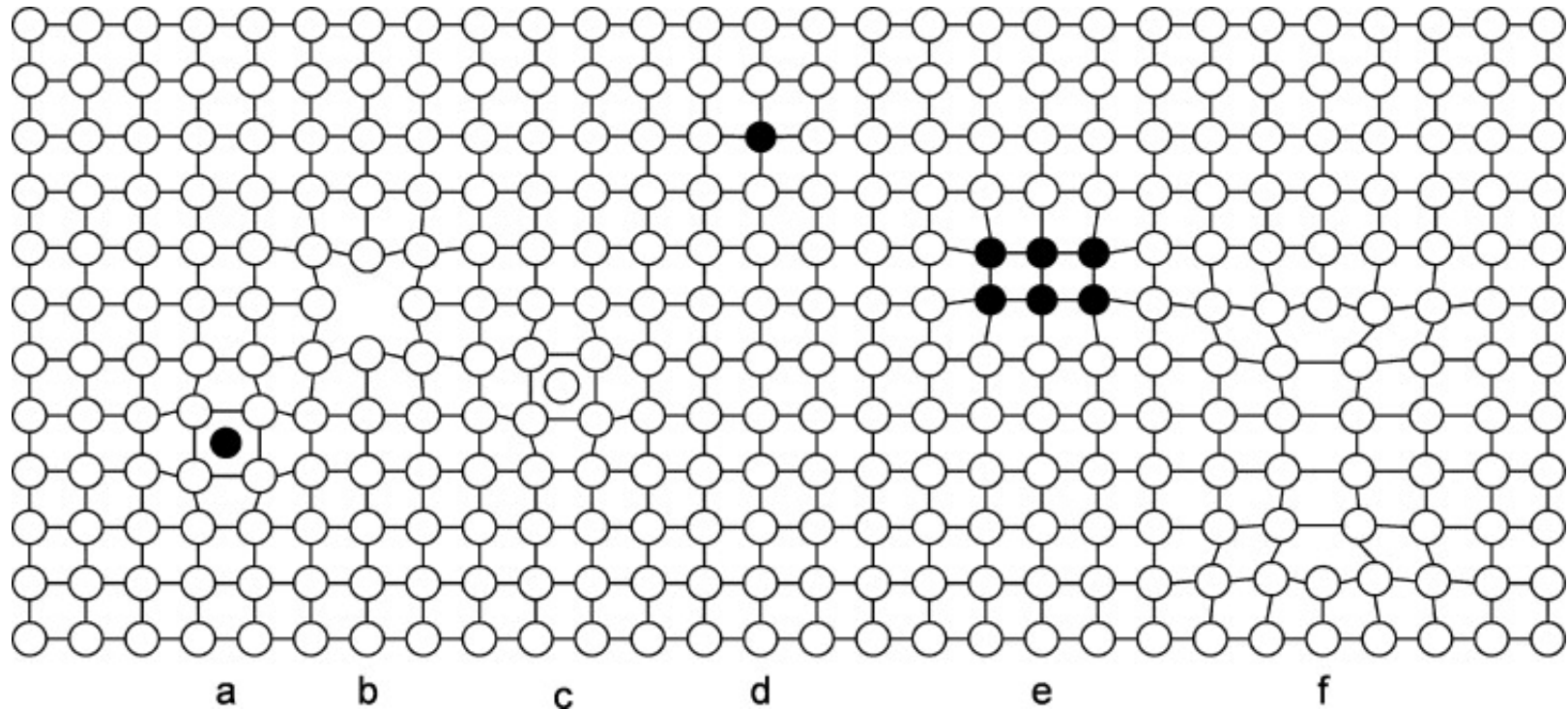
*Axcelis Ultra  
Wafer Loading Station*

*Axcelis. Optima HD: High-Dose Implanter*

# Ion implantation: effect



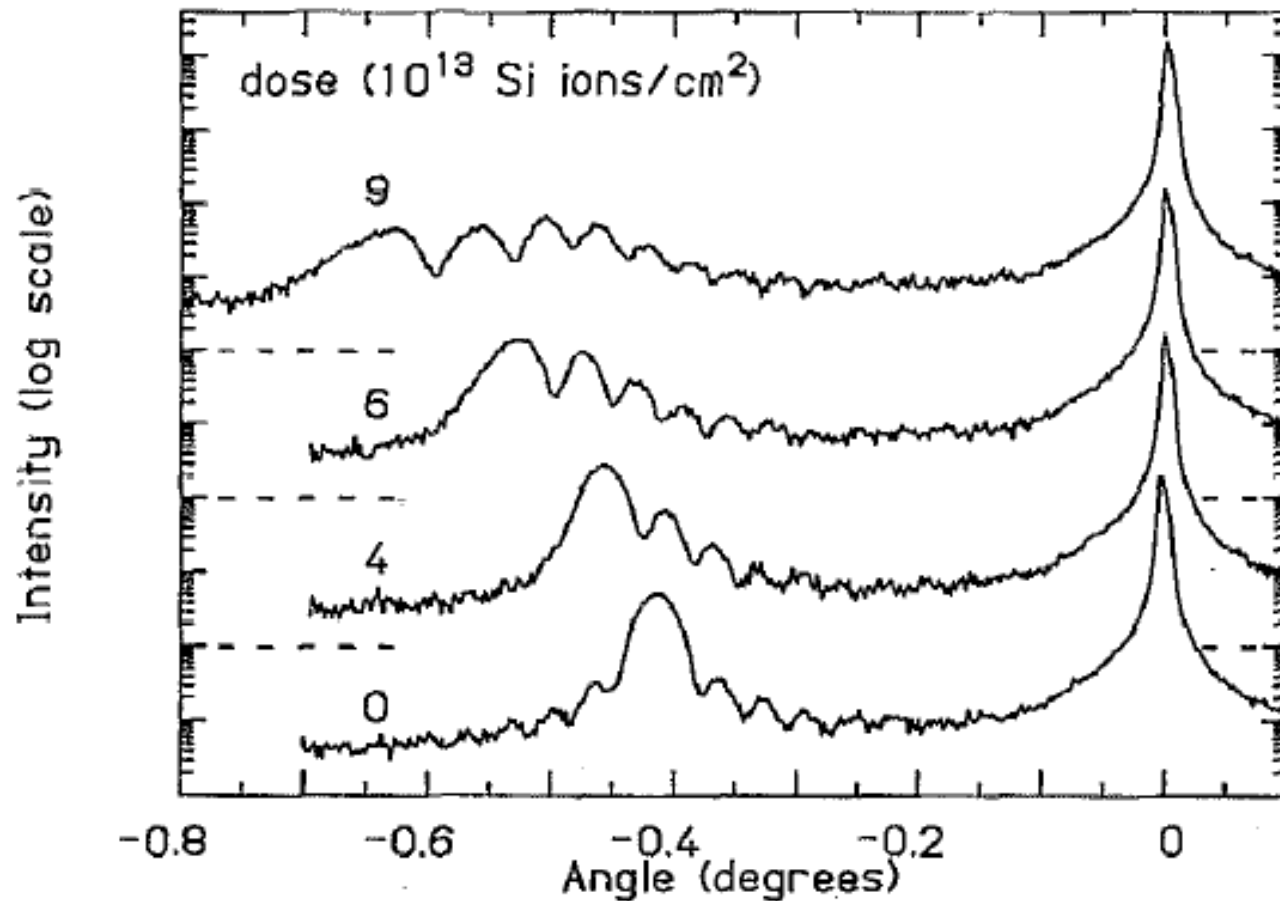
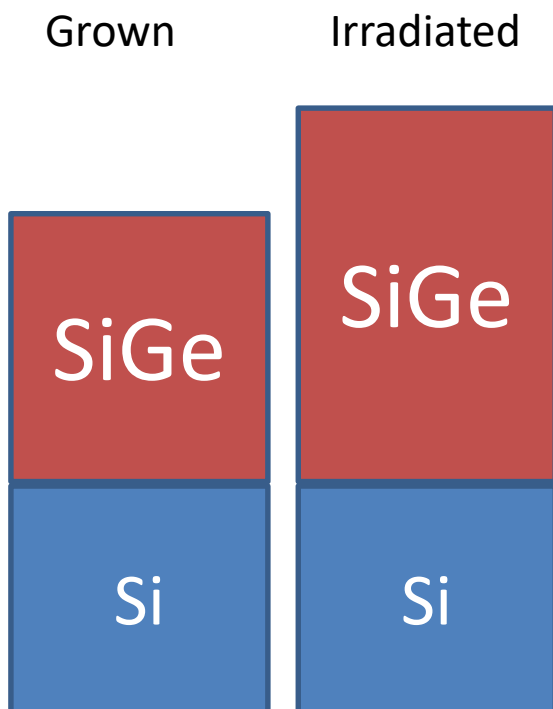
# Ion implantation: effect



Common defects in materials

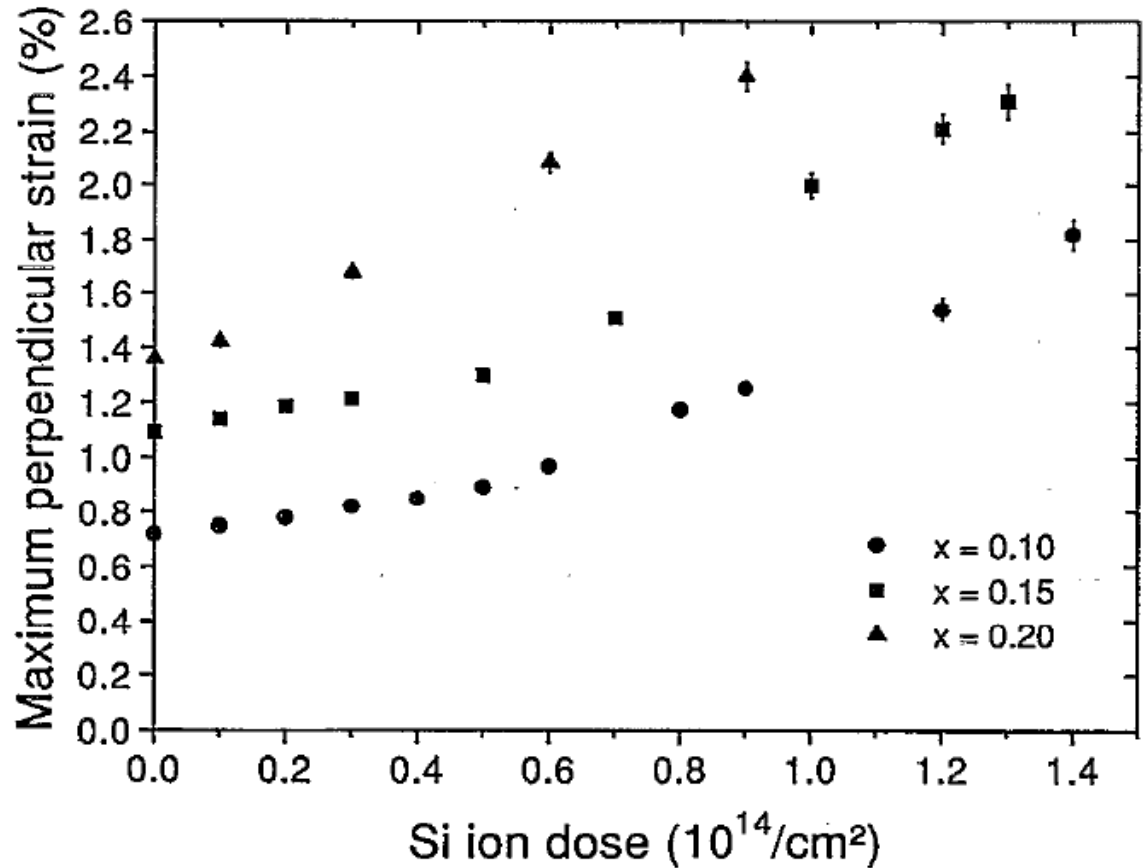
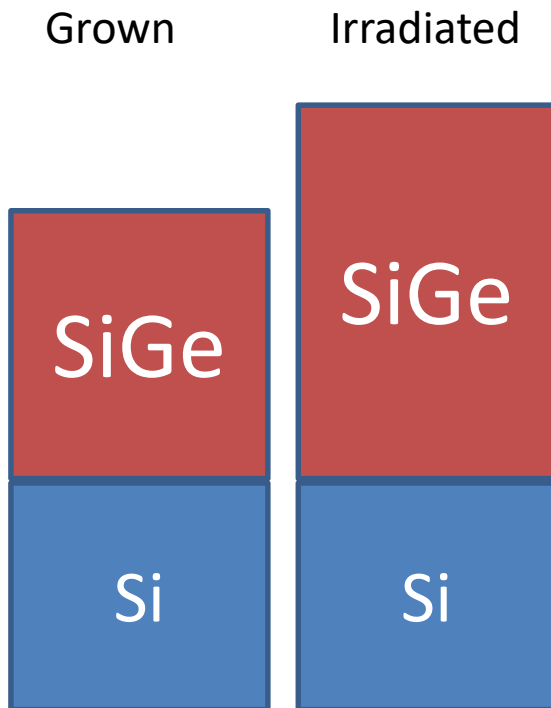
# Ion implantation: effect

More than 20 years ago in Si...



# Ion implantation: effect

More than 20 years ago in Si...

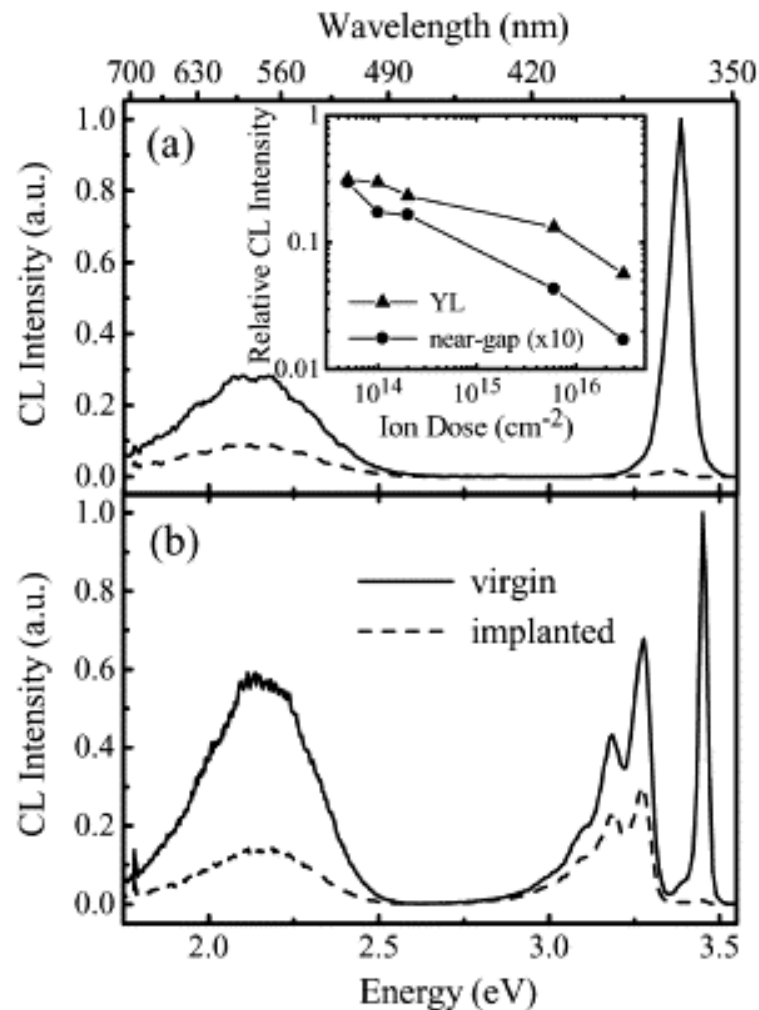




# Ion implantation: effect

More than 20 years ago in Si, GaAs and GaN

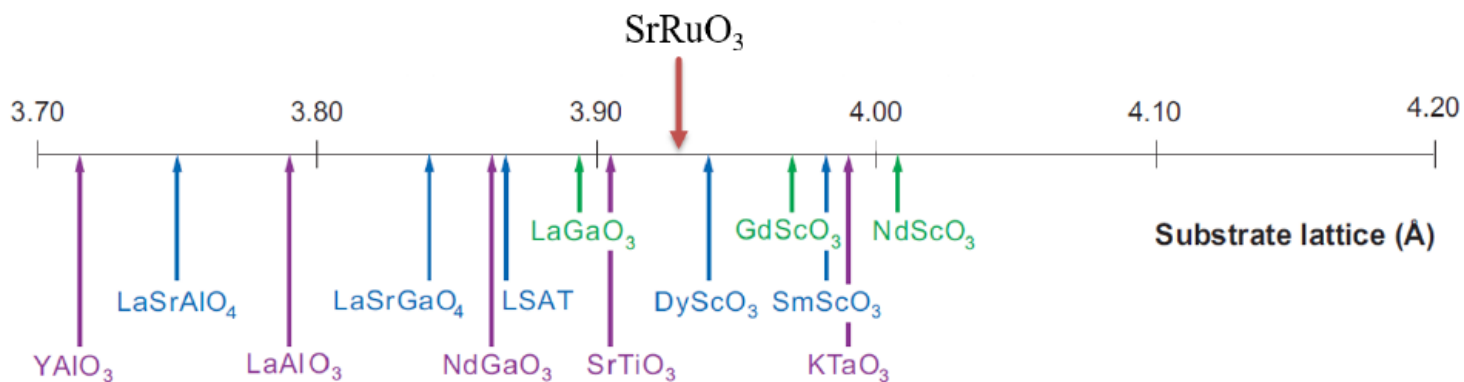
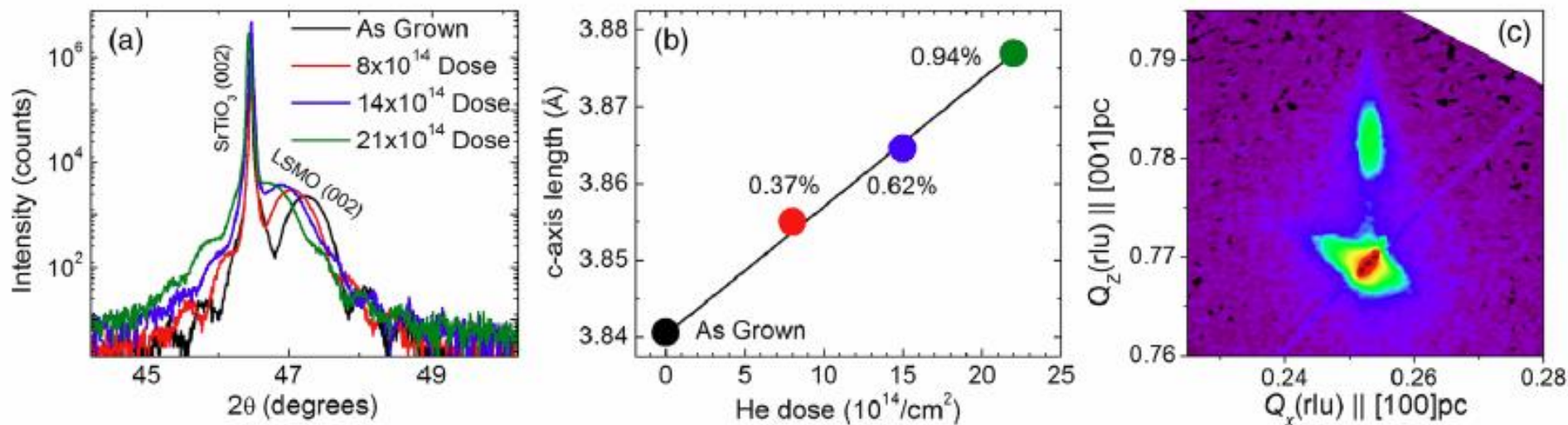
- Mobility ↘
- Photoluminescence ↘



Carbon ion dose:  $1 \times 10^{14} \text{ cm}^{-2}$

# Ion implantation: effect

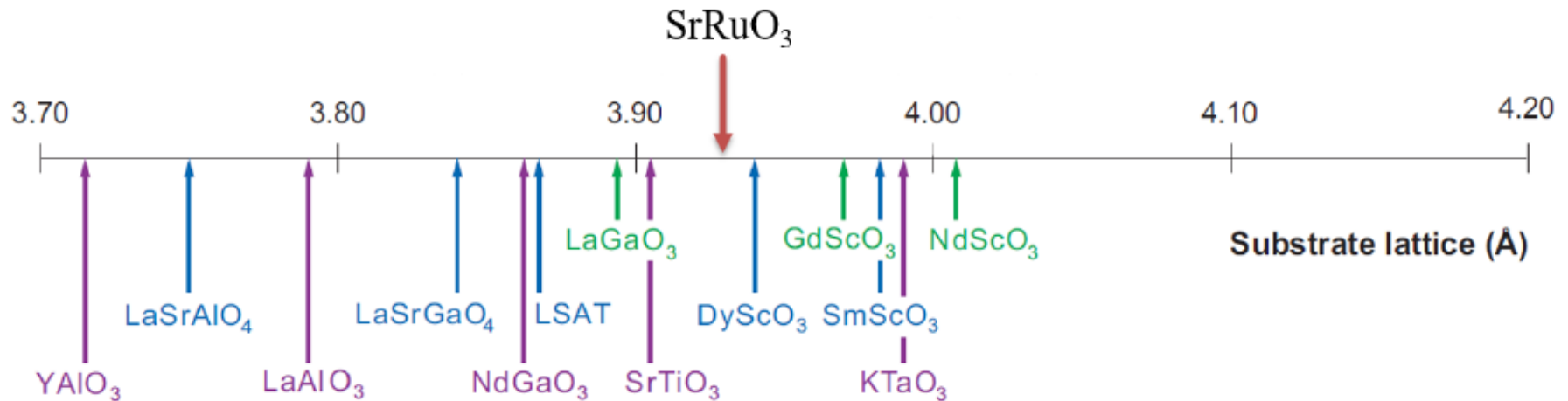
Recently: in oxides



01 (2015)

# Ion implantation: effect

Recently: in oxides



Using different substrates: only discrete choice

<http://dx.doi.org/10.5772/intechopen.70125>

MML ■ IN-HOUSE RESEARCH

Shengqiang Zhou  
Institute of Ion Beam Physics and Materials Research

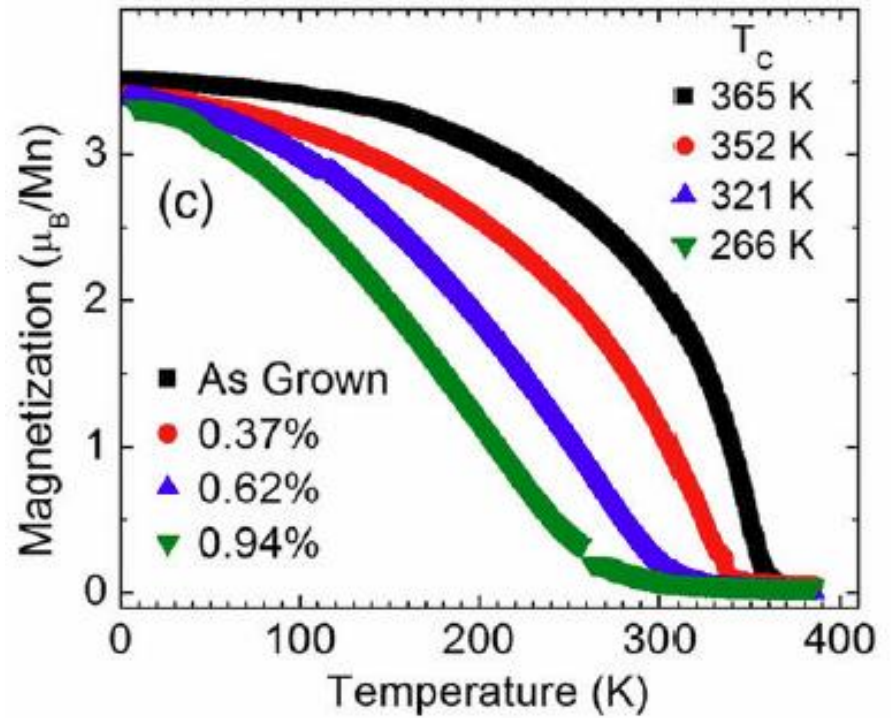
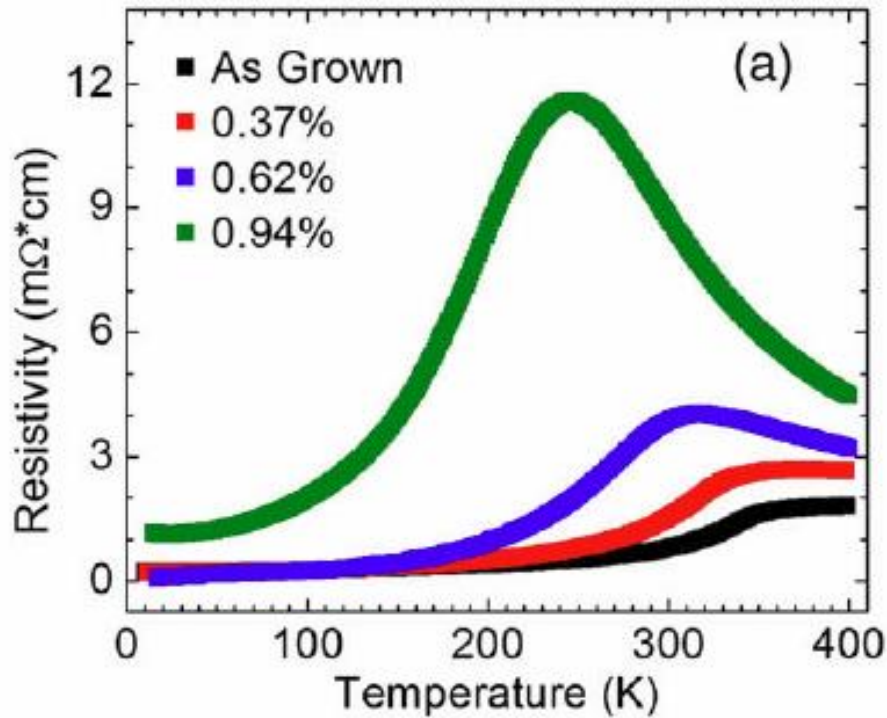
HZDR

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# Defect engineering by irradiation

Helium irradiation shifts the metal-insulator transition and Curie temperature in  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  (LSMO) film.

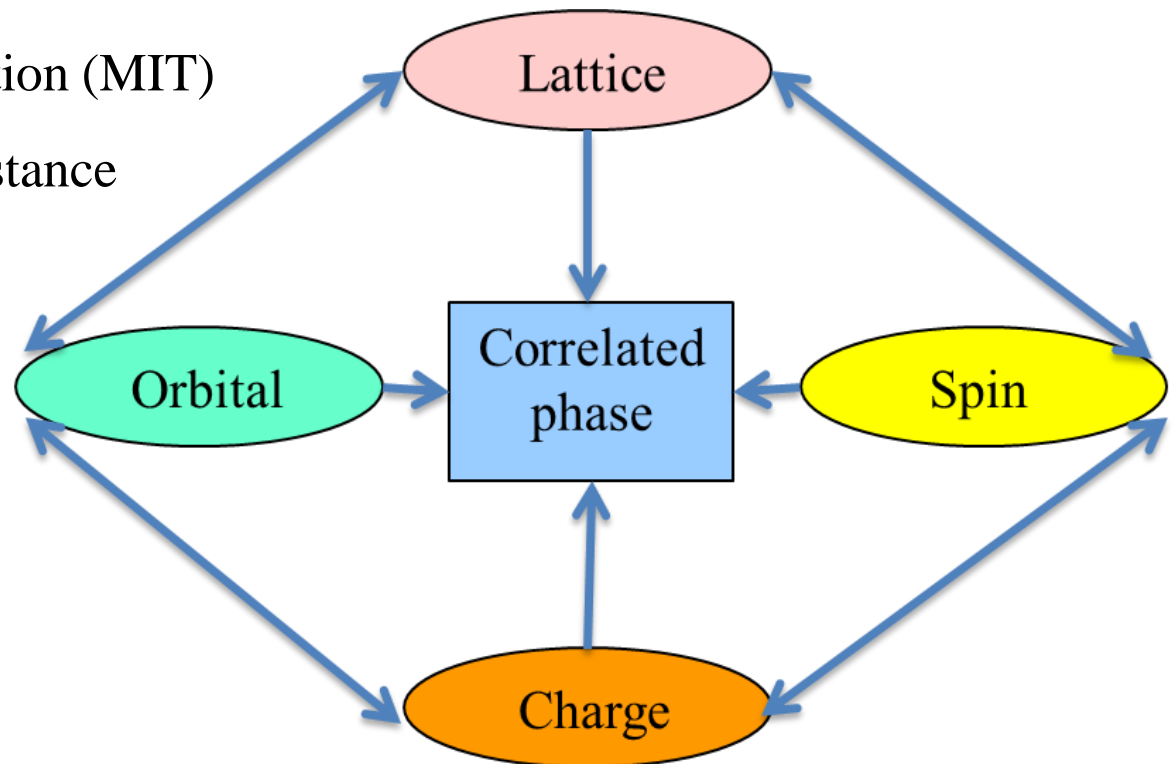


H. Guo. et al. Phys. Rev. Lett **26**, 256801 (2015)

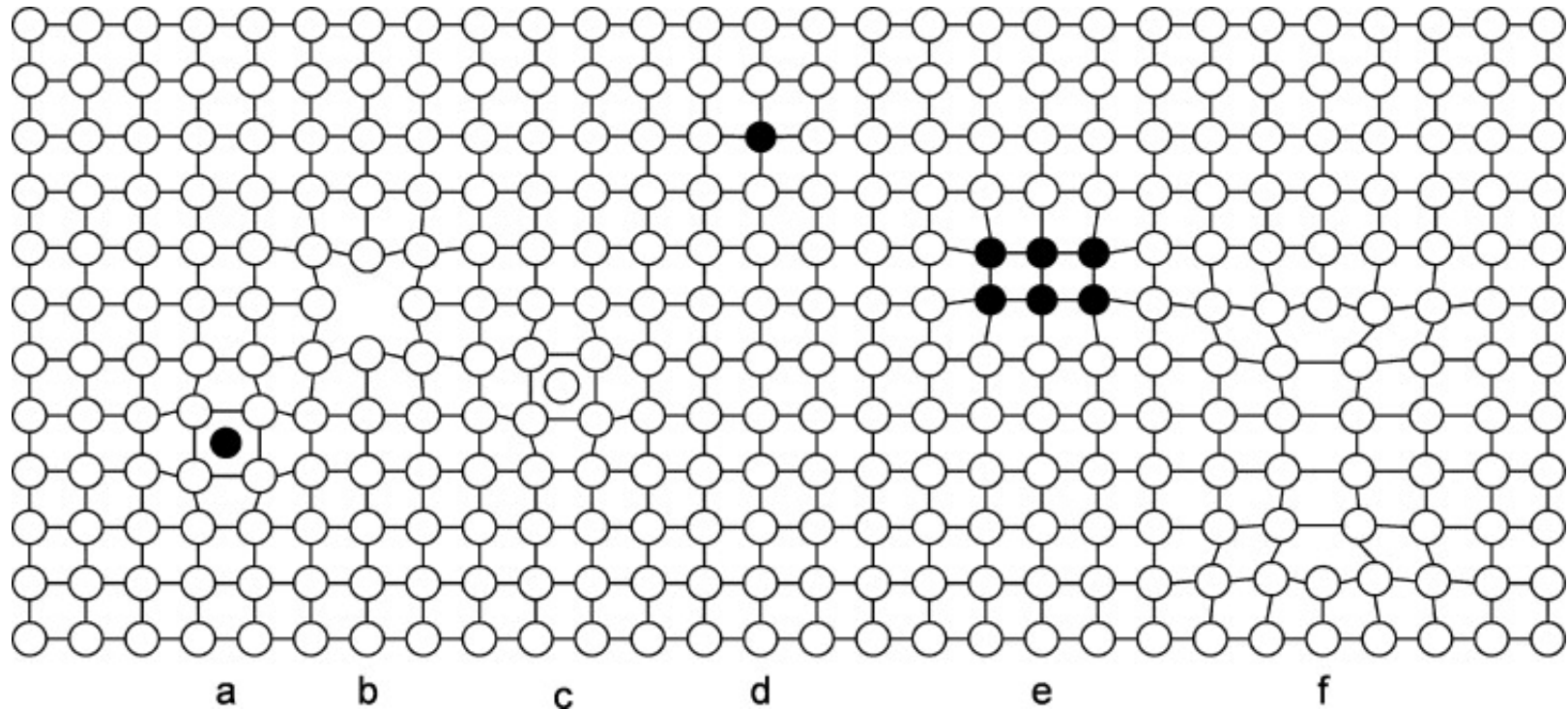
# Correlated oxides

Complex oxides show strong correlations among spin, charge, lattice and orbital degrees of freedom.

- Superconductivity
- Metal-insulator transition (MIT)
- Colossal magnetoresistance
- Multiferroicity



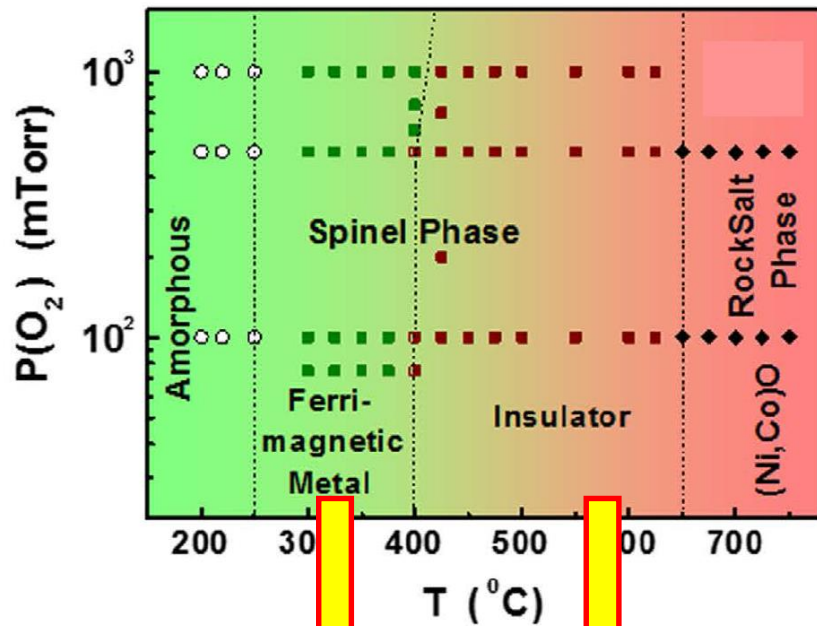
# Ion implantation: effect



Common defects in materials

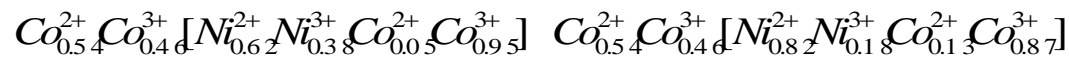
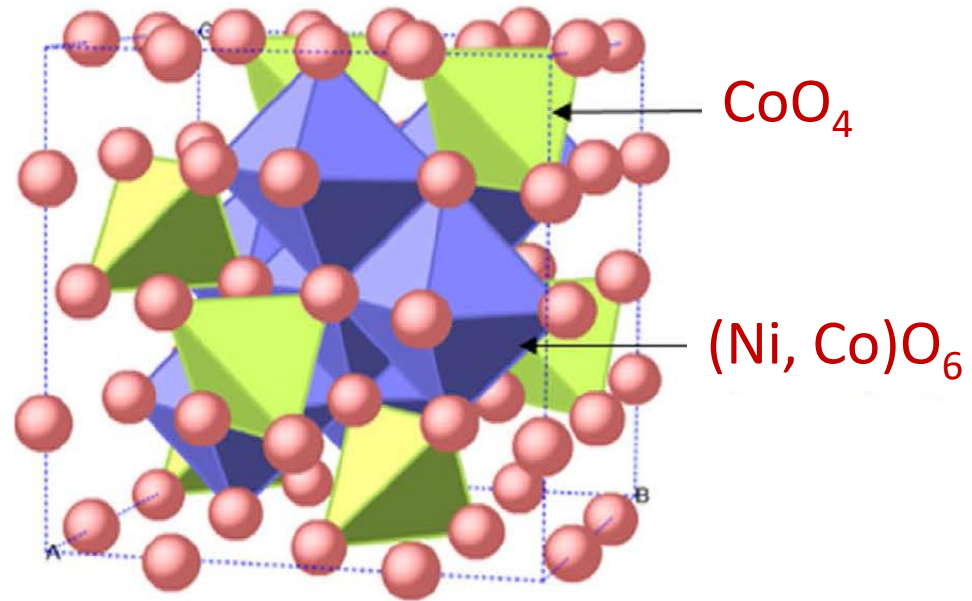
# 1. NiCo<sub>2</sub>O<sub>4</sub>

- NiCo<sub>2</sub>O<sub>4</sub> (NCO) exhibits an inverse spinel structure. NCO displays better electronic conductivity.
- NCO is widely used in various technological applications such as photo-detector, infrared-transparent electrode, supercapacitor

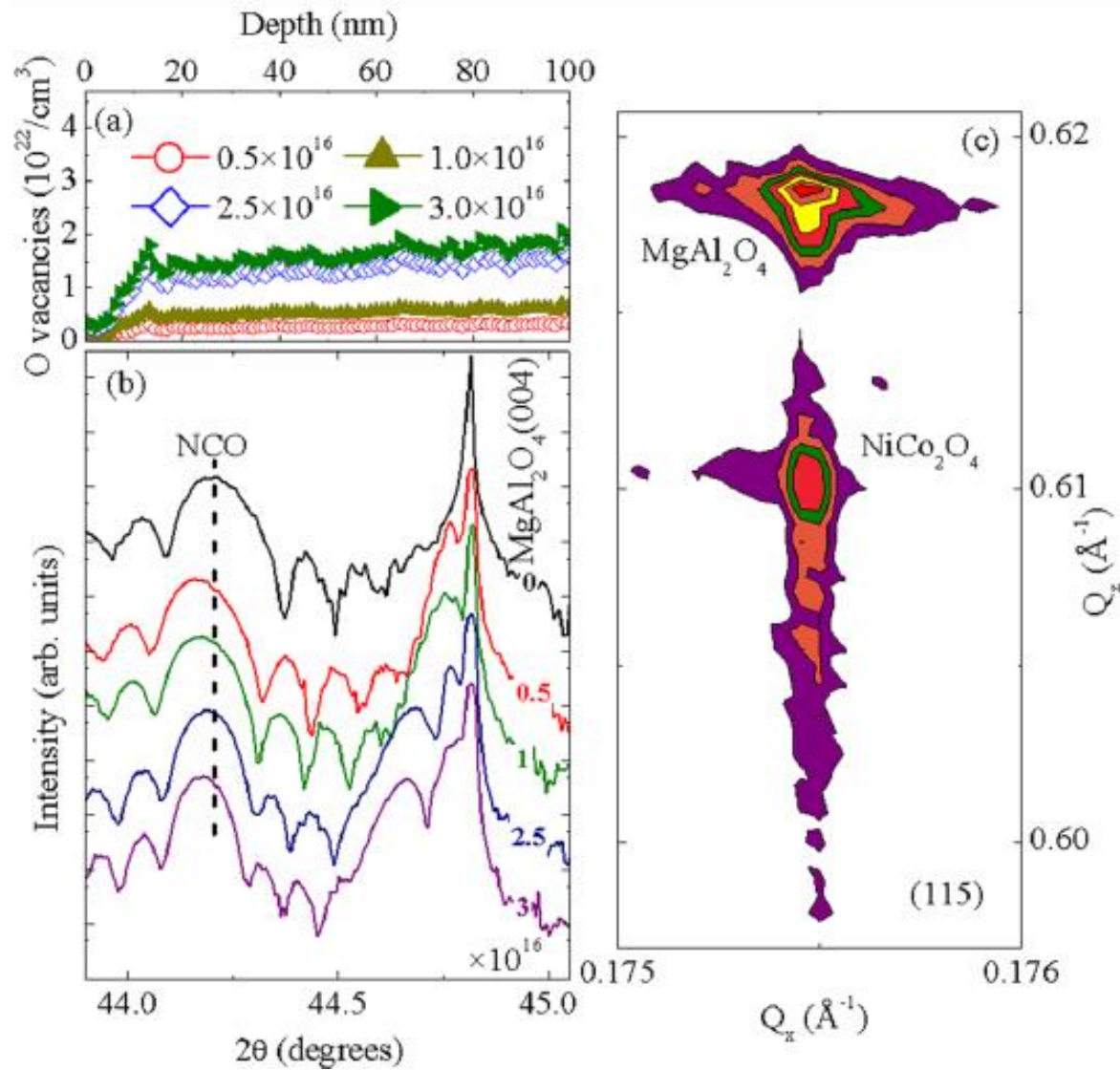


$T_c = 305 \text{ K}$

$T_c = 90 \text{ K}$

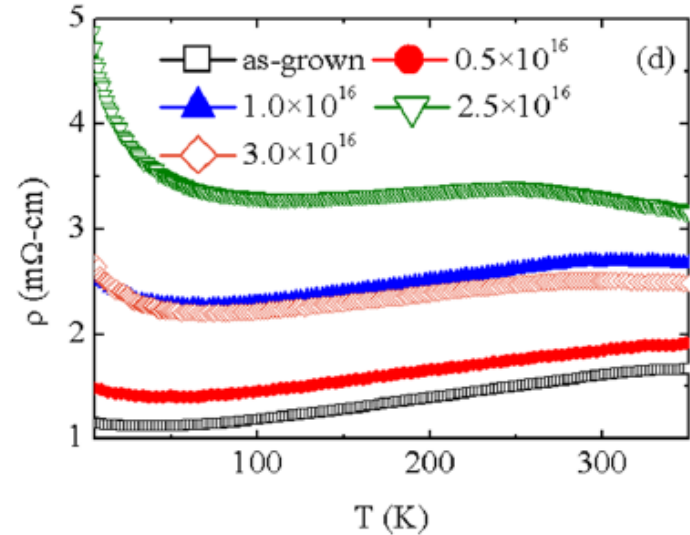
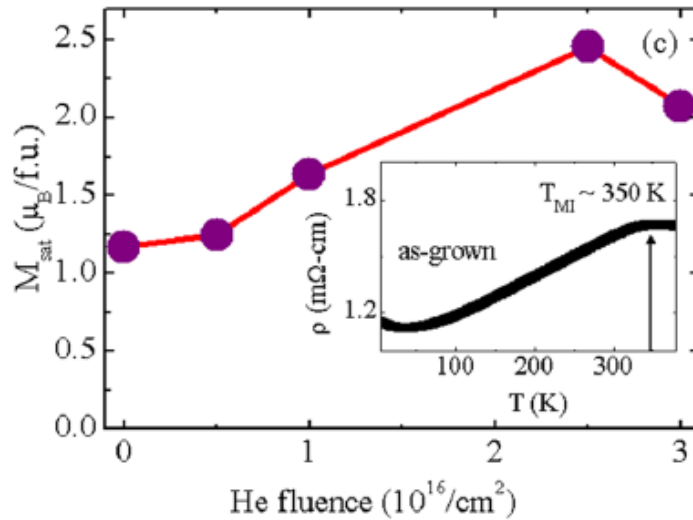
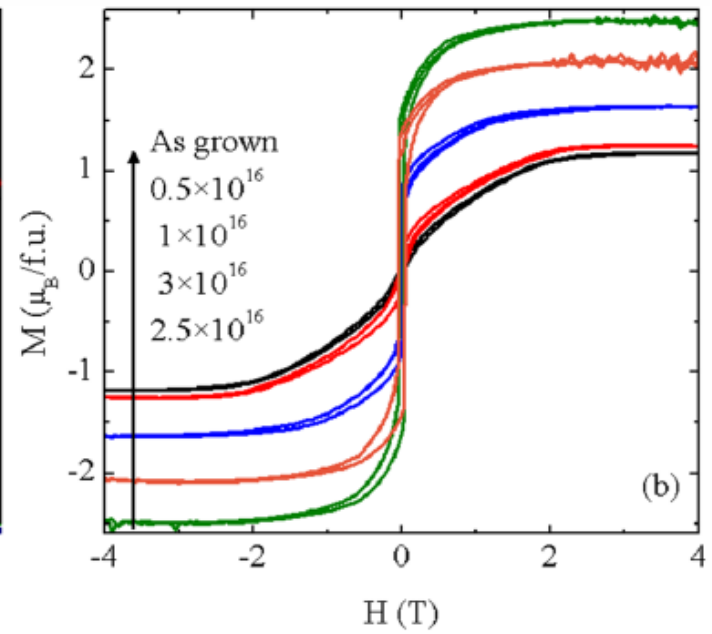
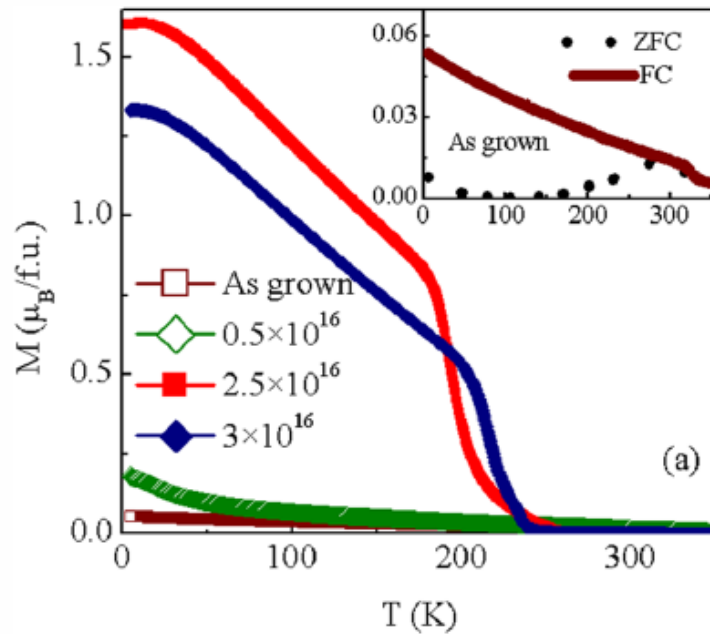


# 1. NiCo<sub>2</sub>O<sub>4</sub>





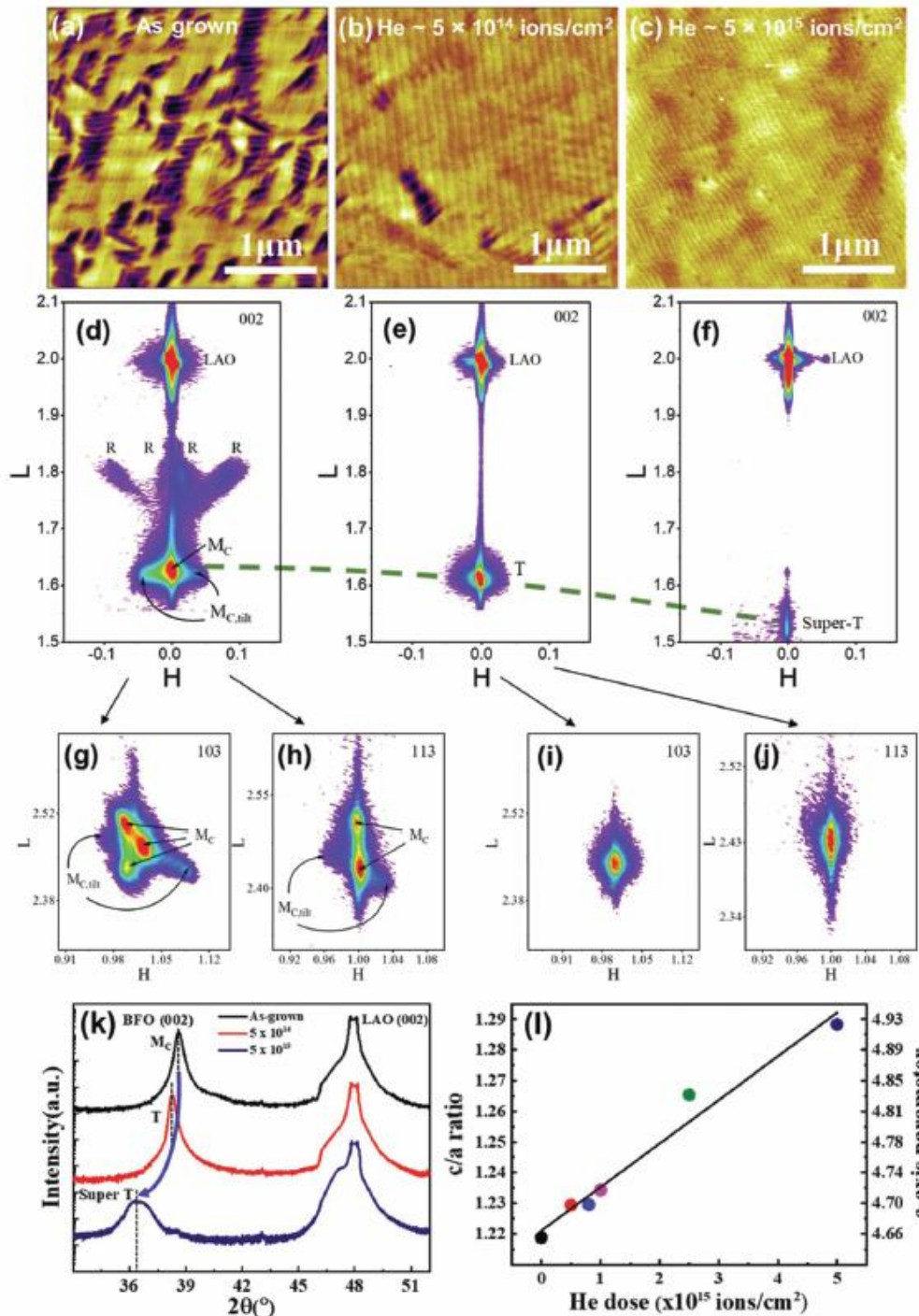
# 1. NiCo<sub>2</sub>O<sub>4</sub>



# 2. BiFeO<sub>3</sub>

Phase transition from the as-grown mixed rhombohedral-like (R) and tetragonal-like (M<sub>C</sub>) phase to true tetragonal (T) symmetry.

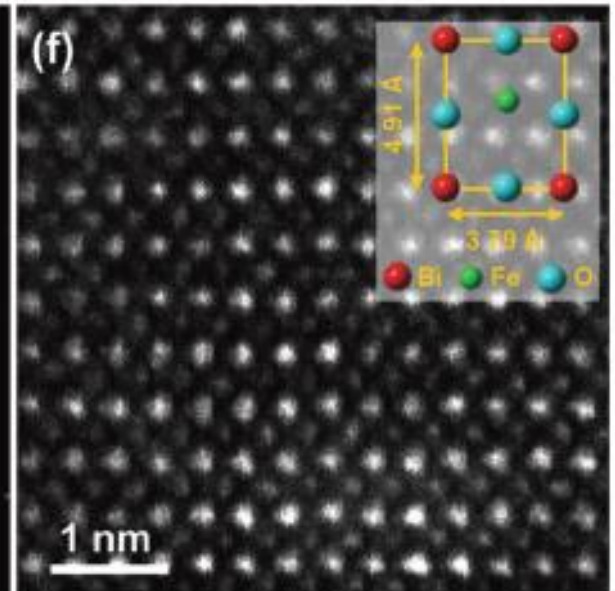
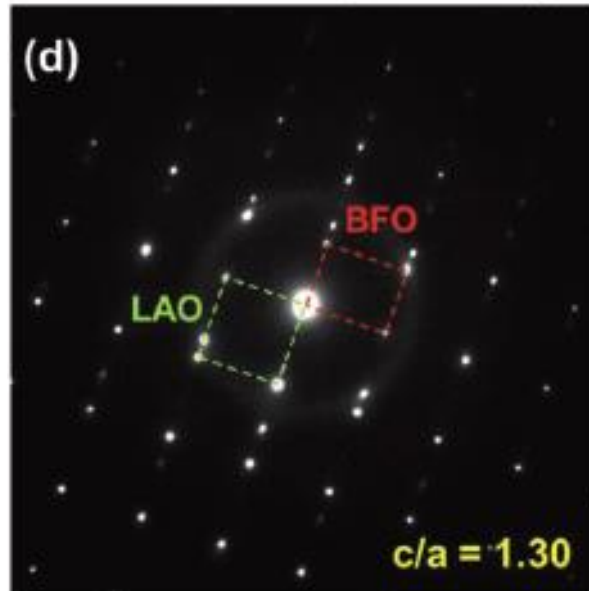
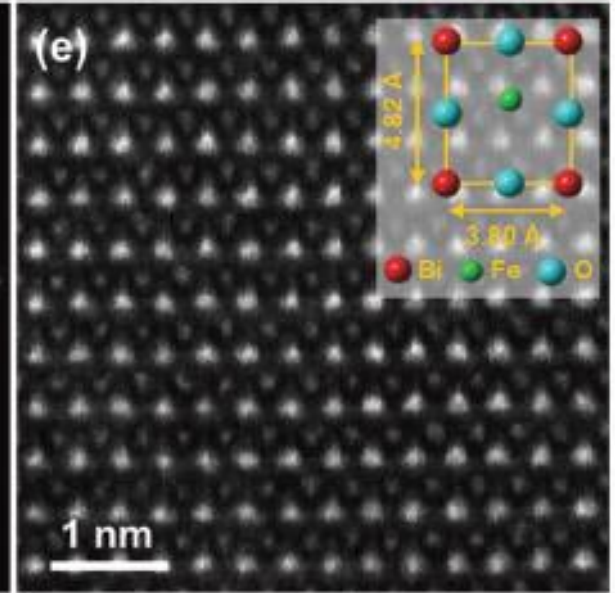
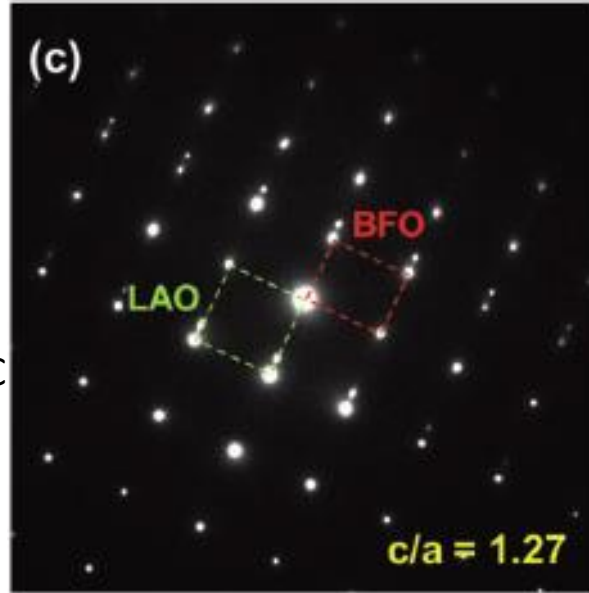
The stripe multi-nanodomains to a single domain state



# 2. BiFeO<sub>3</sub>

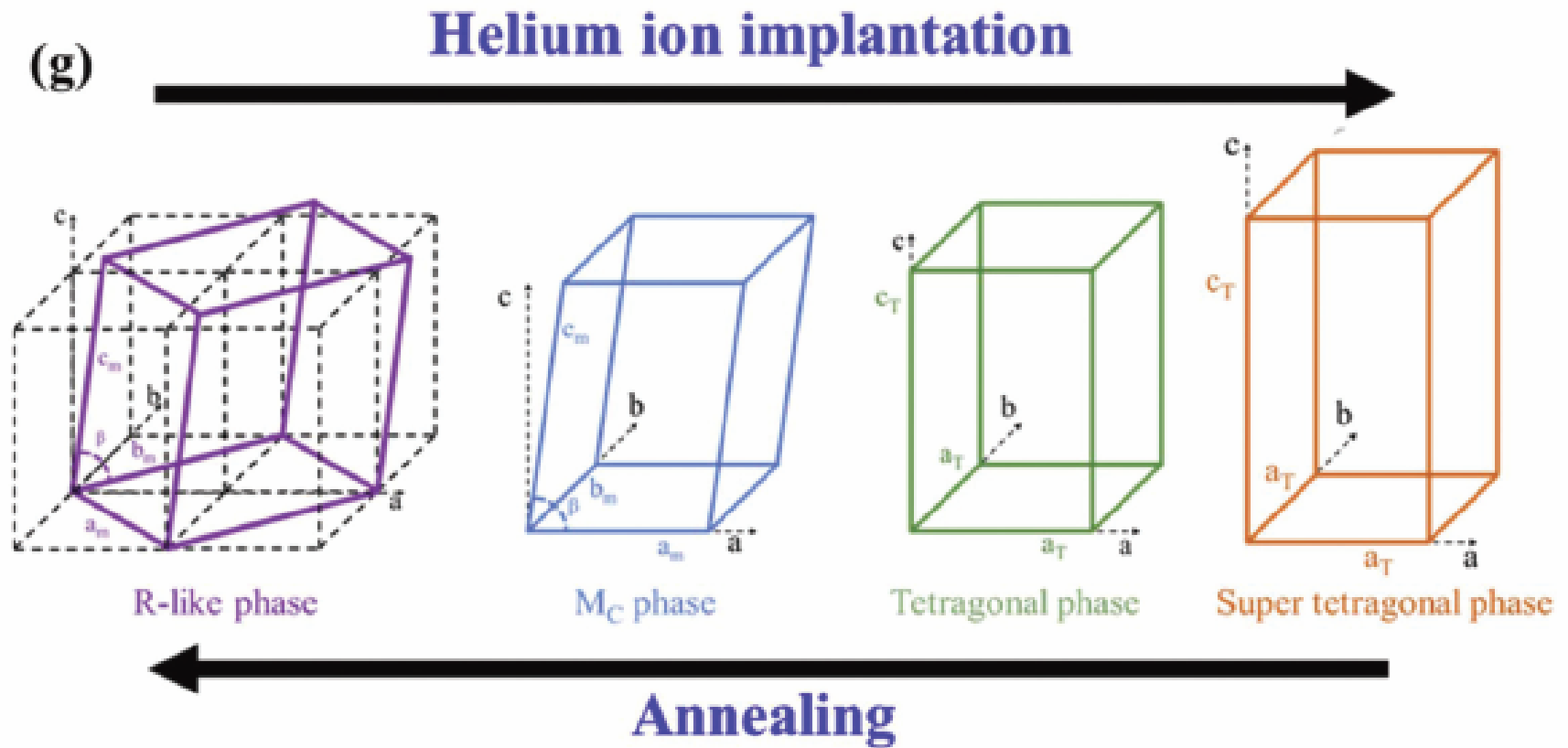
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The stripe multi-nanodomains to a single domain state



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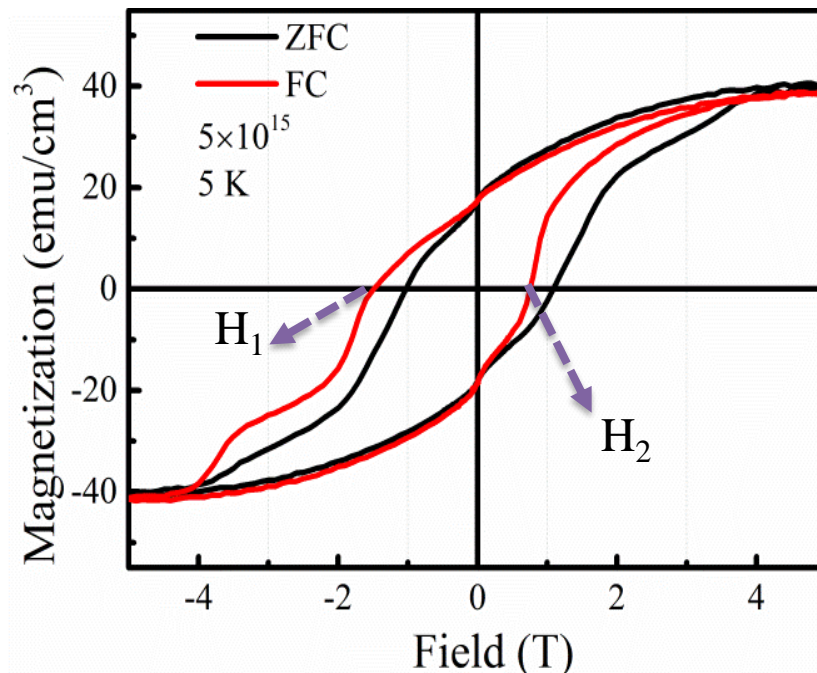
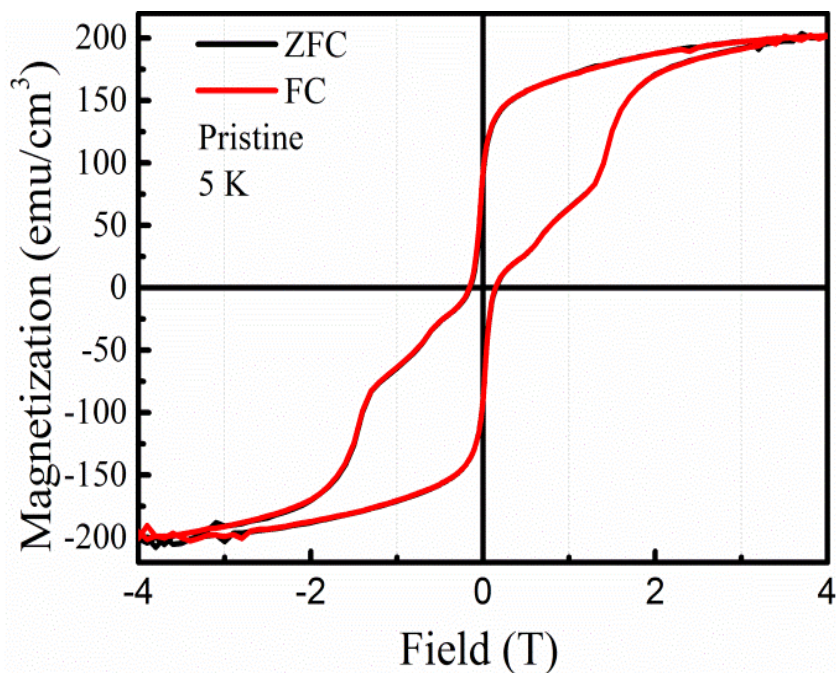
Transition is reversible



# 3. SrRuO<sub>3</sub>

ZFC: zero-field cooling

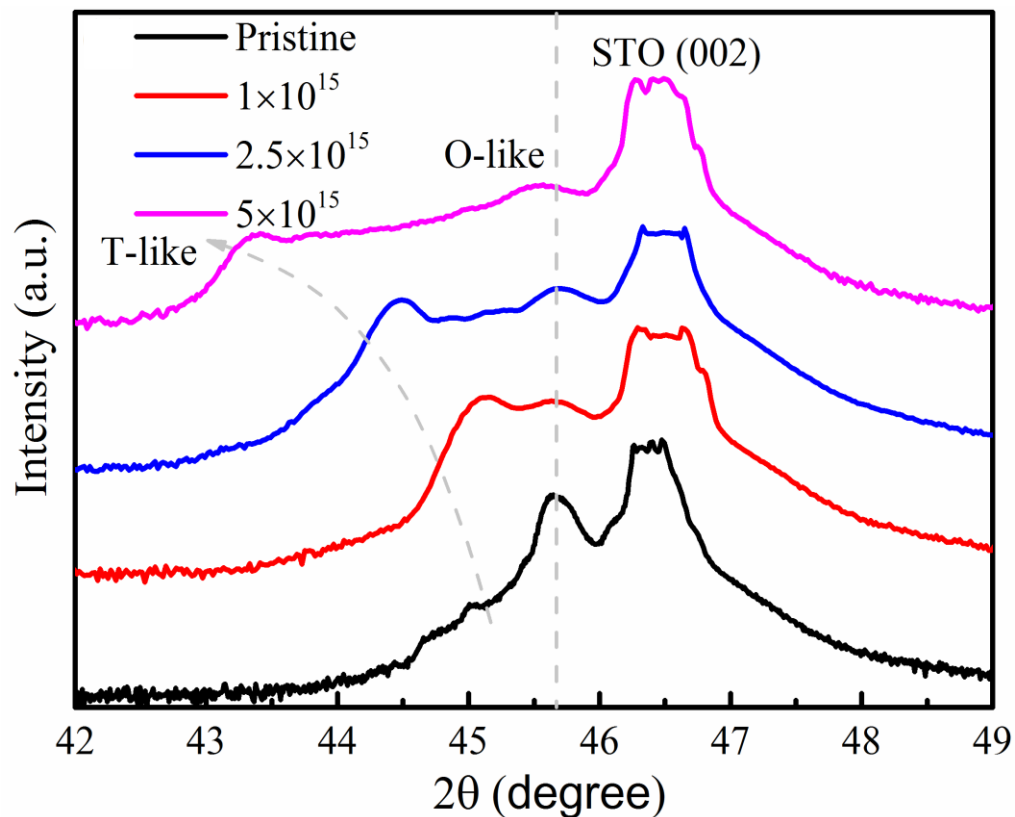
FC: field cooling



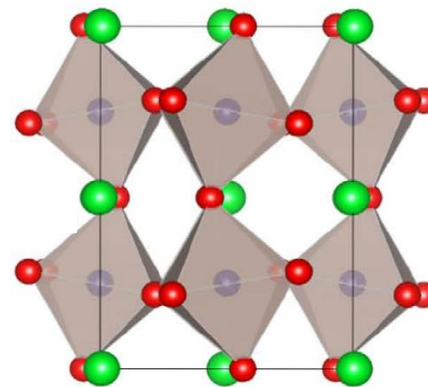
$$H_{\text{EB}} = |(H_1 + H_2)/2|$$

A large exchange bias field  $H_{\text{EB}}$  up to  $\sim 0.36$  T.

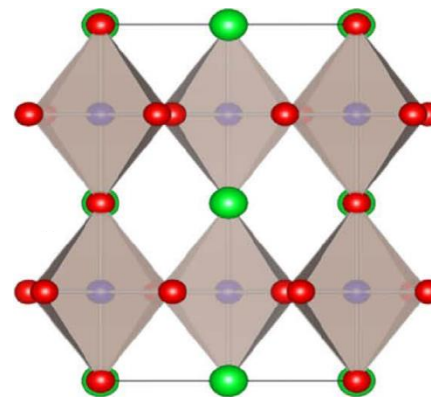
# 3. SrRuO<sub>3</sub>



The irradiation triggers a transition from an **O-like phase to a T-like one.**

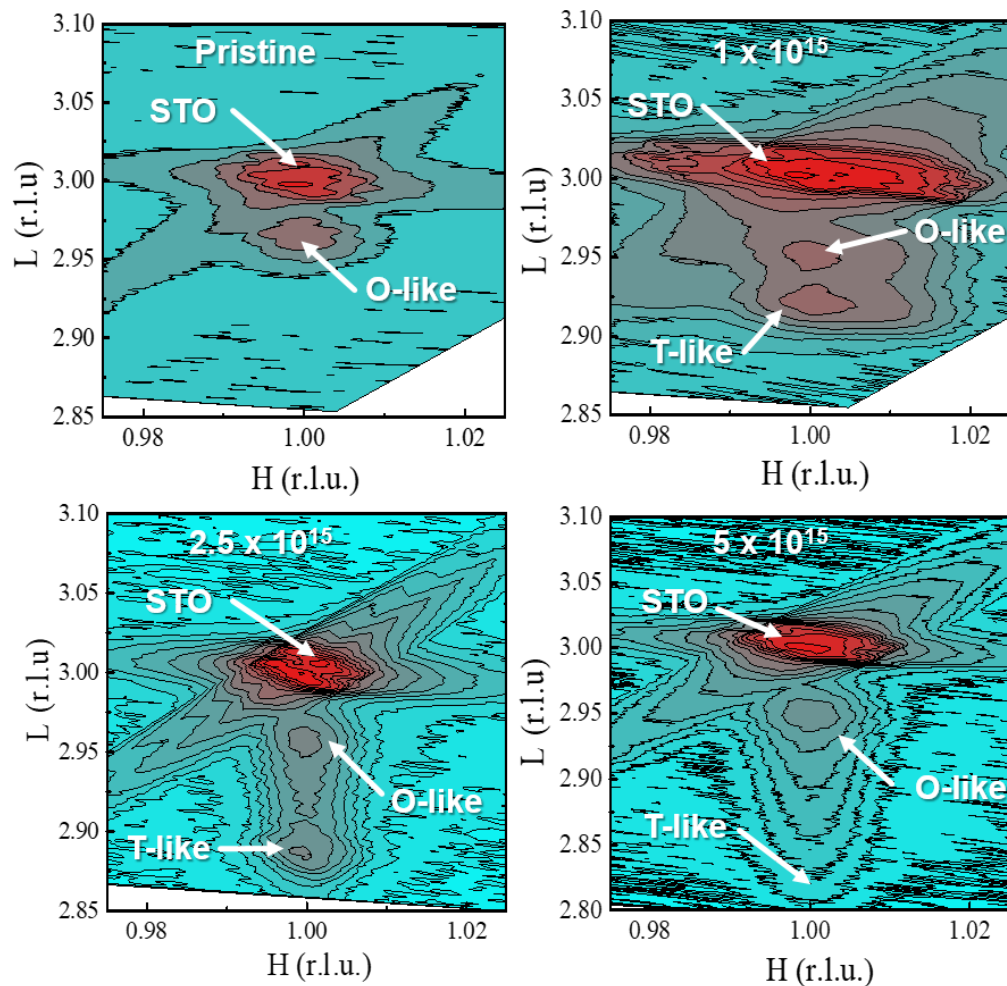


O-like:orthorhombic-like



T-like:tetragonal-like

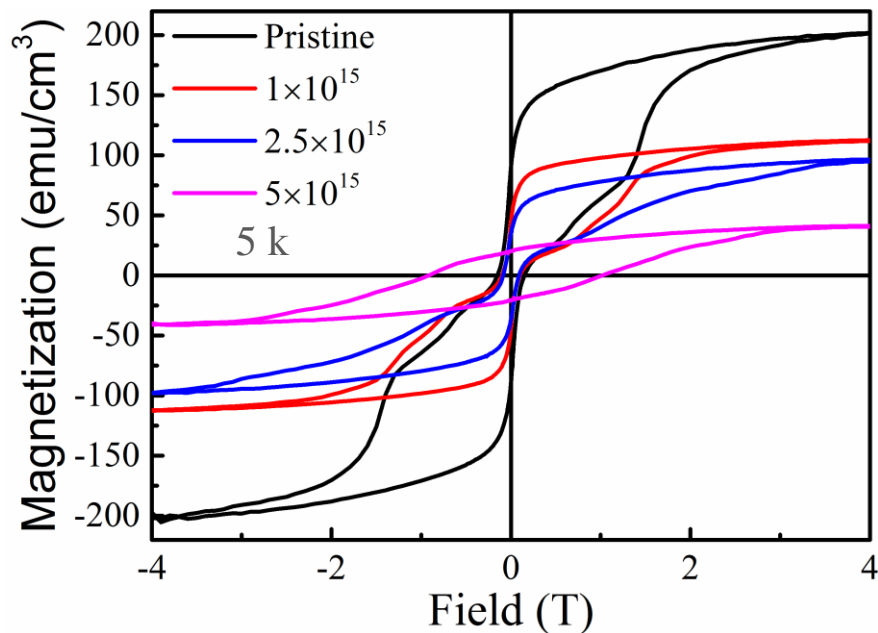
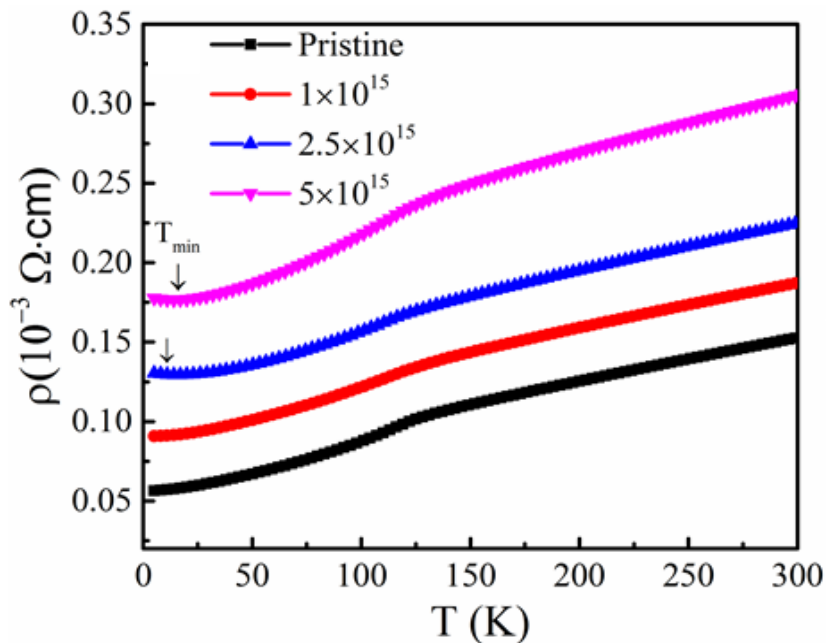
# 3. SrRuO<sub>3</sub>



- The irradiation only induces uniaxial lattice expansion.
- Two peaks for irradiated SRO films in RSMs indicate the **existence of two phases.**

# 3. SrRuO<sub>3</sub>

- Electrical and magnetic properties in SRO films with He ion irradiation.



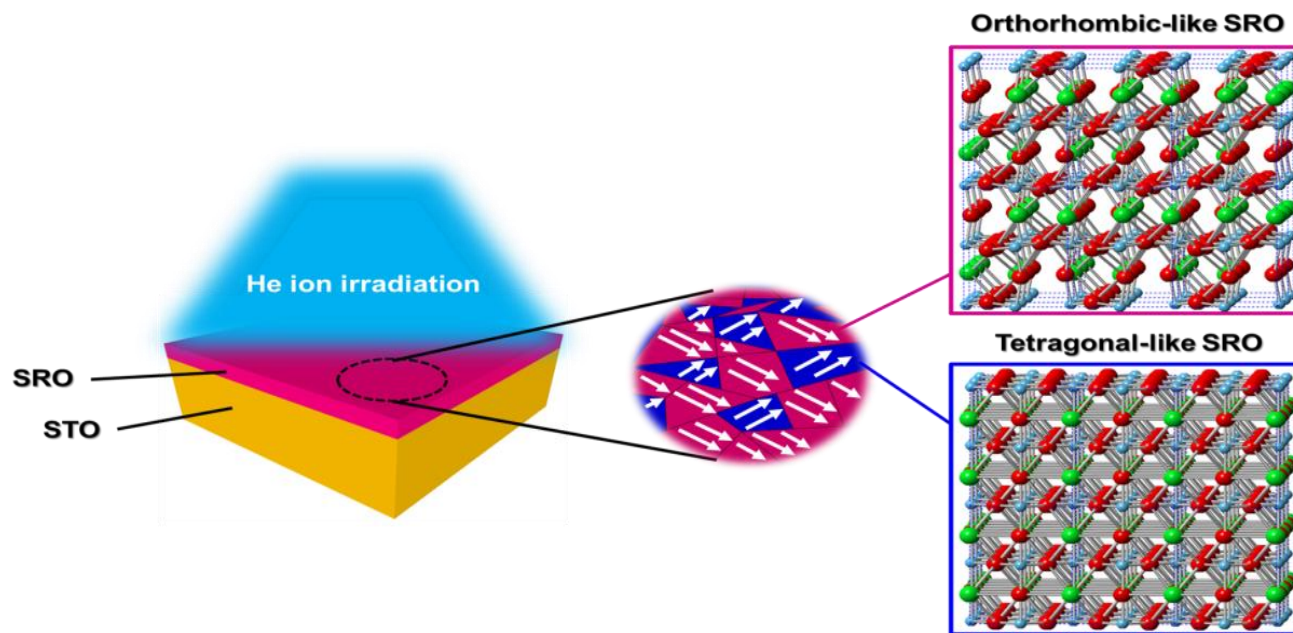
- The resistivity increases continuously as the fluence of ions increases.
- The magnetization decrease with the increase of the irradiation fluence.



# 3. SrRuO<sub>3</sub>

## ➤ How to understand exchange bias in irradiated SRO films?

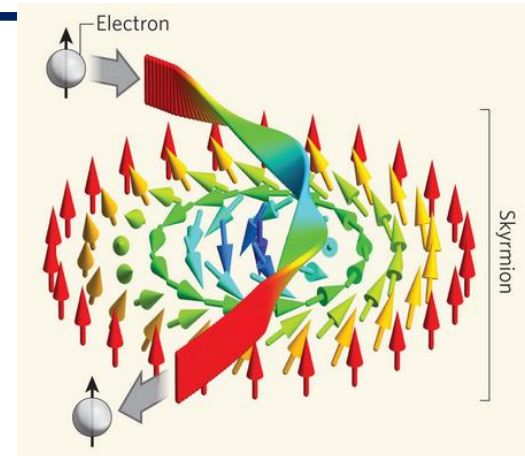
The magnetic phases with different easy axes in an irradiated SRO film.



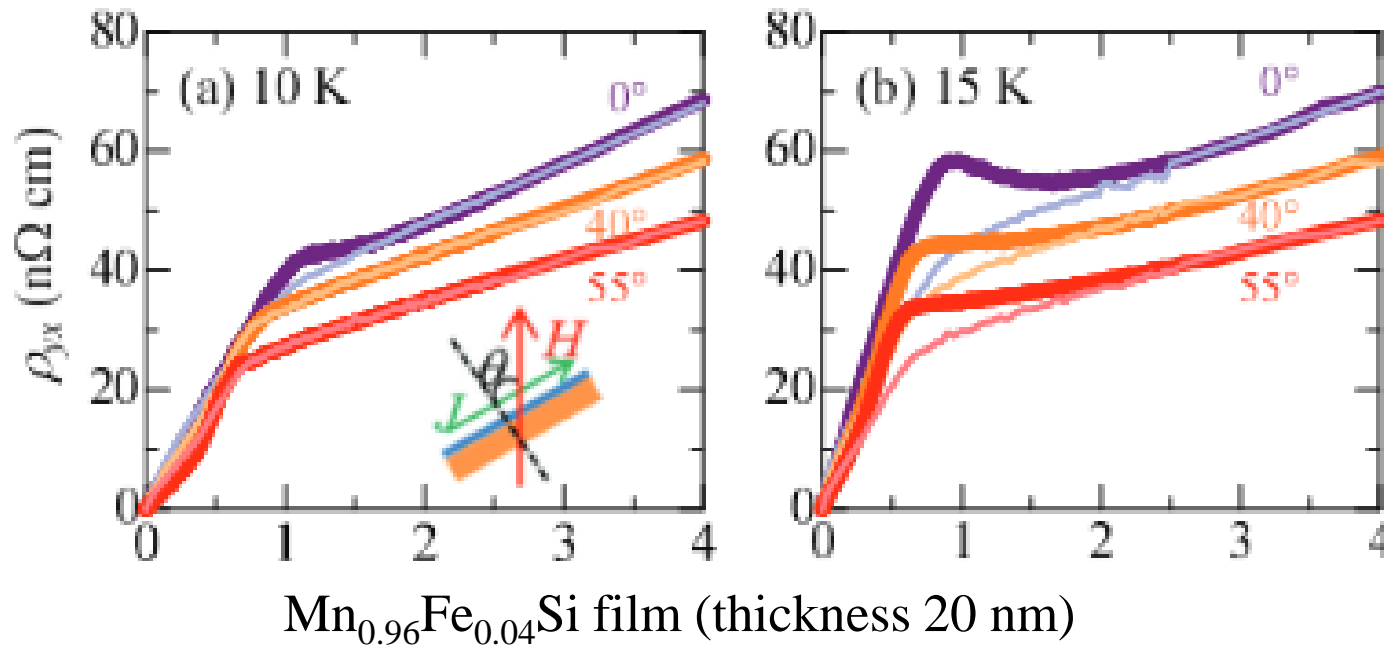
1. The O-like phase and the T-like phase have different **magnetic anisotropy**.
2. Disorder induced by the ion irradiation may drive an **antiferromagnetic phase** in SRO.

# 3. SrRuO<sub>3</sub>

**Topological Hall effect (THE)** is proportional to neither magnetic field nor magnetization. It is generated by non-coplanar or non-collinear spin arrangements such as domain walls, helices or skyrmions.



$$\rho_{xy} = R_H B + R_S M + \rho_H^T$$



T. Yokouchi et al. *Phys. Rev. B.* **89**, 064416 (2014)

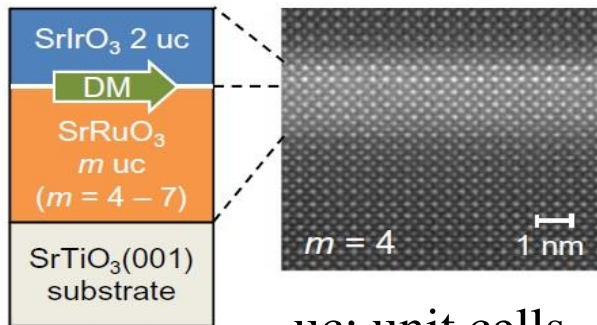
T. Yokouchi et al. *Phys. Rev. B.* **89**, 064416 (2014)

[www.christophschuette.com/phycis](http://www.christophschuette.com/phycis) (Introduction to emergent electrodynamics)

# 3. SrRuO<sub>3</sub>

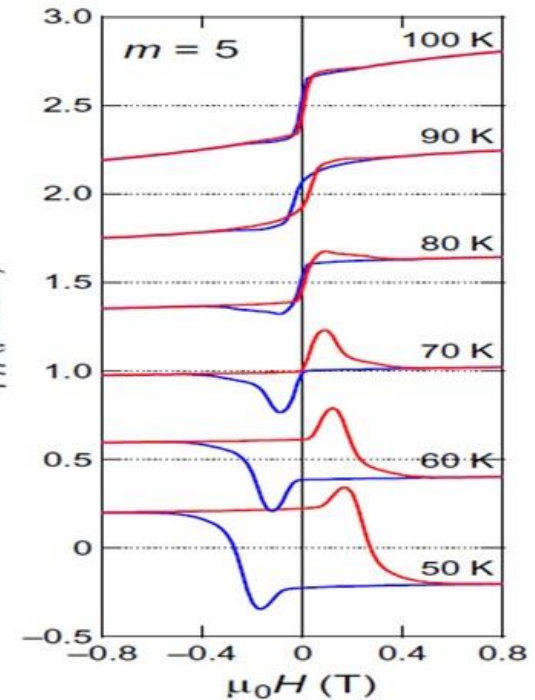
In previous report:

Heterostructure:

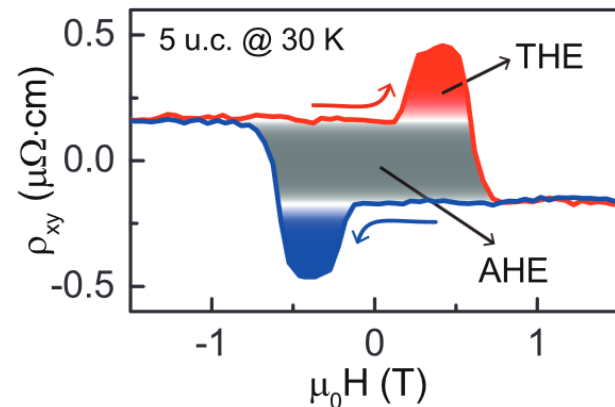
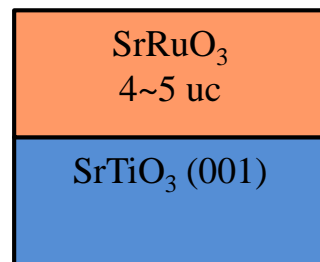


uc: unit cells

DM: Dzyaloshinskii-Moriya interaction



Ultrathin SRO system:

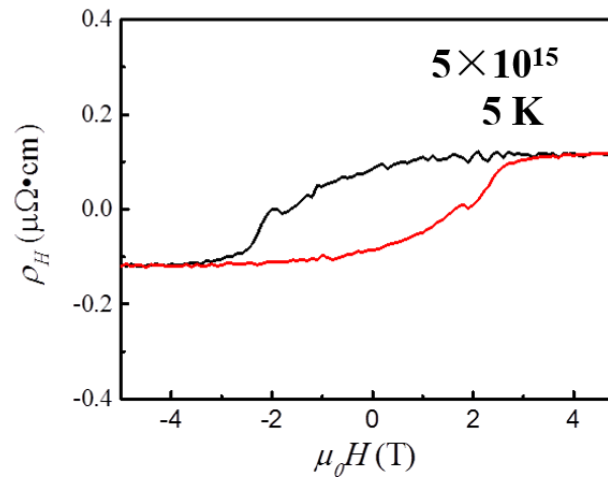
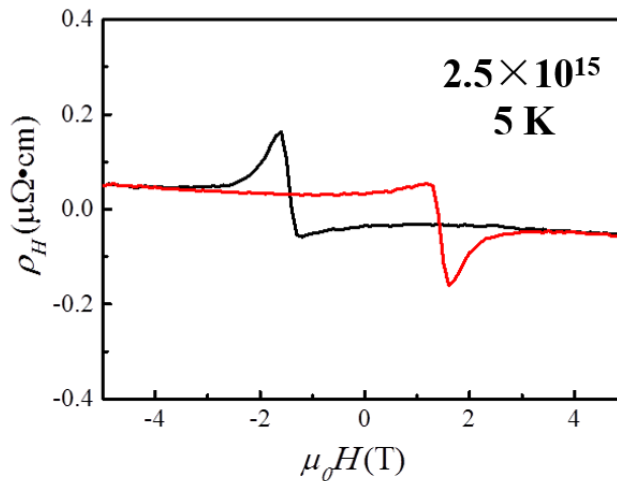
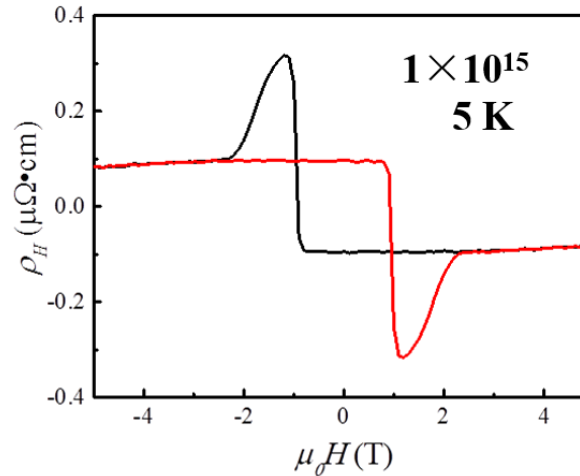
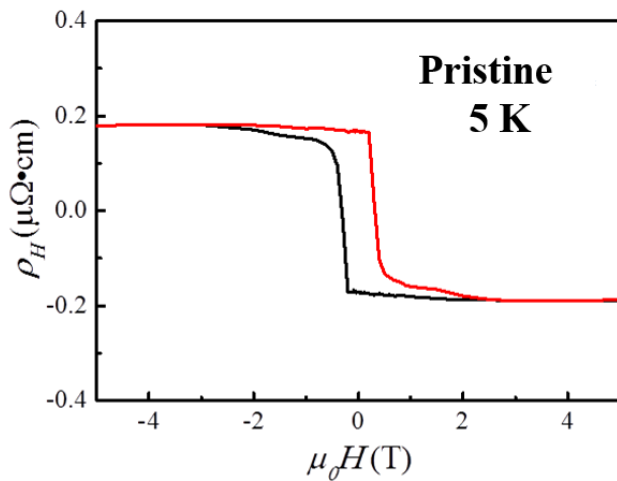


A **heterostructure** system or the SRO layer thickness is limited to only a **few nanometers** to show a measurable THE

# 3. SrRuO<sub>3</sub>

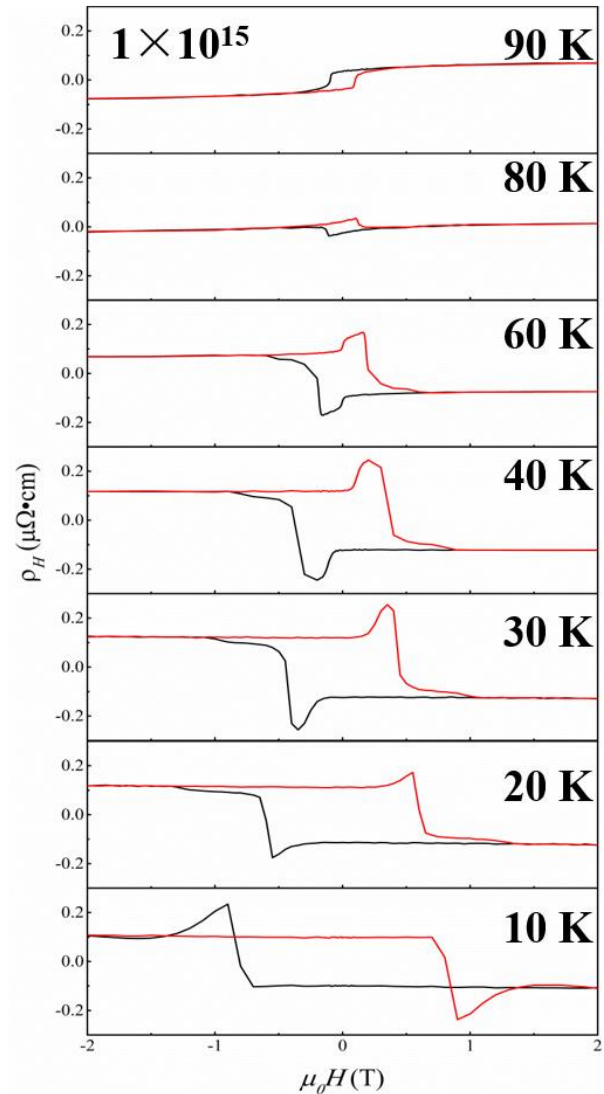
- **THE** appear in a **single and thick (~ 60 nm)** SRO films with He ion irradiation.

Sweep direction

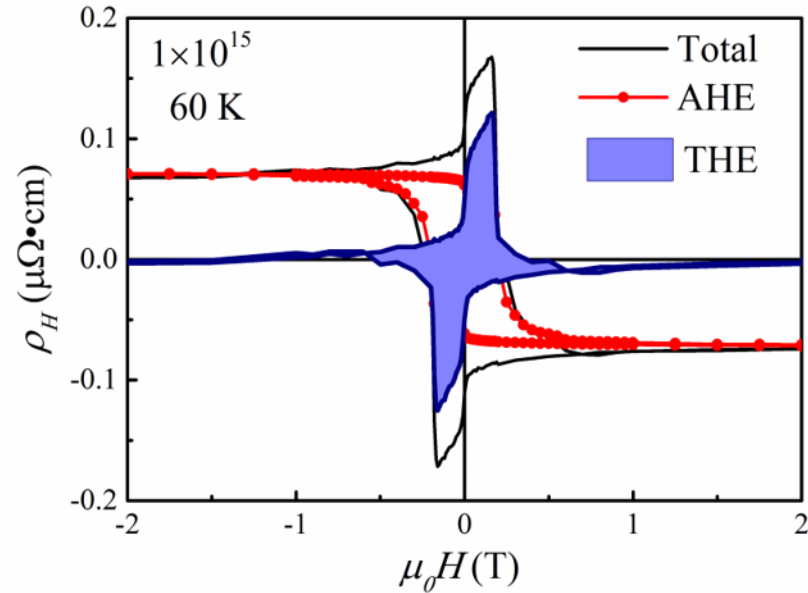


# 3. SrRuO<sub>3</sub>

➤ Hall effect for the sample  $1 \times 10^{15}$

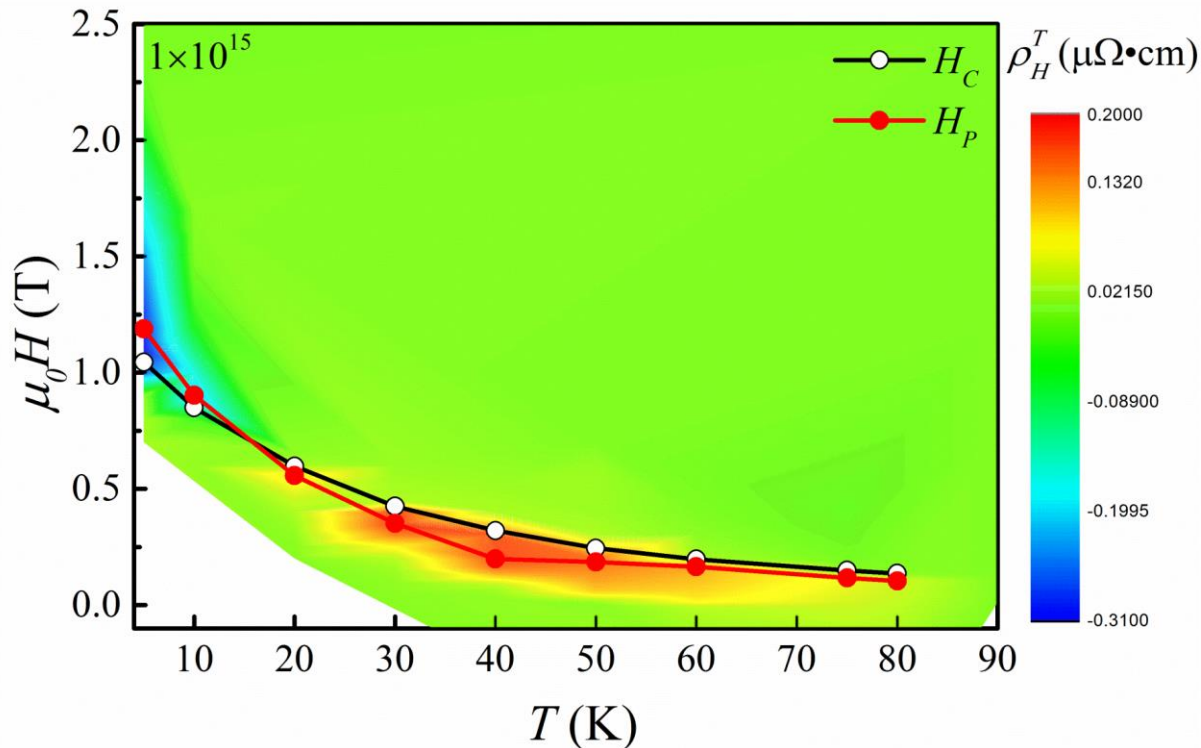


Contribution from AHE and THE for the  $1 \times 10^{15}$



# 3. SrRuO<sub>3</sub>

- Color map of topological Hall resistivity in the T-H plane for the sample  $1 \times 10^{15}$



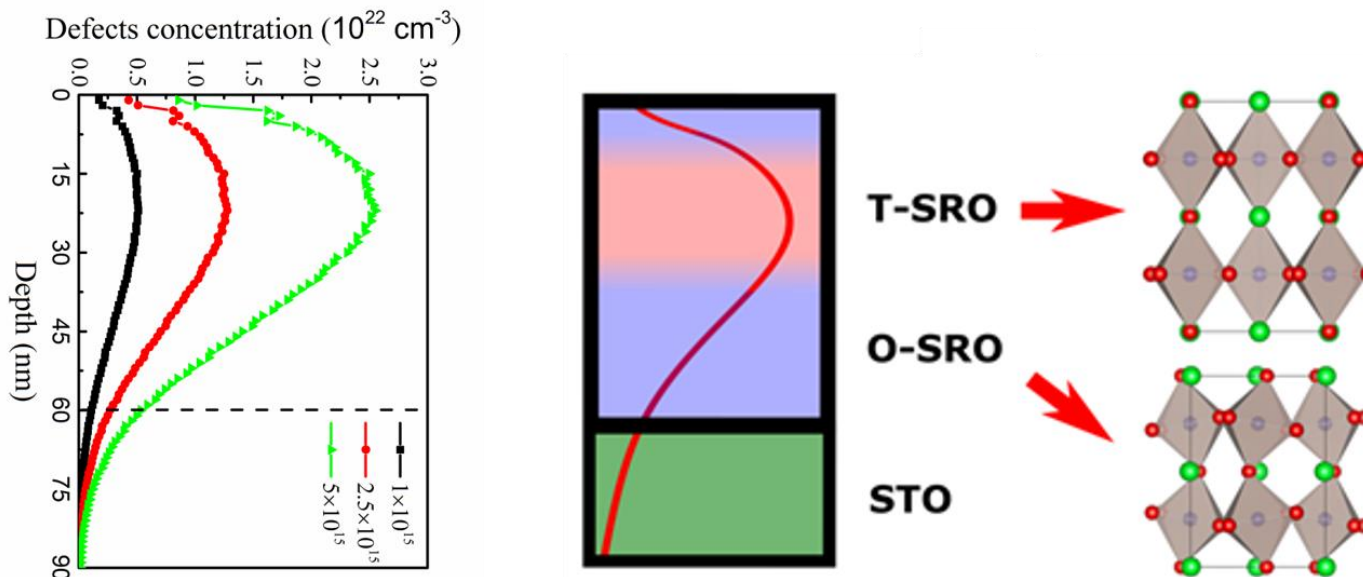
$H_C$ : coercivity at M-H loops

$H_P$ : magnetic field of peak at THE

**A pronounced THE is observed in a wide temperature range from 5 to 80 K.**

# 3. SrRuO<sub>3</sub>

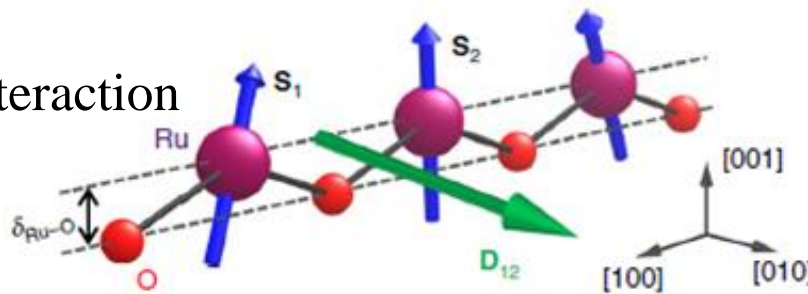
- The observed THE is attributed to **inversion symmetry breaking** due to defect engineering.



A gradient in the density of defects lead to the **local structural distortion**.

The change of oxygen octahedral rotation at the O-T phase boundary.

Dzyaloshinskii-Moriya interaction



L. F. Wang et al. *Nat. Mater.* 2018, 7, 1087-1094

# Ion irradiation effect in complex oxides: Another degree of freedom or complexity?

Who play the major role?

Defects? Strain? Oxygen-vacancy? Ion occupations?



# Acknowledgement

From my group: Changan Wang, Dr. Parul Pandey

Prof. Ching-Hao Chang:

Prof. Ying-Hao Eddie Chu: National Jiaotong University

Prof. Deyang Chen: South China Normal University

**IBC.**

 **HELMHOLTZ**  
ZENTRUM DRESDEN  
ROSSENDORF



**DFG**

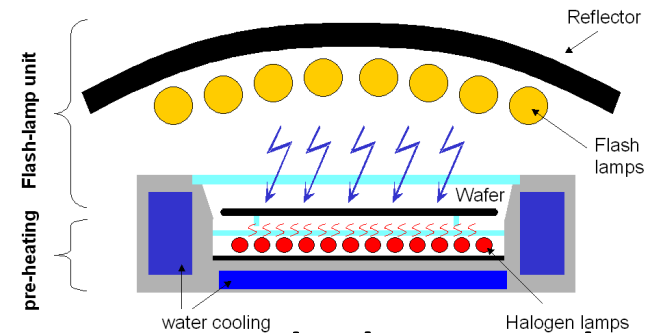
ZH 225/10-1

Thank you for your attention!  
Looking forward to cooperation!

**s.zhou@hzdr.de**

# Resources: Semiconductor materials

## Material processing: laser and flash lamp annealing



## Material characterization: magnetic and electrical



SQUID-VSM  
SQUID-MPMS  
Lakeshore Hall Measurement system  
1.8-400 K  
up to 7 T

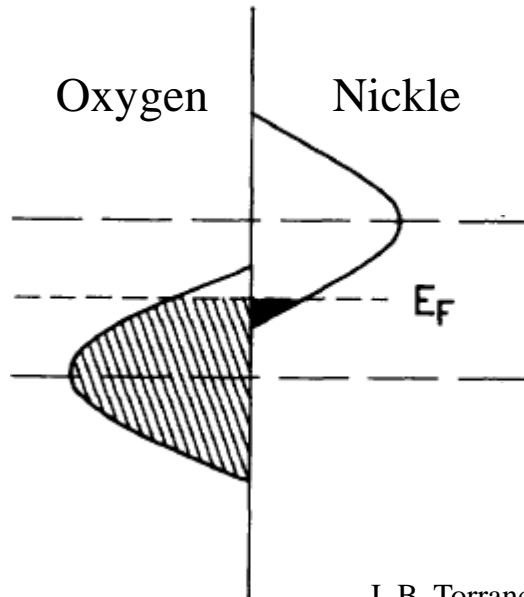


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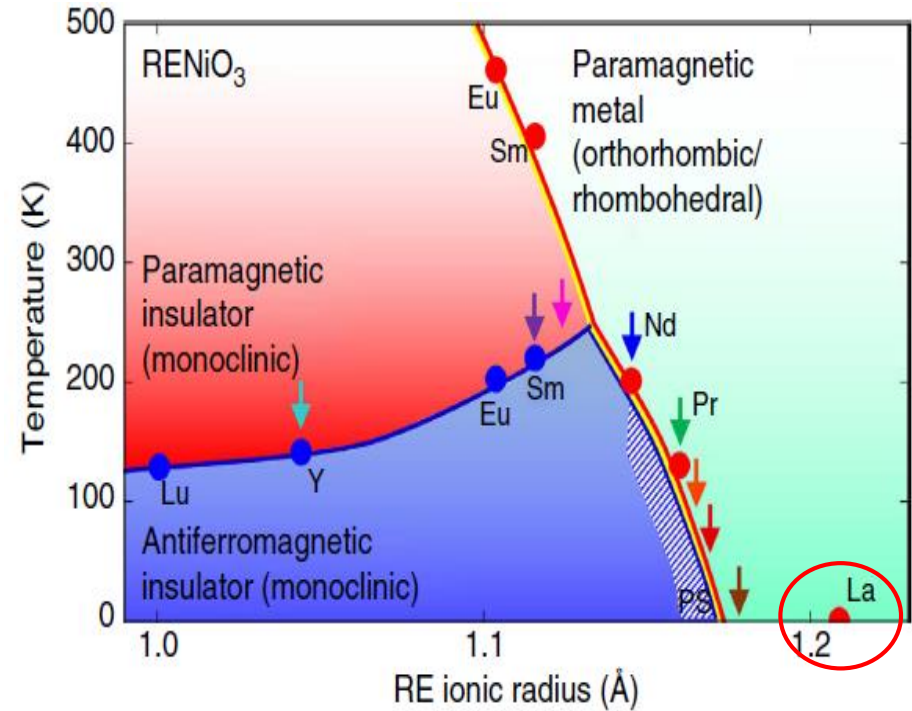
And the user facilities: ion beam center

# 3. $\text{LaNiO}_3$

- Paramagnetic oxide
- No metal insulator transition
- Metallic behavior down to 0.4 K

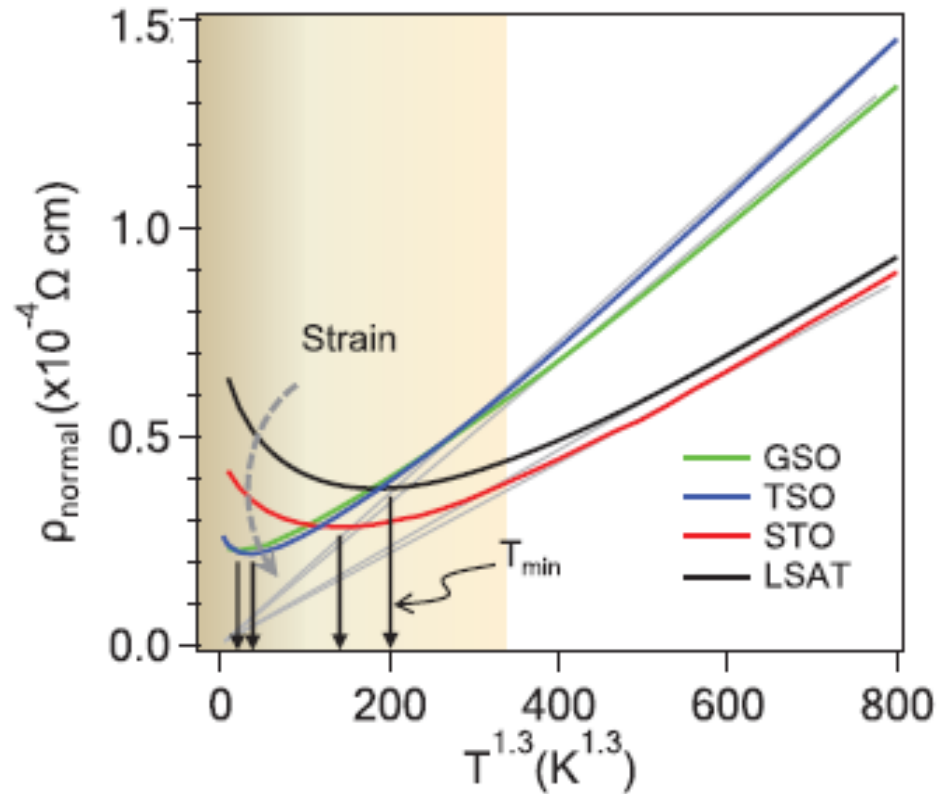
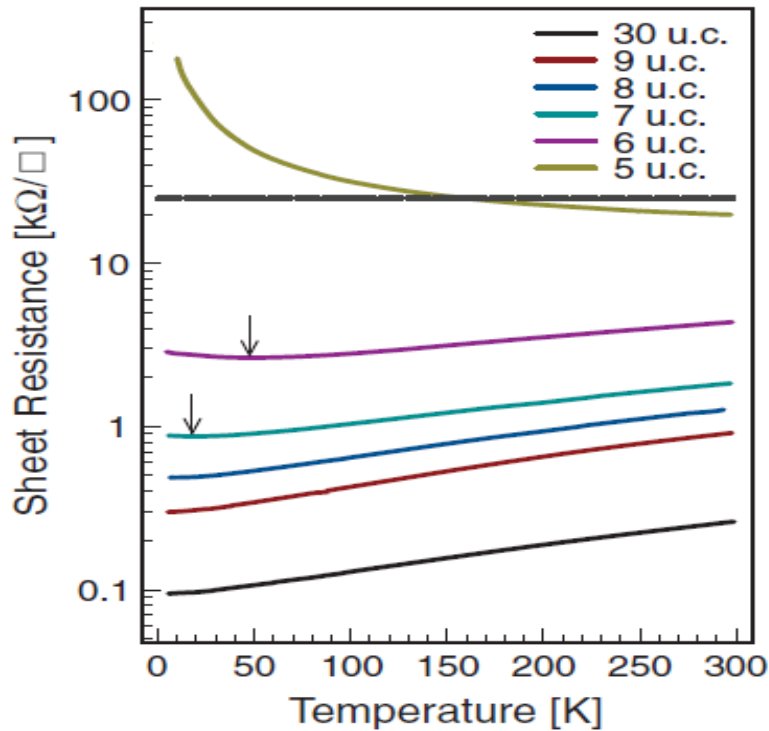


J. B. Torrance. et al. Phys. Rev. B **45**, 8209 (1992)



B. A. Frandsen. et al. Nat. Commun **7**, 12519 (2016)

# 3. $\text{LaNiO}_3$



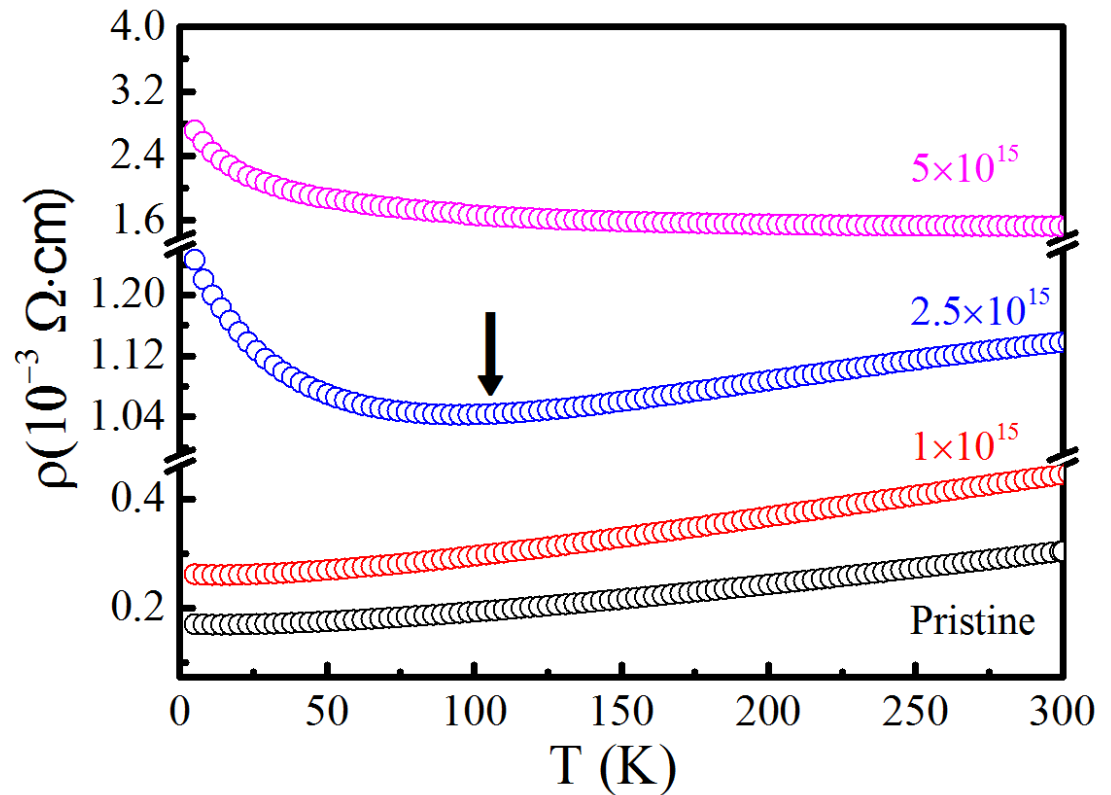
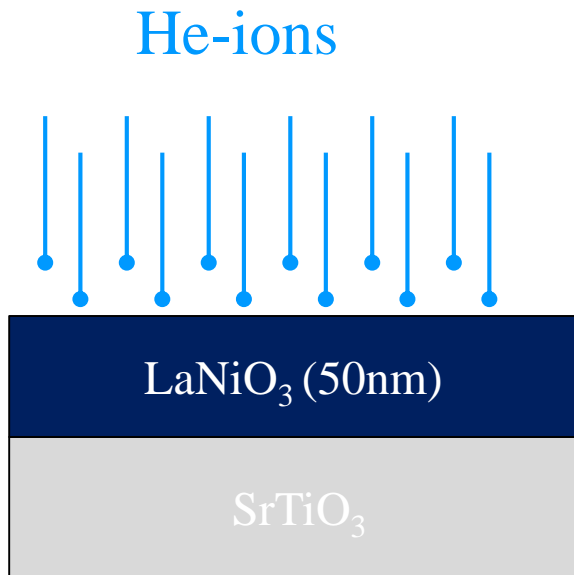
LNO-based heterostructures have been grown and transport measurements have revealed a MIT as the thickness is reduced to 3-5 monolayer.

Weak localization can also be driven in LNO films by strain.

R. Scherwitzl. et al. Phys. Rev. Lett **106**, 246403 (2011)

E. J. Moon. et al. New. J. Phys. 13, 073037(2011)

# 3. $\text{LaNiO}_3$

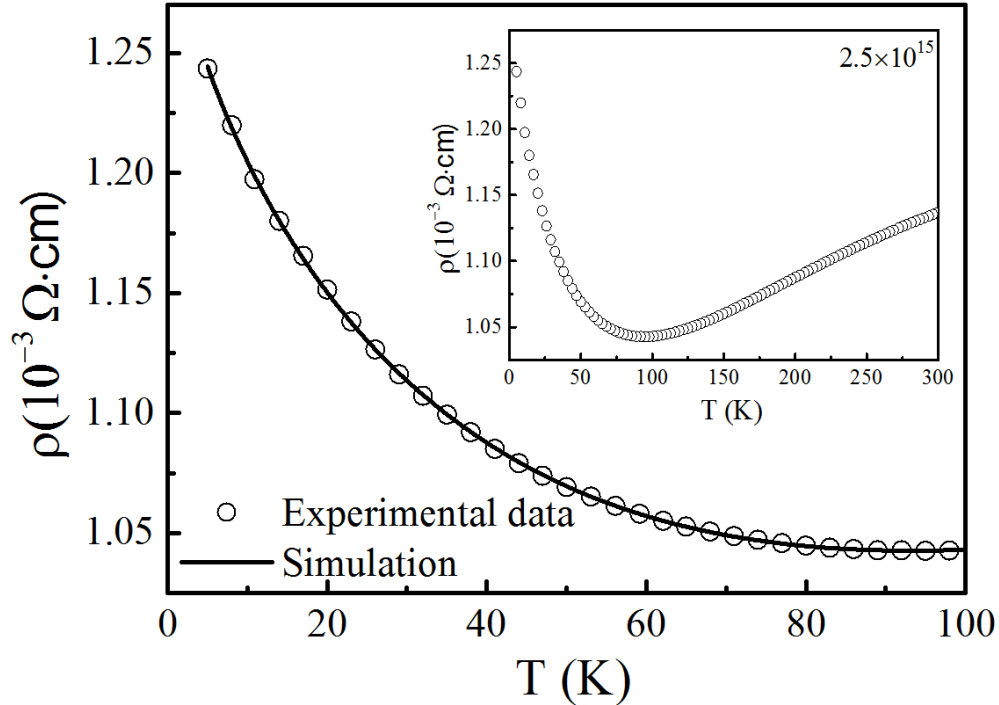


Pristine and  $1 \times 10^{15}$  show metallic behavior ( $d\rho/dT > 0$ ).

$2.5 \times 10^{15}$  displays an upturn in resistivity at around 100 K.

$5 \times 10^{15}$  shows insulating behavior ( $d\rho/dT < 0$ ).

# 3. $\text{LaNiO}_3$

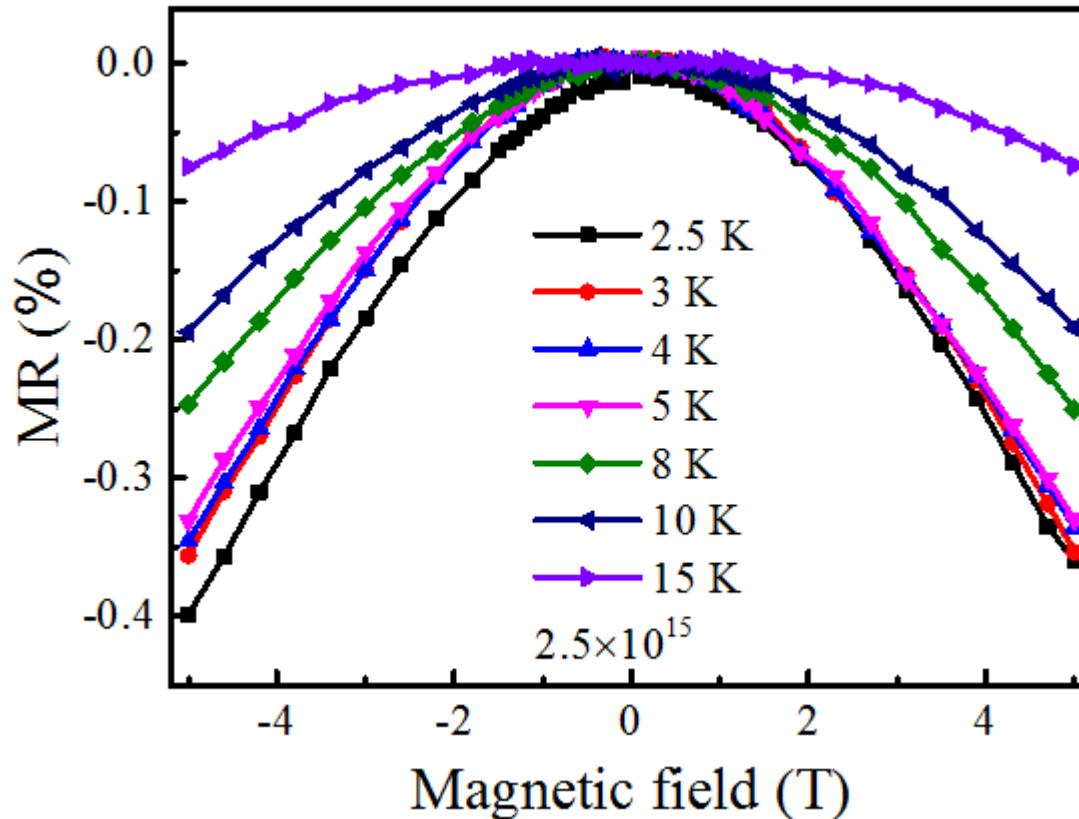


- $\rho_0$ : the remnant resistance;
- the second and third terms represent the weak localization correction in three dimensions and inelastic scattering due to electron-boson interaction;
- $bT^2$  is the classical Boltzmann term.

$$\rho = \rho_0 - \alpha T^{3/4} + \beta T^{3/2} + bT^2$$

Dominated by electron-defects interaction rather than the electron-electron interaction

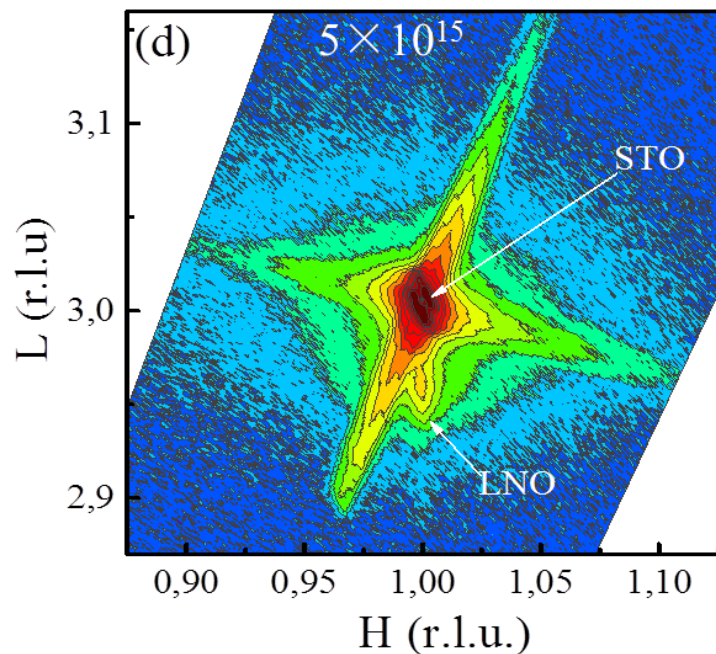
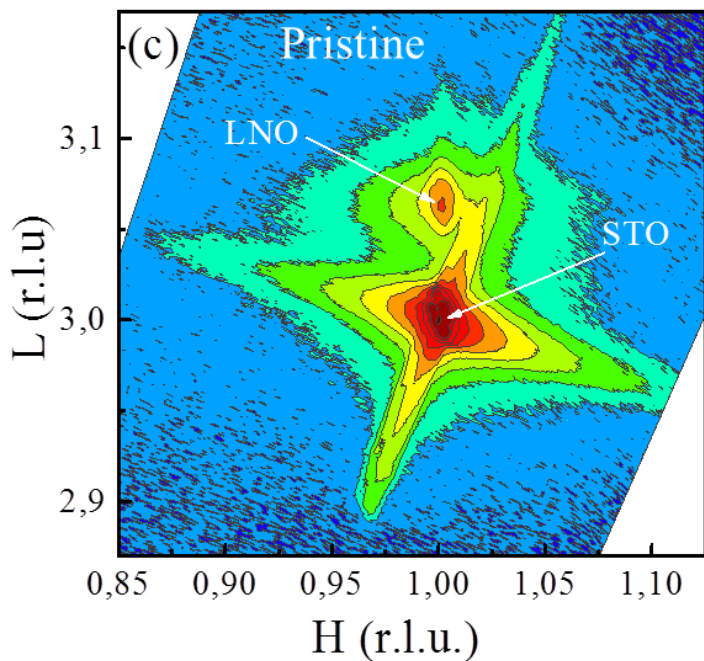
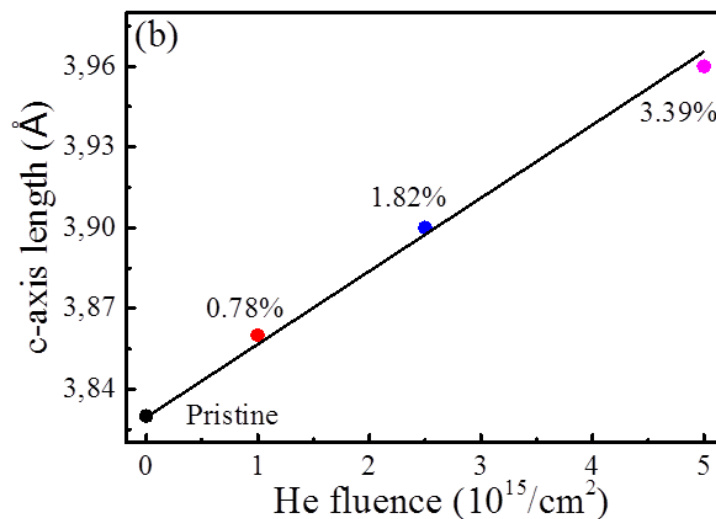
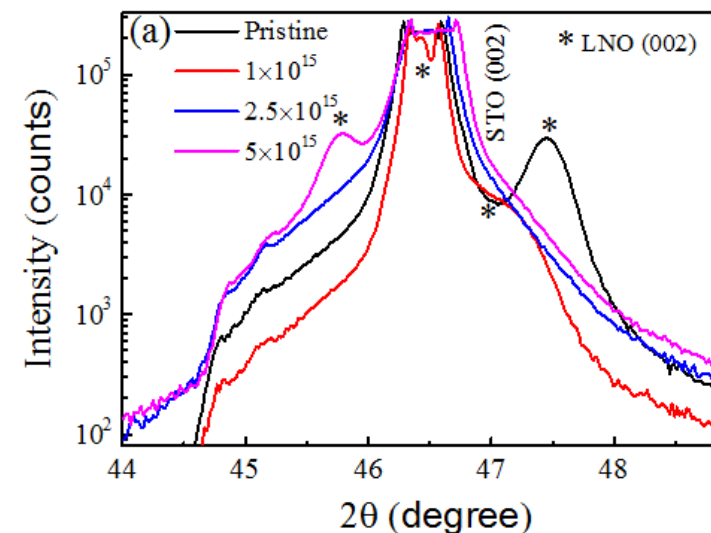
# 3. $\text{LaNiO}_3$



The negative MR is also an evidence that the dominant scattering mechanism is not electron-electron interaction.

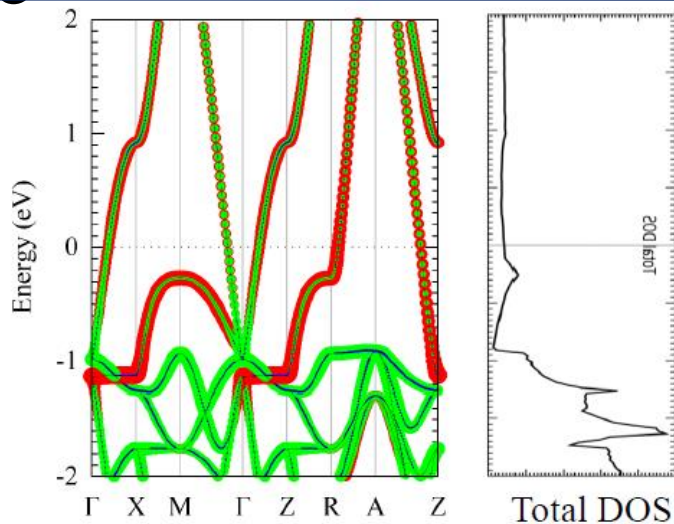


# 3. $\text{LaNiO}_3$

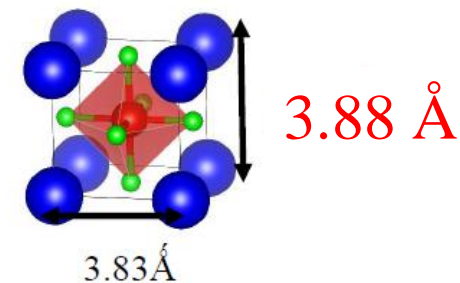
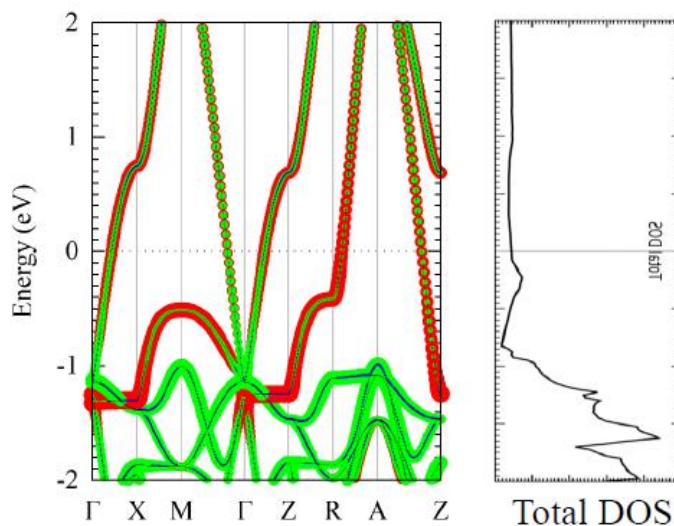
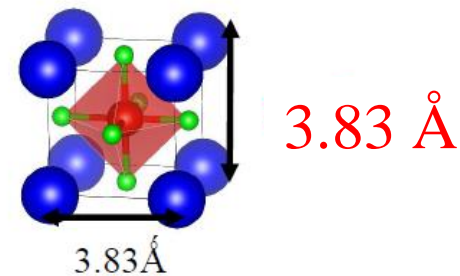


# 3. $\text{LaNiO}_3$

- $\text{Ni } d$
- $\text{O } p$



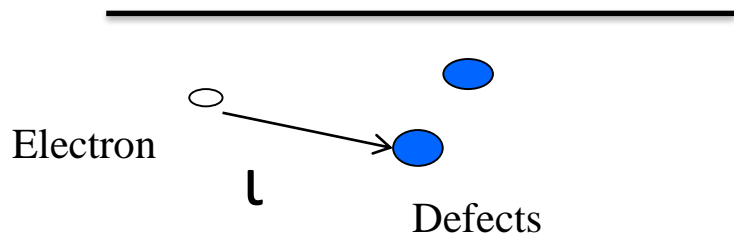
$\text{LaNiO}_3$  (stress in c axis)



Strain induced by defects does not open the band gap in LNO.

# 3. $\text{LaNiO}_3$ Defects / impurities are winners

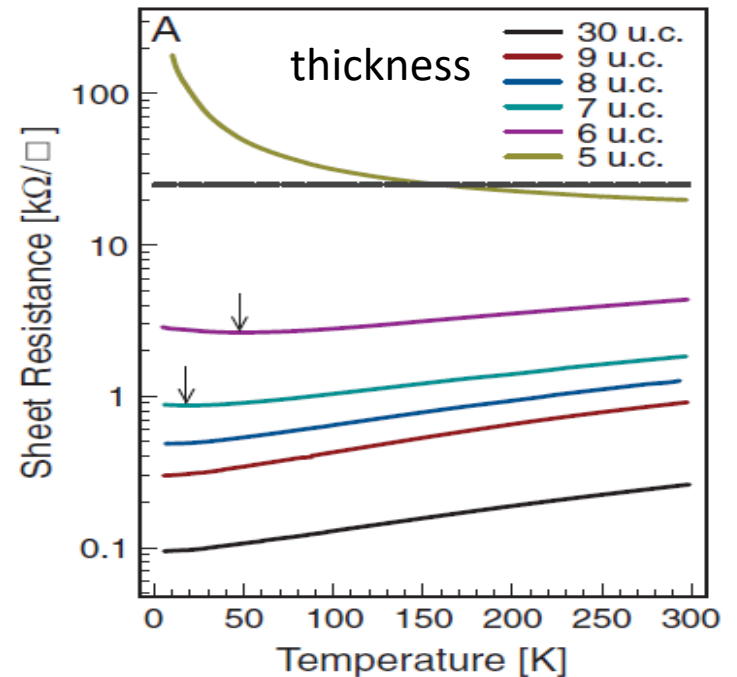
Defects are responsible for electrical phenomena in LNO



Mean free path :  $\tau$

Mean free path reduced, then rise the resistivity as  $\rho \propto \tau^{-1}$

$\tau$  approaches the interatomic spacing  $a$



R. Scherwitzl. et al. Phys. Rev. Lett **106**, 246403 (2011)

The usual transport theory (the Drude formula) break down.  
This is so-called Mott-Ioffe-Regel (MIR)

Phys. Rev. Mater. 3, 053801 (2019)

## 2. $\text{BiFeO}_3$

