Ferromagnetism in CuO nanowires on the top of CuO nanograins

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General Properties of Bulk Cupric oxide (CuO)

- Cupric oxide is a p-type semiconductor with a narrow band gap .

- Semiconducting properties along with FM ordering functionality have been the focus of great attention;

- Different magnetism is observed in nanosize materials.

Outline

CuO nanowires preparation

Structural and Morphological Characterization

Magnetization Susceptibility Results

Conclusions

Nanowires production

❖Metal wires of Cu with 99.99% purity

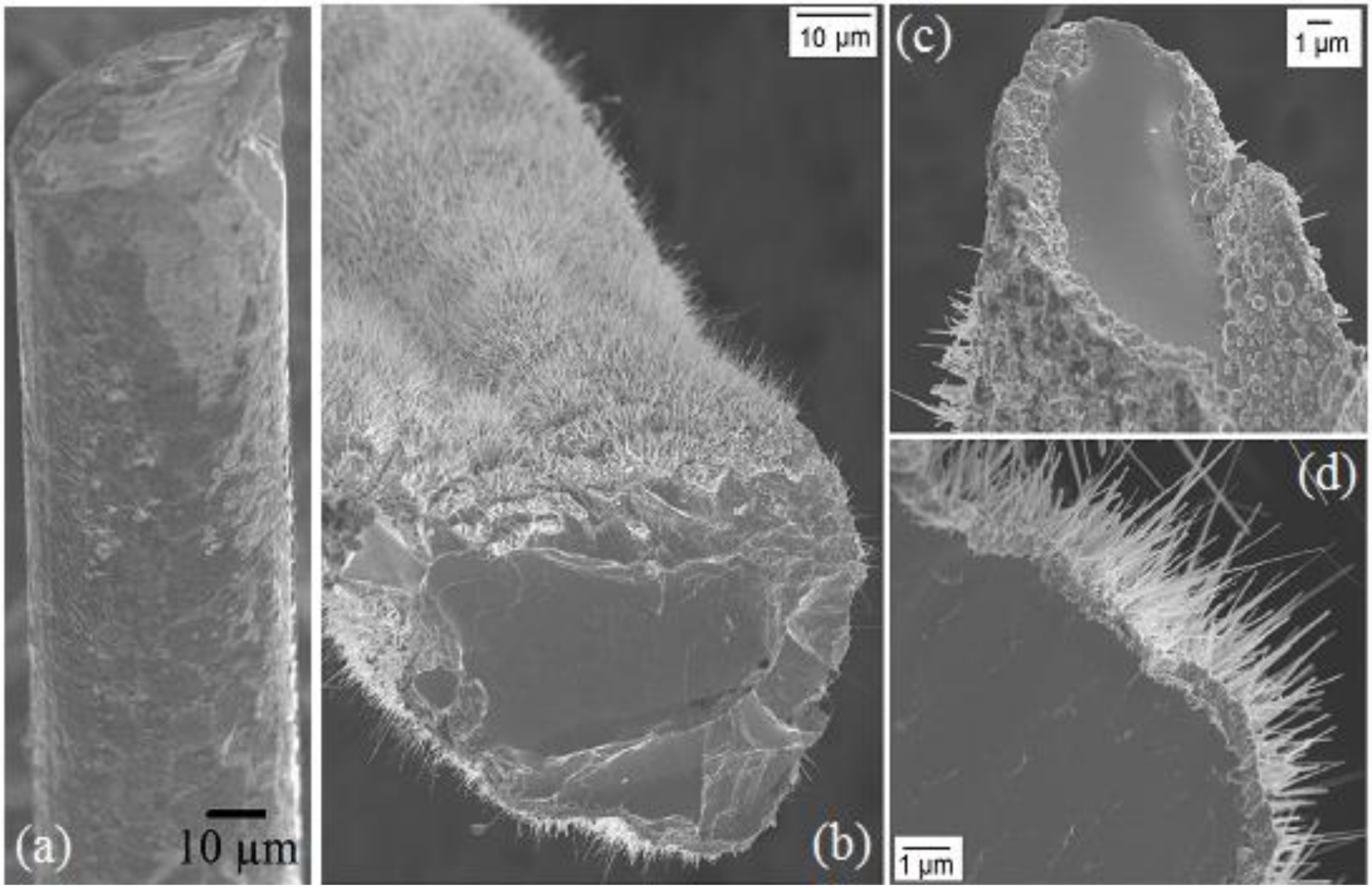
❖The synthesis of nanowires was carried out by resistive heating and thermal oxidation methods

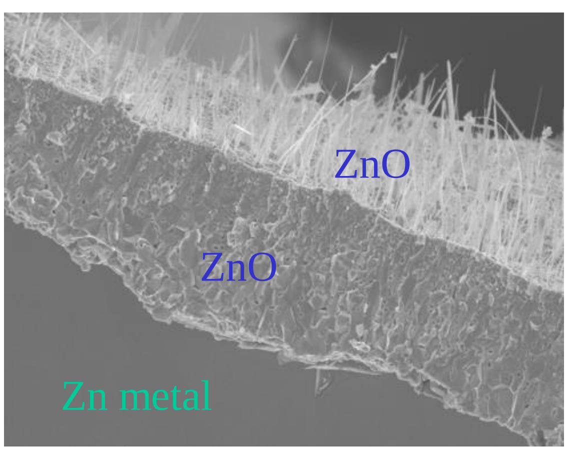
❖The as-received pure metal wires, suspended by two electric contacts, were heated by direct electric current or just put into a furnace.

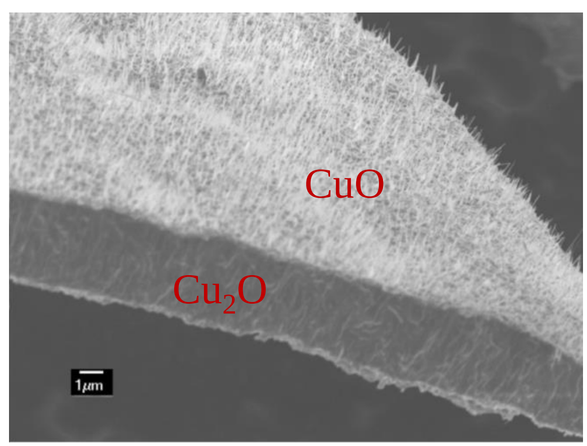
Power Supplies

Furnace

Scanning electron microscopy



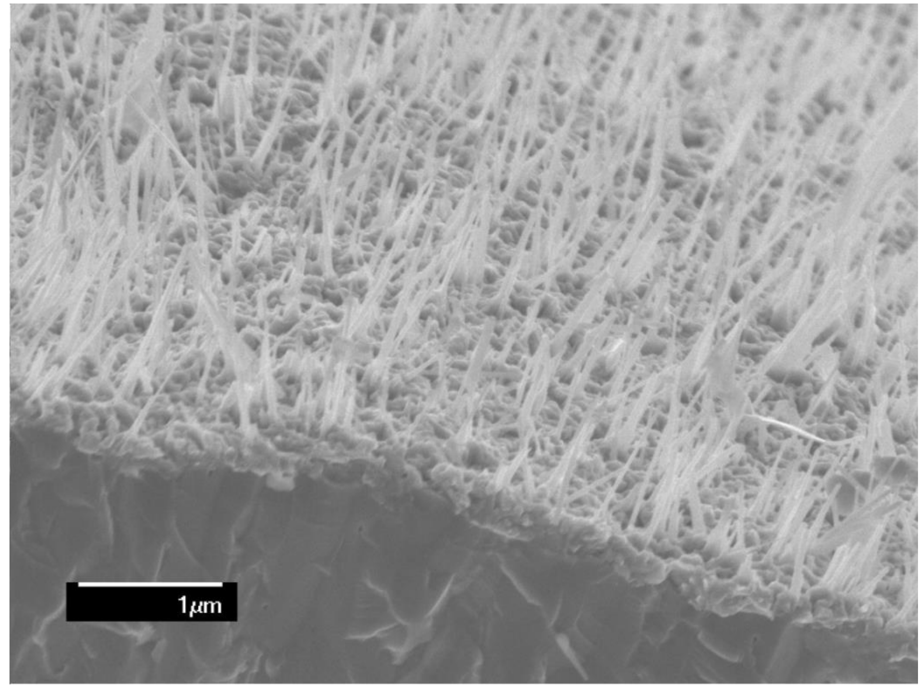




Several kinds of nanostructure of transition metal oxide can be produced by these methods

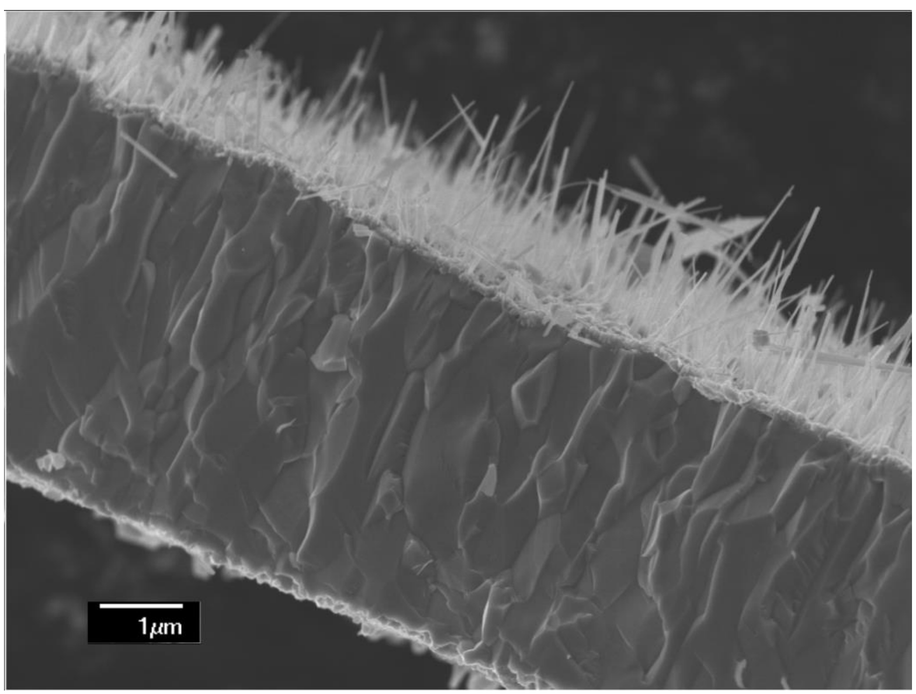
Scanning electron microscopy

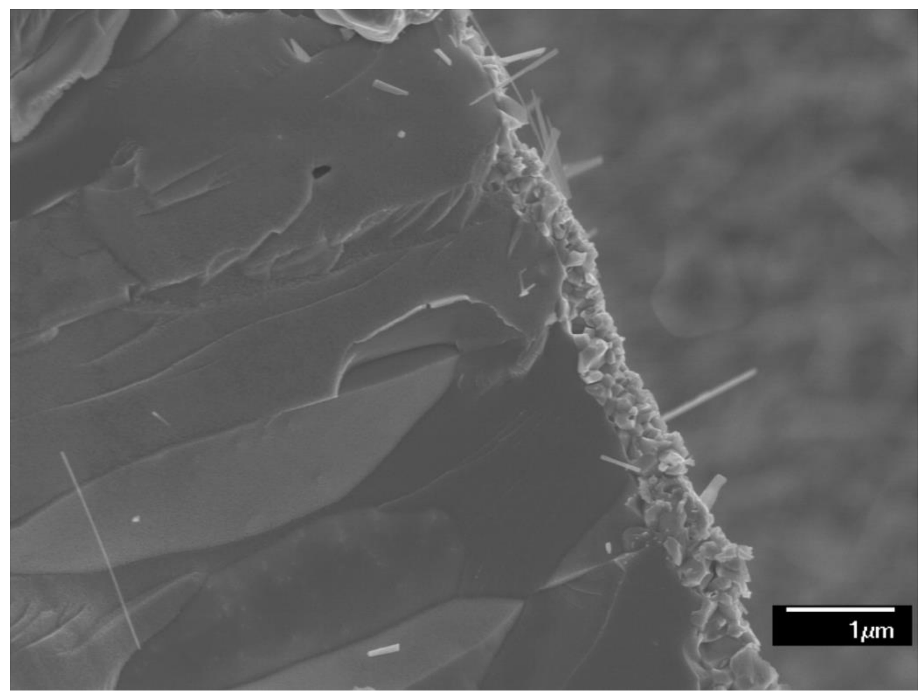
The electrical current magnitude and exposed time play an important role regarding the morphology and number of nanowires.



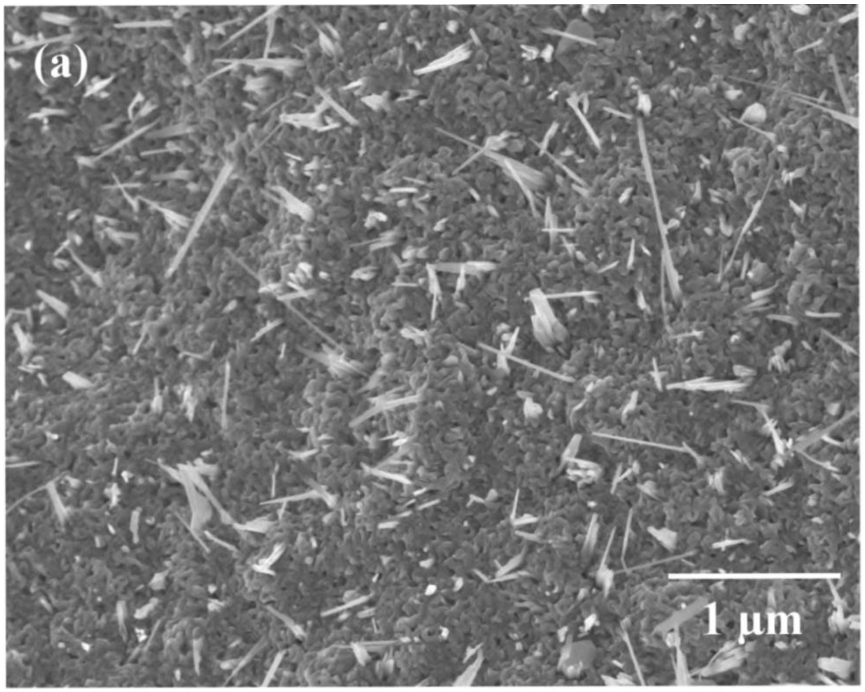
CuO nanowires
60-120 nm of diameter
1-2 μm in length

CuO nanowires
Thin layer of CuO
Cu_2O layer

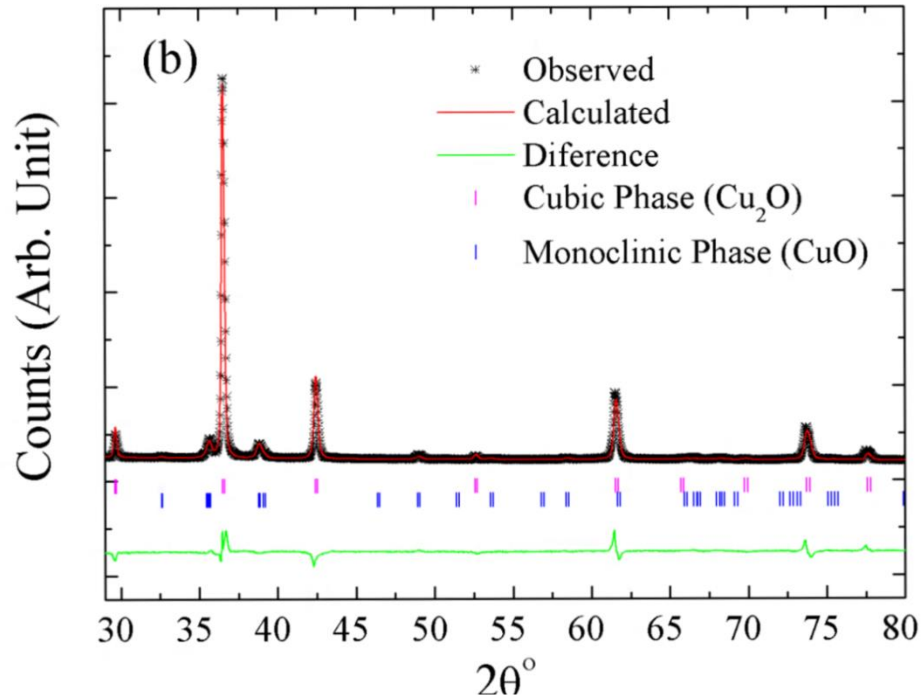


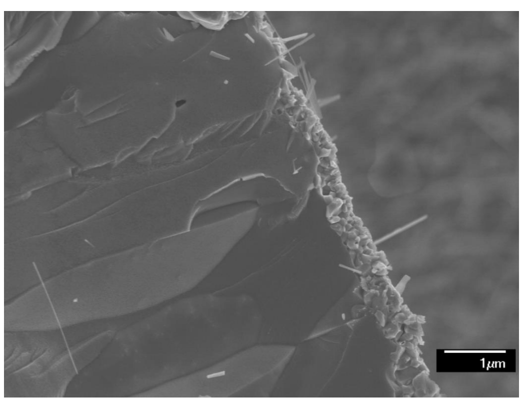


First sample: Cu_2O + CuO grains



X-ray Powder Diffraction

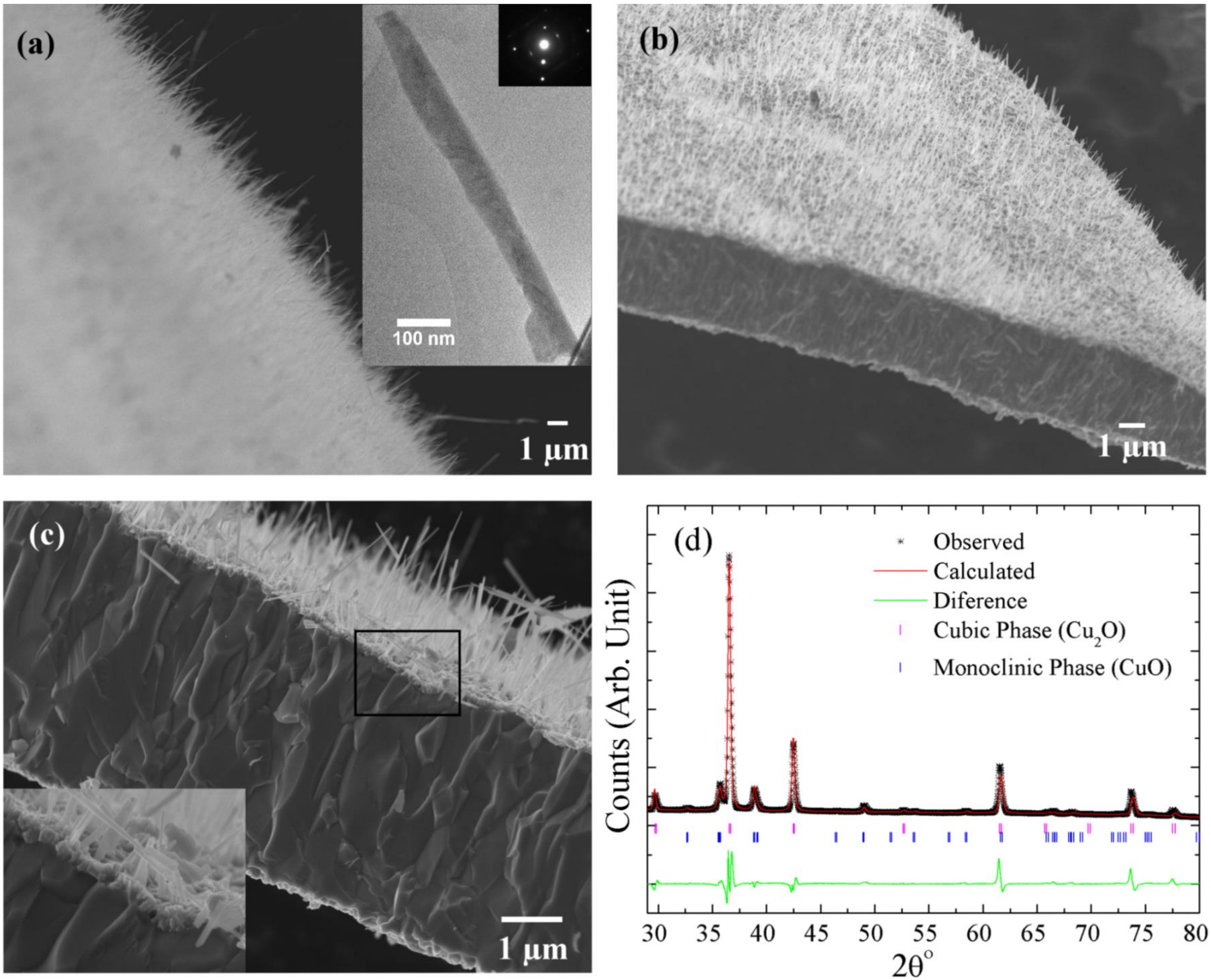




- Majority phase Cu_2O - 86 %
- Minority phase CuO - 14 %

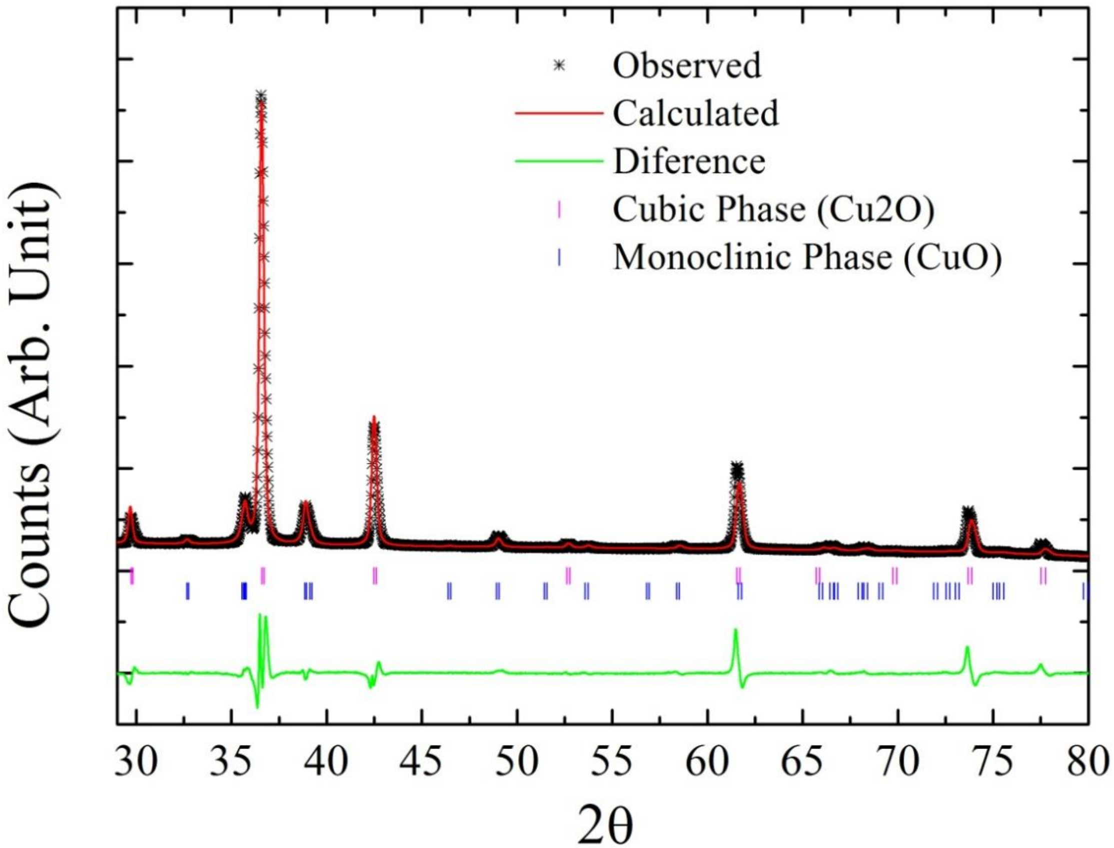
Second sample: Cu2O layer + CuO nanograins + CuO nanowires

SEM and TEM



X-ray Powder Diffraction

X-ray Powder Diffraction



Phase	Cu_2O	CuO
S. G.	*Pn-3m* cubic	*C2/c* monoclinic
a **(Å)**	4.2529 (1)	4.664 (2)
b **(Å)**	4.2529 (1)	3.411 (1)
c **(Å)**	4.2529 (1)	5.115 (2)
V **(Å³)**	76.9 (1)	80.2 (3)
α	90	90
β	90	90.41 (2)
γ	90	90
χ^2	55.44	55.44
wRp	9.85	9.85
Rp	5.25	5.25

- Majority phase Cu_2O - 77 %
- Minority phase CuO - 23 %

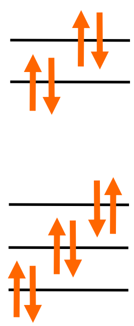
Electronic Structure of Cu_2O and CuO

Cu [Ar] $3d^{10}$ $4s^{1}$

$Cu_2^{1+}O^{2-}$

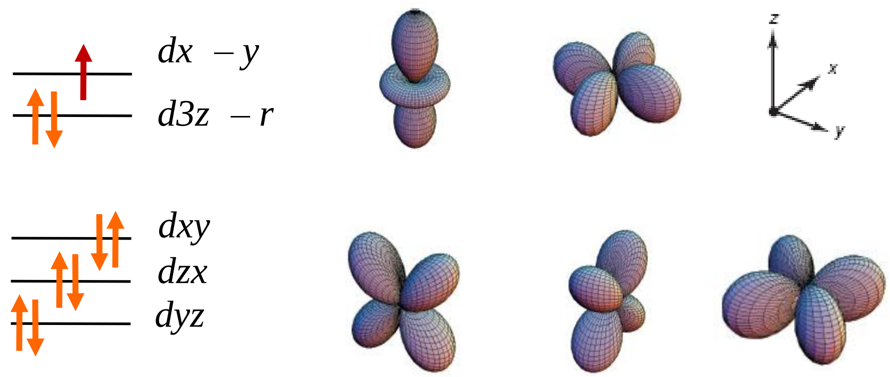
$Cu^{2+}O^{2-}$

Cu^{1+}



S = 0

Cu^{2+}



S = 1/2

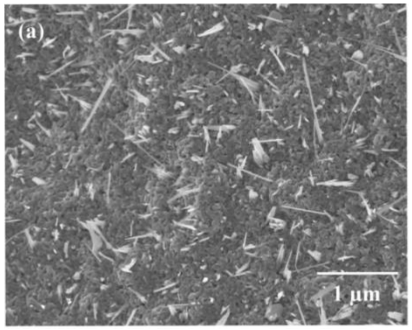
dyz dzx dxy

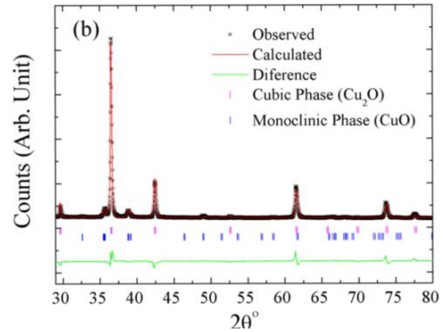
Diamagnetic
Negative contribution

Paramagnetic

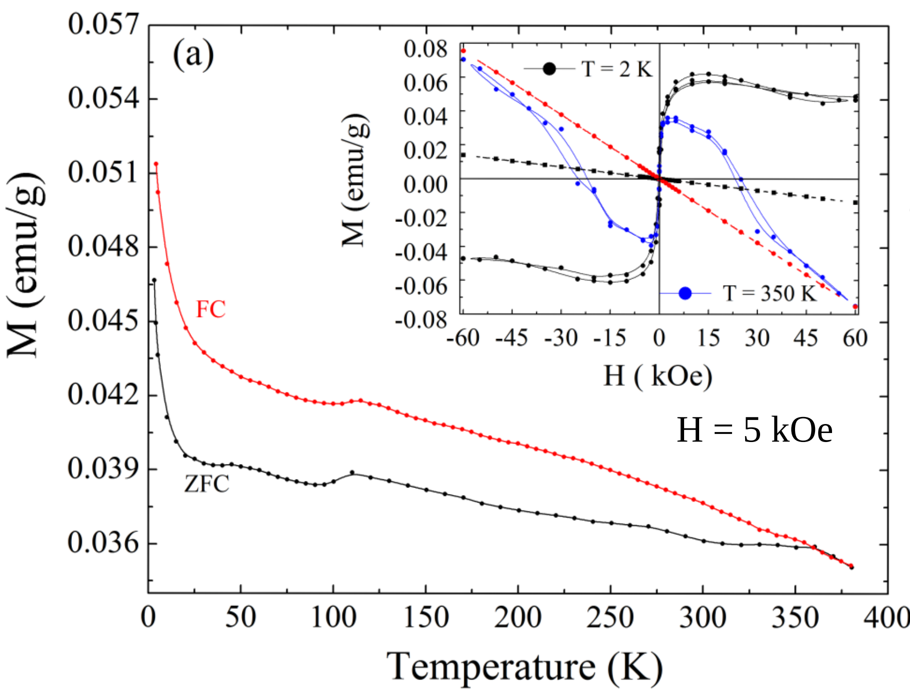
➢ Bulk CuO: PM to AFM phase transition at T = 230 K

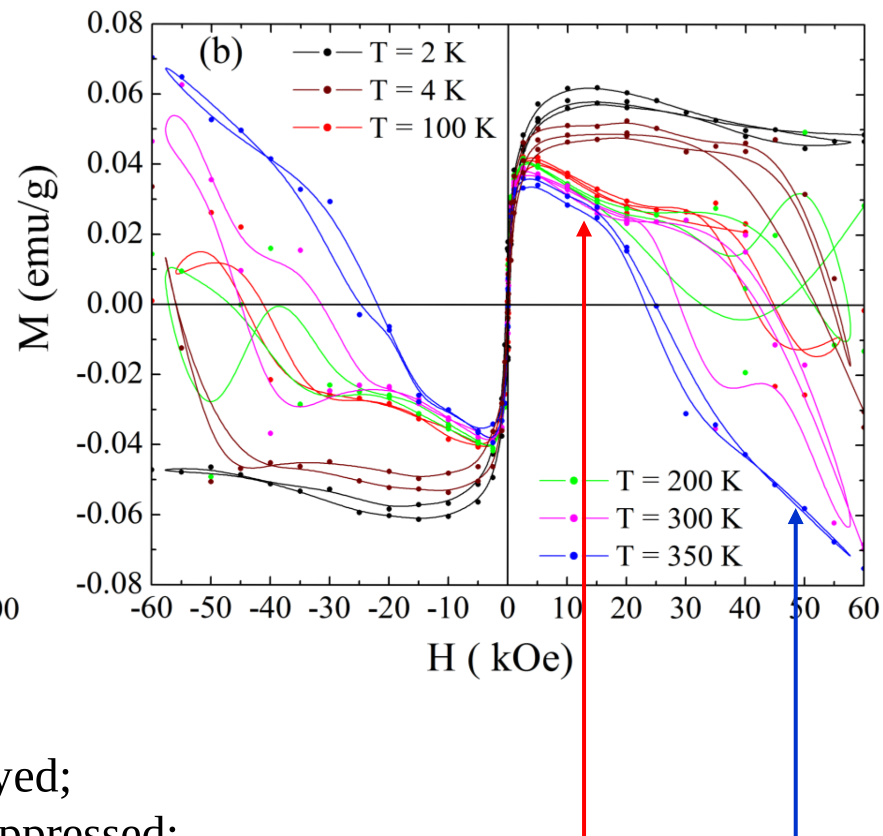
Magnetic Properties: First sample





CuO nanograins (14%) +
Cu_2O layer (86%)



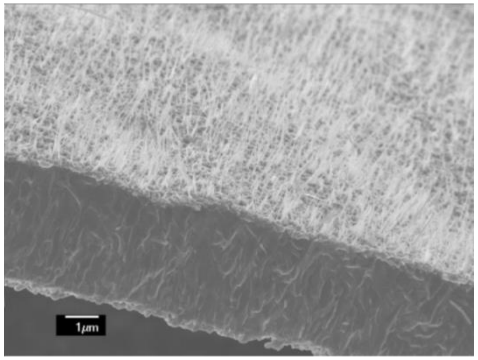


- ✓ Curie law is not obeyed;
- ✓ AFM transition is suppressed;
- ✓ Ferromagnetic-like behavior
- ✓ Diamagnetism $-1.4x10^{-4}$ emu/mole.Oe

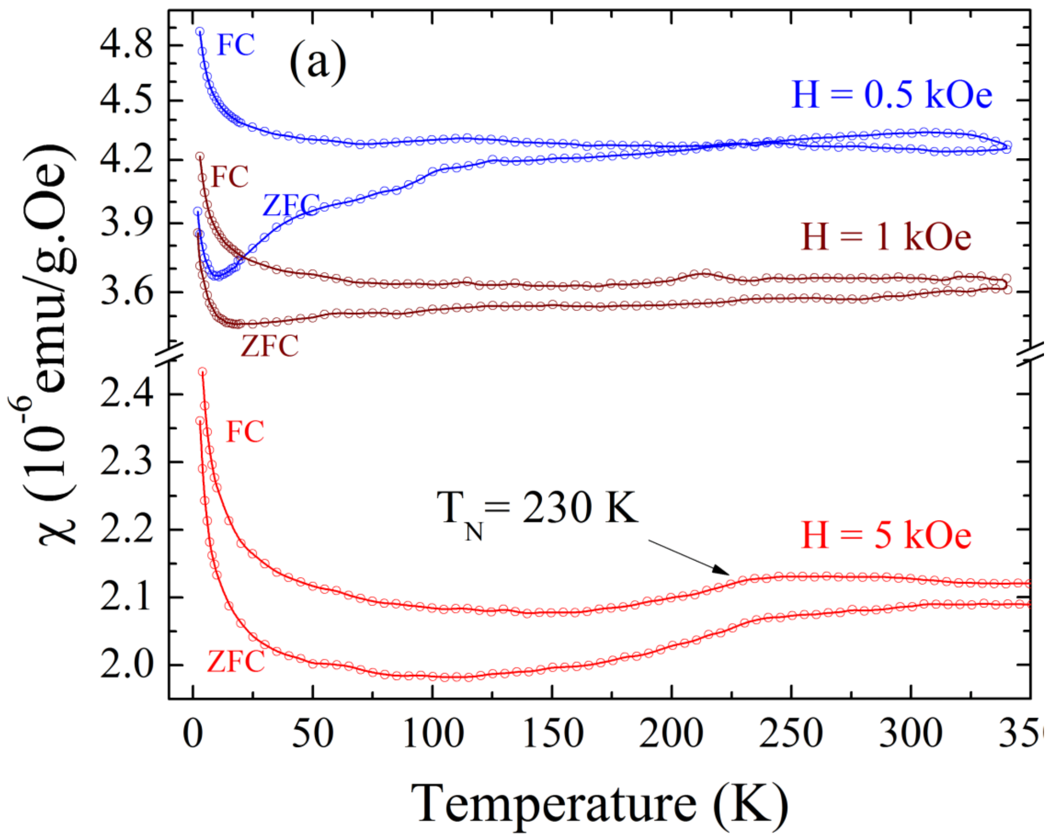
CuO FM

Cu_2O Dia

Magnetic Properties



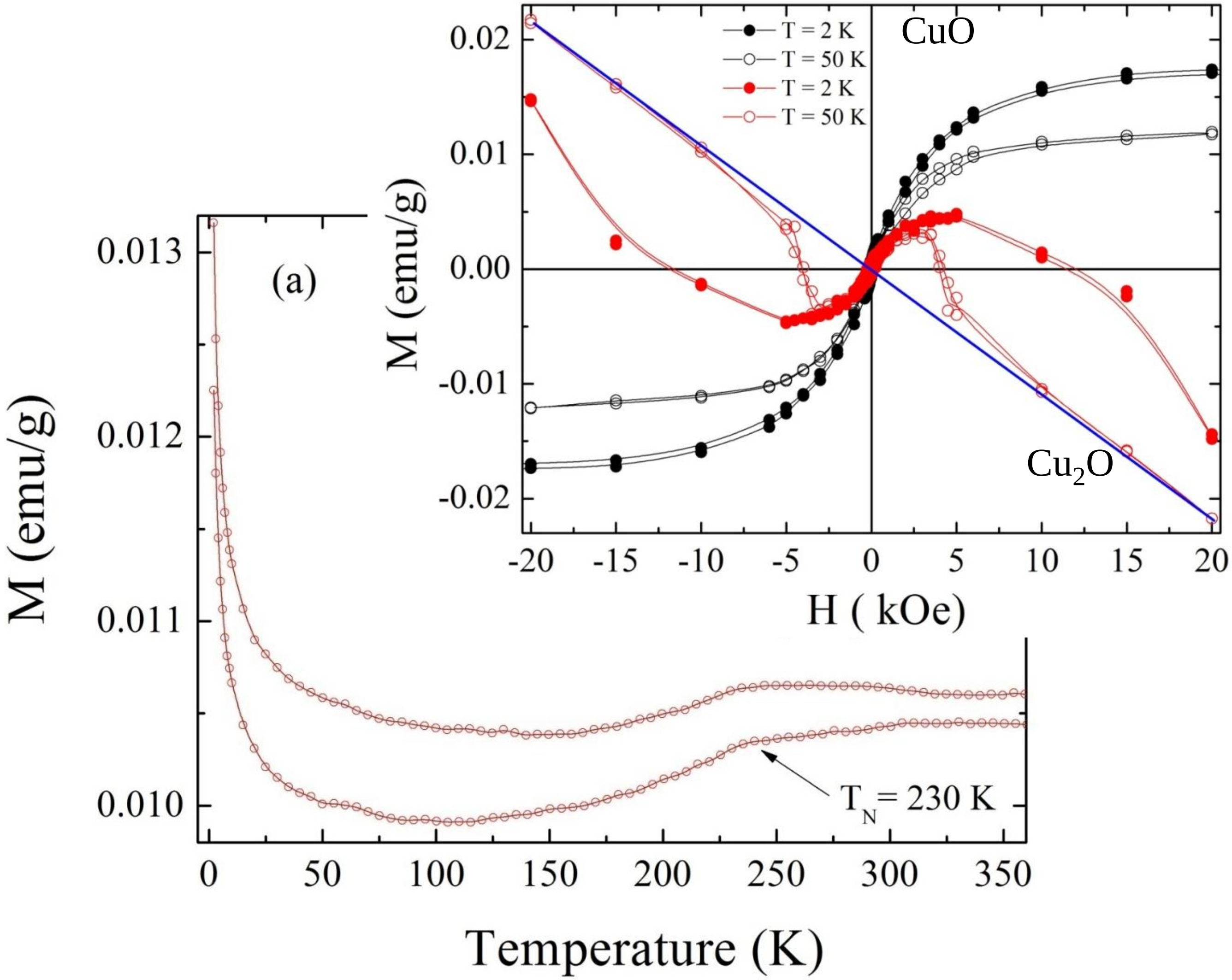
- Increased the phase CuO to 23 %
  - Majority phase Cu_2O - 77 %



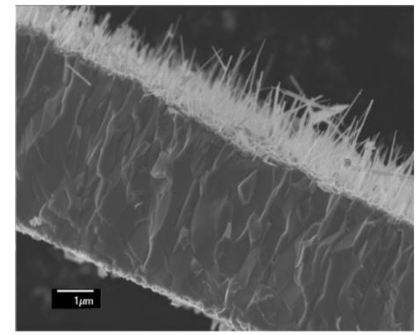
AFM transition is induced at H = 5 kOe !!!

✓The antiferromagnetic phase transition is observed at T = 230 K
✓A huge paramagnetic-like contribution is also observed at low T

Magnetization Susceptibility M(T,H)



increase and saturate
FM Behavior

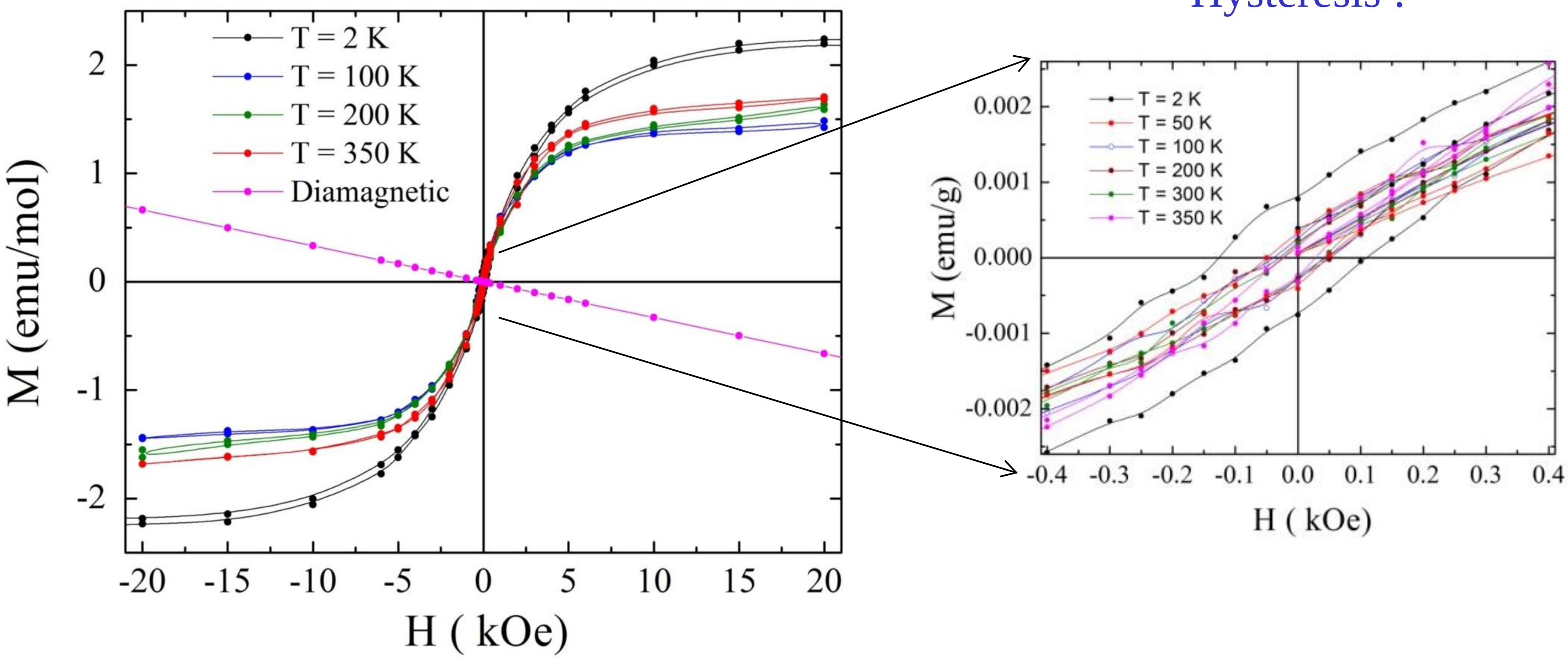


$CuO + Cu_2O$

- ✓At low field a ferromagnetic-like contribution is observed;
- ✓At high field the diamagnetic contribution starts to be pronounced;
- ✓The results suggest ferromagnetic alignment in a AFM matrix.

The ferromagnetic-like contribution remains present up to 350 K regardless the onset of AFM transition at T = 230 K!

Hysteresis !



✓Presence of AFM ordered core and a FM-like contribution coming from uncompensated spins at the surface of nanostructures.

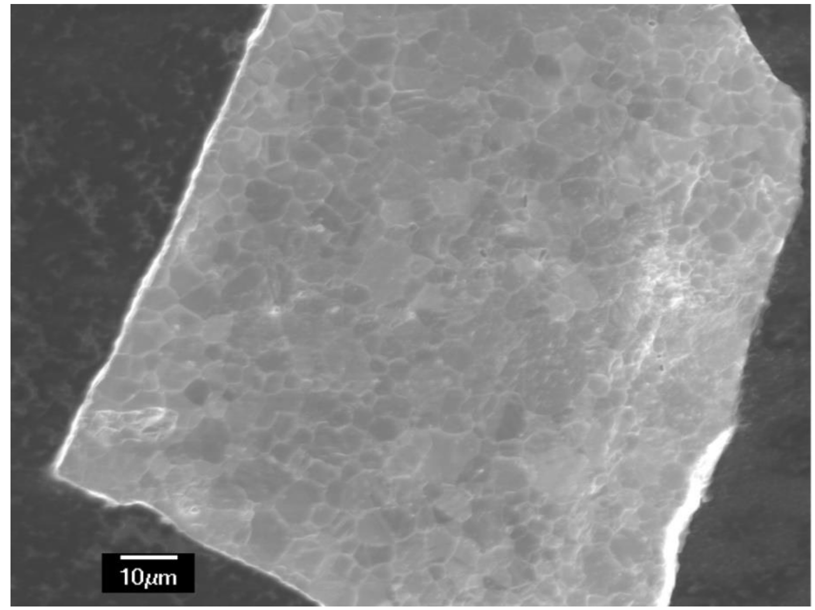
✓Presence of defects throughout the sample: lattice mismatch, crystalline boundary, formation of a twin boundary in CuO nanowires

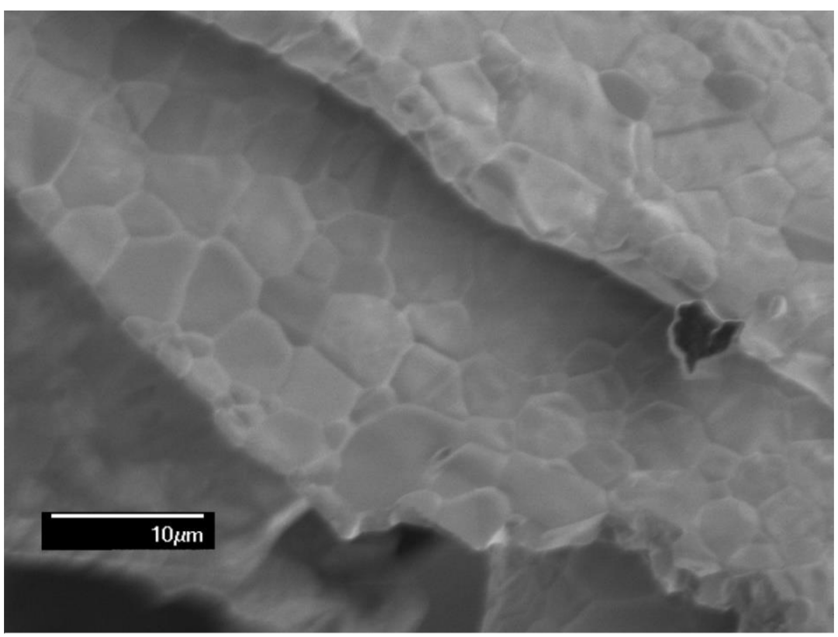
Scanning electron microscopy

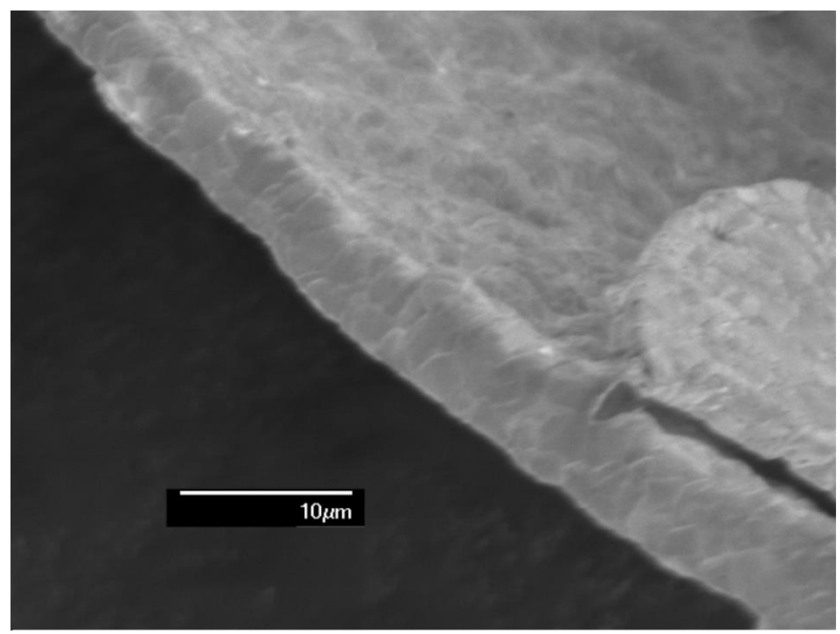
$CuO + Cu_2O$

Heat treated in air at 900 °C for 90 minutes

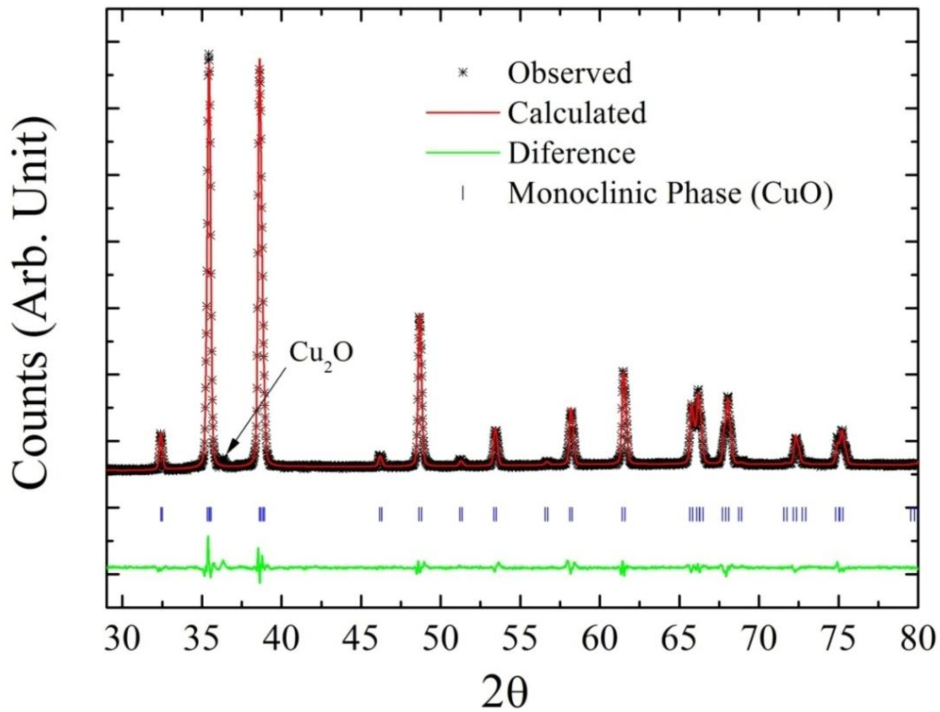
CuO nanowires disappeared





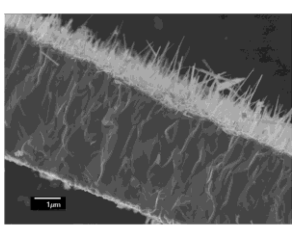


X-ray Powder Diffraction



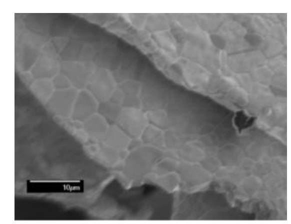
Phase	CuO
Space Group	*C2/c* (monoclinic)
a **(Å)**	4.6842 (1)
b **(Å)**	3.4202 (1)
c **(Å)**	5.1279 (1)
V **($Å^3$)**	81.044 (1)
χ^2	3.017
α	90
β	99.44 (1)
γ	90
wRp	3.57
Rp	2.79

- Majority phase CuO 99 %



CuO nanowires
CuO thin layer
Cu_2O thick layer

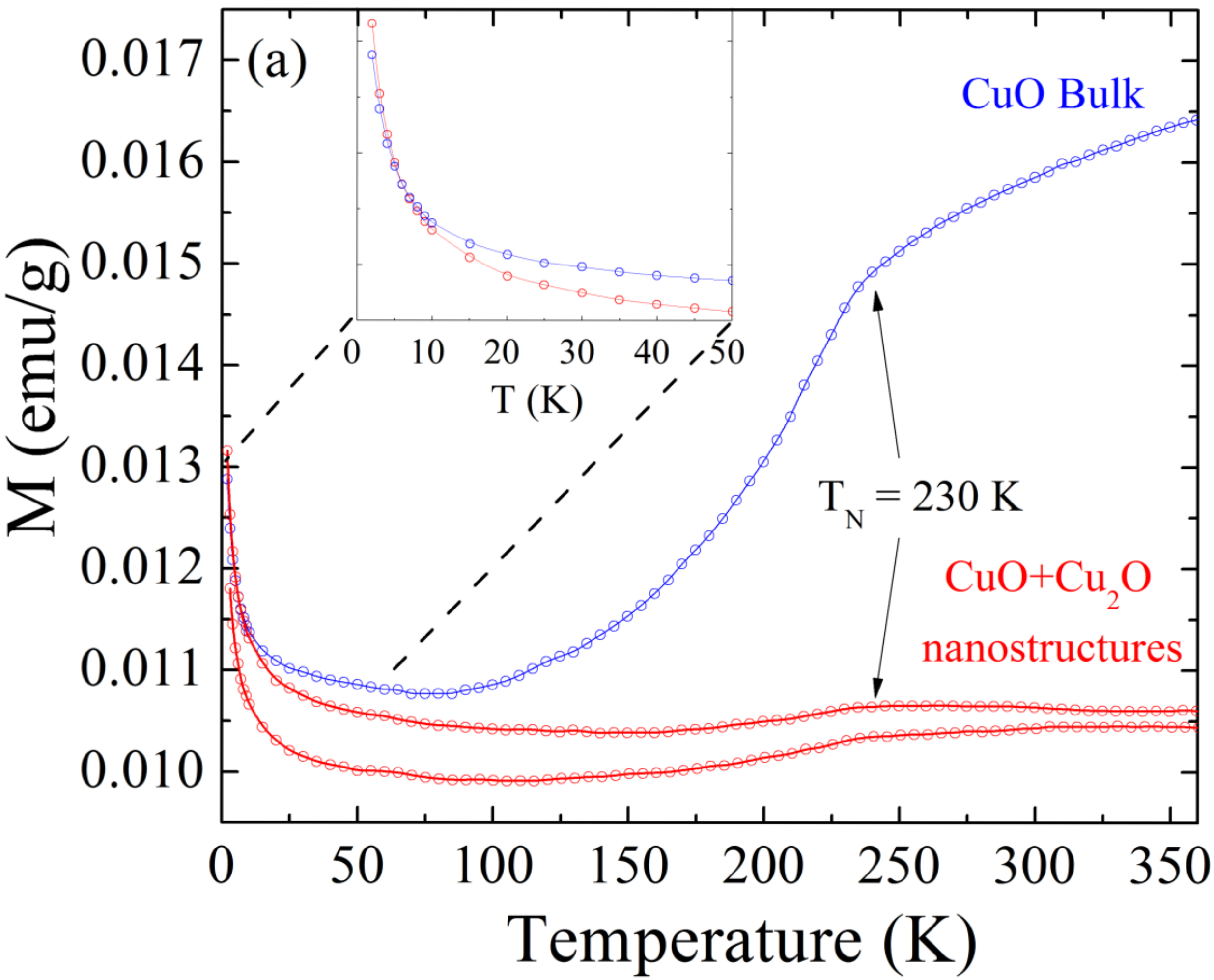
T = 900 C for 90 minutes

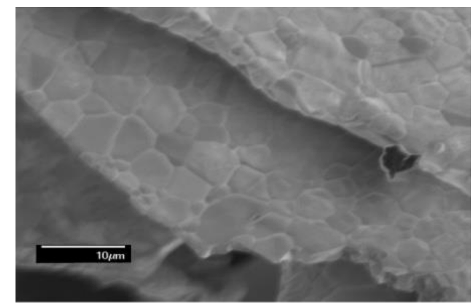


CuO bulk (thick layer)

Magnetization Susceptibility M(T,H)

Heat treated in air at 900 ºC for 90 minutes



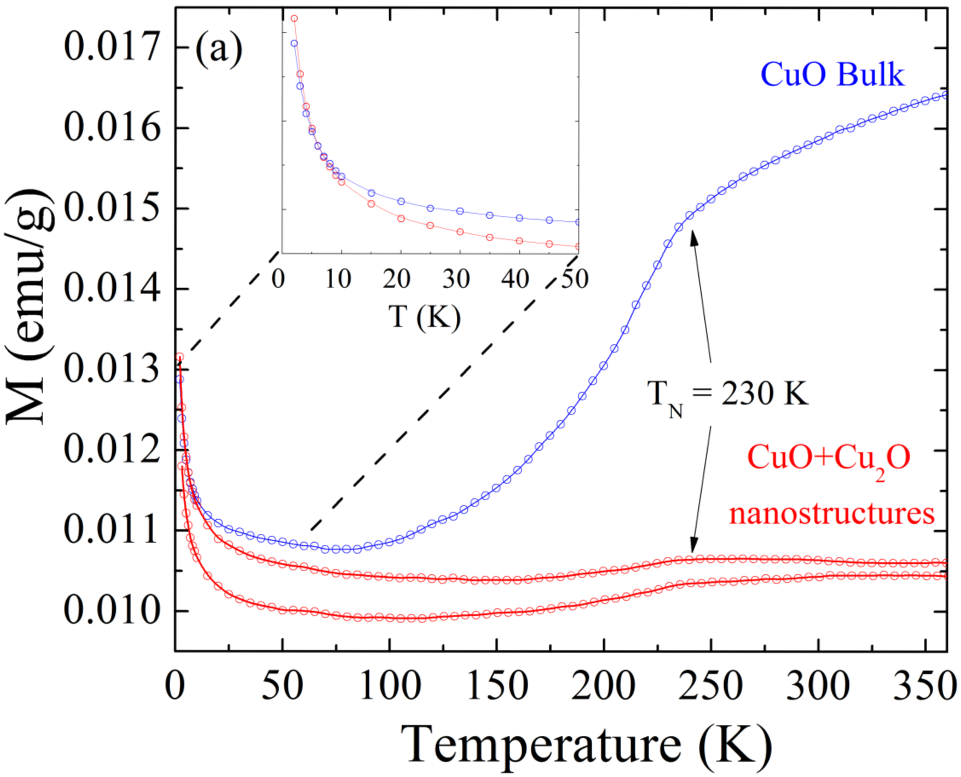


CuO

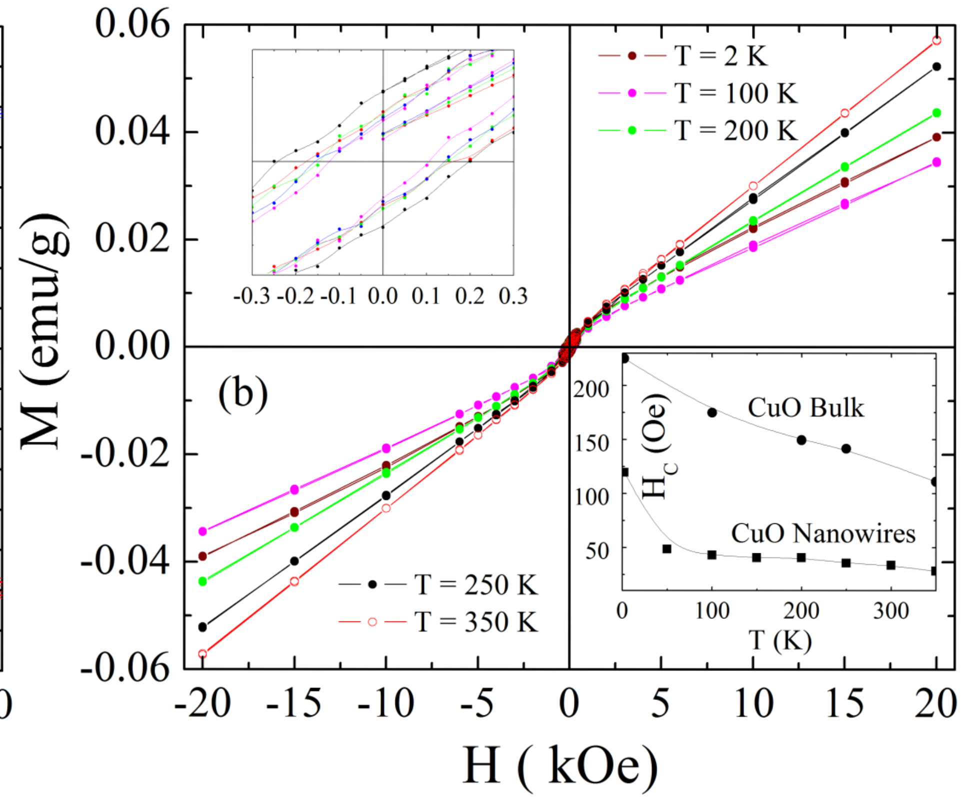
The same sample!

- ✓The AFM transition is more pronounced;
- ✓The paramagnetic-like contribution is still there;
- ✓We suggest that it may come from uncompensated charge - Cu^{3+}

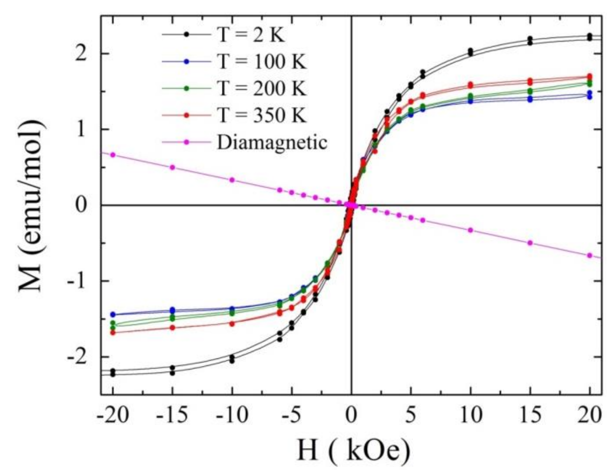
Hysteresis M vs. H at several temperatures



AFM behavior



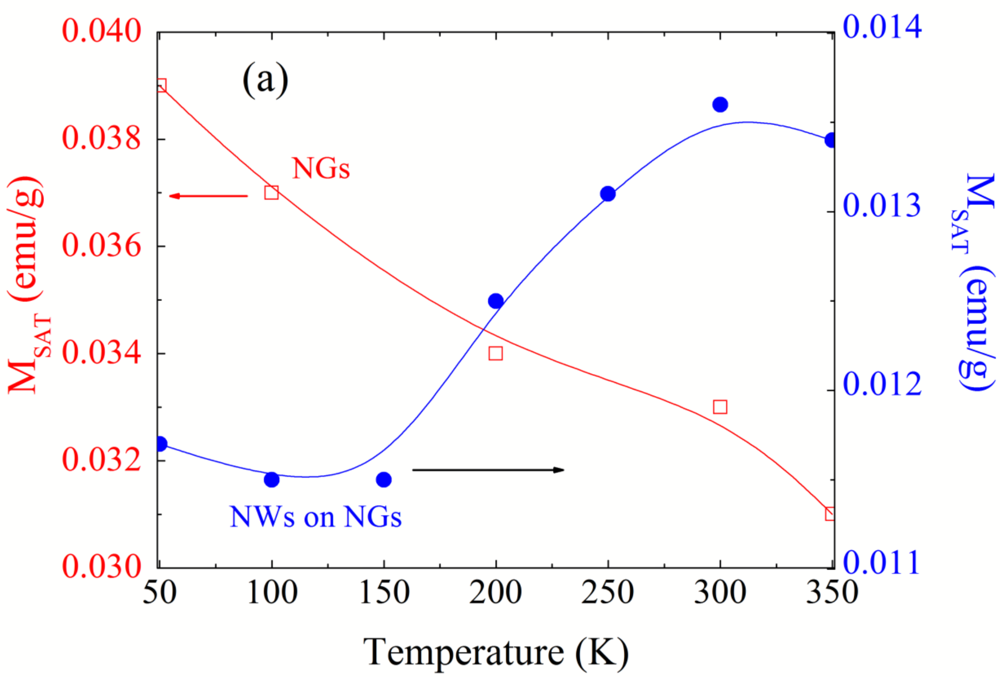
FM behavior



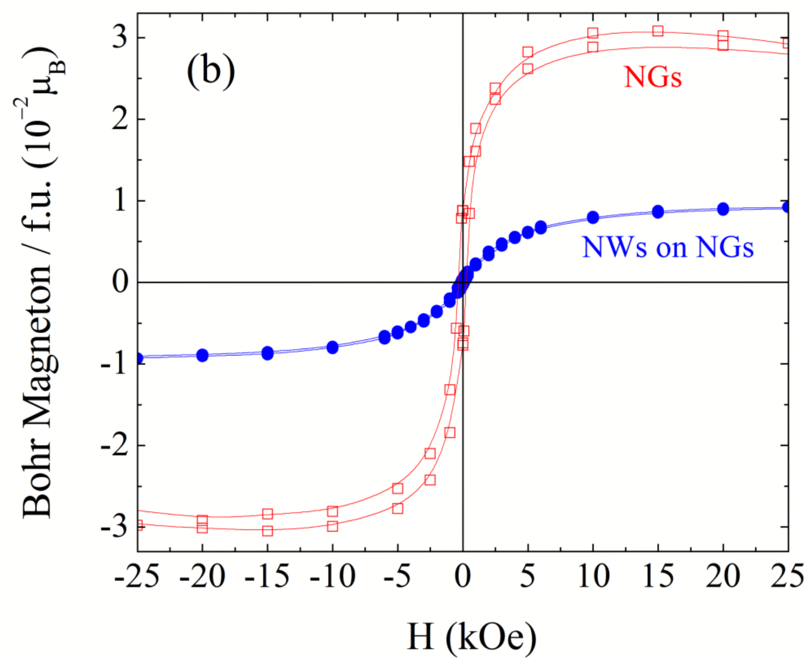
✓The AFM transition shows coercive field !
✓Several papers claim that coercive field comes from FM contribution in nanostructured systens.

Effective Magnetic Moment

✓Saturation magnetization for both samples



✓Bohr magneton at low temperature



Conclusions

- ✓The AFM phase transition is suppressed in nanograins;

- ✓The AFM phase transition shows up in nanowires at H = 5 kOe;

- ✓A FM-like effect is observed in an AFM matrix;

- ✓The effective magnetic moment is robust;

- ✓The huge paramagnetic-like contribution is not related to nanoscale phenomena; it may come from uncompensated charge - Cu^{3+}.

Condensed Matter Laboratory at UFABC - Students

Dr. Gabriel – Post-doc

Fabian - PhD student

Cesar – PhD student

Emersson – Master student

Cynthia – Master student

João – Undergrad student

Gustavo – Undergrad student

Thank you for attention!

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FAPESP

CAPES