

**Magnetism & Superconductivity Group (MSG)**  
**Department of Physics**  
**Quaid-i-Azam University, Islamabad**



# ***Magnetic and optical studies of nano scale zinc oxide.***

**S. K. Hasanain**

**Magnetism & Superconductivity Group (MSG)**  
**Department of Physics**  
**Quaid-i-Azam University, Islamabad**



## *Introduction to ZnO*

- *A hexagonal Wurtzite structure*
- *Wide bandgap  $E_g=3.37\text{eV}$ .*
  - *suited for applications with short wavelength light*
- *Transparent in the visible region*
- *ZnO has n-type character, even in the absence of intentional doping. Native defects such as oxygen vacancies or zinc interstitials are often assumed to be the origin of this, but the subject remains controversial.*
- *Capability to be grown at low temperatures*



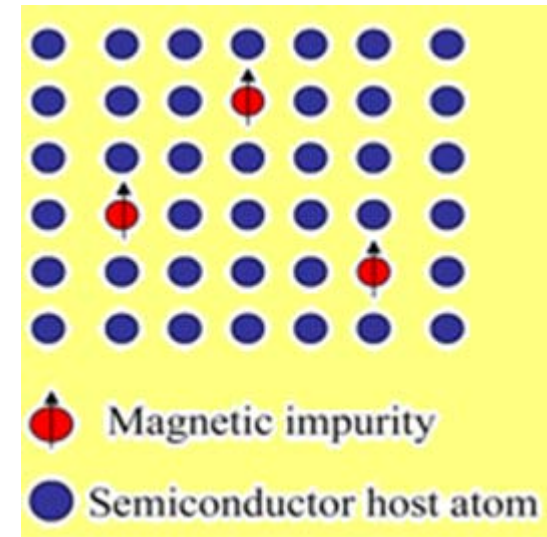
## *Introduction to ZnO*

- *Large electronegativity of oxygen expected to produce strong p-d exchange coupling between band carriers and localized spins*
- *Due to wide band gap, it has tremendous potential with regard to spintronic applications.*
- *i.e. as room temperature ferromagnetic semiconductor when doped with magnetic impurities e.g. Co, Mn etc*



## *Dilute Magnetic Semiconductors*

- **Semiconductors (non-magnetic) doped substitutionally with small concentrations of magnetic elements (e.g. Co, Ni, Mn) to yield Ferromagnetism.**
- **Examples of DMS:**  
 **$\text{GaAs}+\text{Mn}$ ;  $\text{TiO}_2+\text{Co}$ ;  $\text{ZnO}+\text{Co}$ ;  $\text{ZnO}+\text{Mn}$  etc.**
- **Under suitable conditions room temperature ferromagnetism at 300K can be achieved .**
- **Typically in wide band gap semiconductors e.g.  $\text{ZnO}$ ,  $\text{TiO}_2$ ,  $\text{GaN}$  (Dietl et al. Science 1019 287 (2000))**
- **Room temperature FM has been achieved in the oxide semiconductors. Initially in Co doped  $\text{TiO}_2$  (Rudolph et al Appl.Phys. Lett. 4516 82 (2003); Matsumoto et al Science 854 291 (2001))**





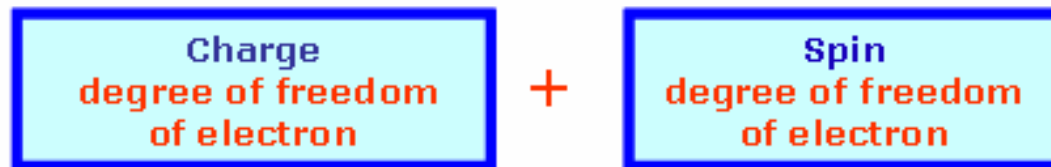
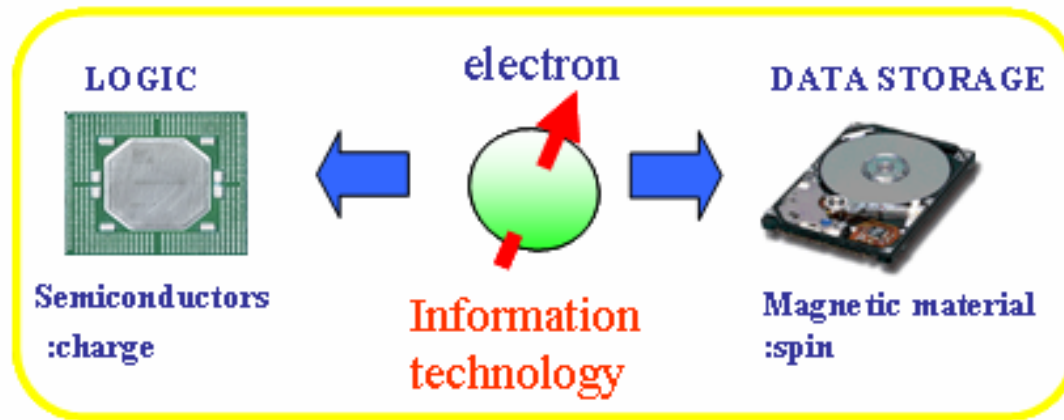
## *Dilute Magnetic Semiconductors*

- *Wide and exciting range of electronic and spintronic applications incorporating both computational logic and memory in the same material and device.*
- *Many issues and controversies remain about the nature of the experimentally observed FM in DMS.e.g.*
  - *truly intrinsic FM or the effect of impurity phases or clustering of magnetic ions.*
  - *nature and mechanism of the ferromagnetic coupling between the magnetic dopants.*
  - *role of the optical band gap and the defect states in the band e.g. due to oxygen vacancy defects.*
  - *how to tailor the magnetic properties and still retain the semiconducting properties at an optimal level.*



# *Applications Potential*

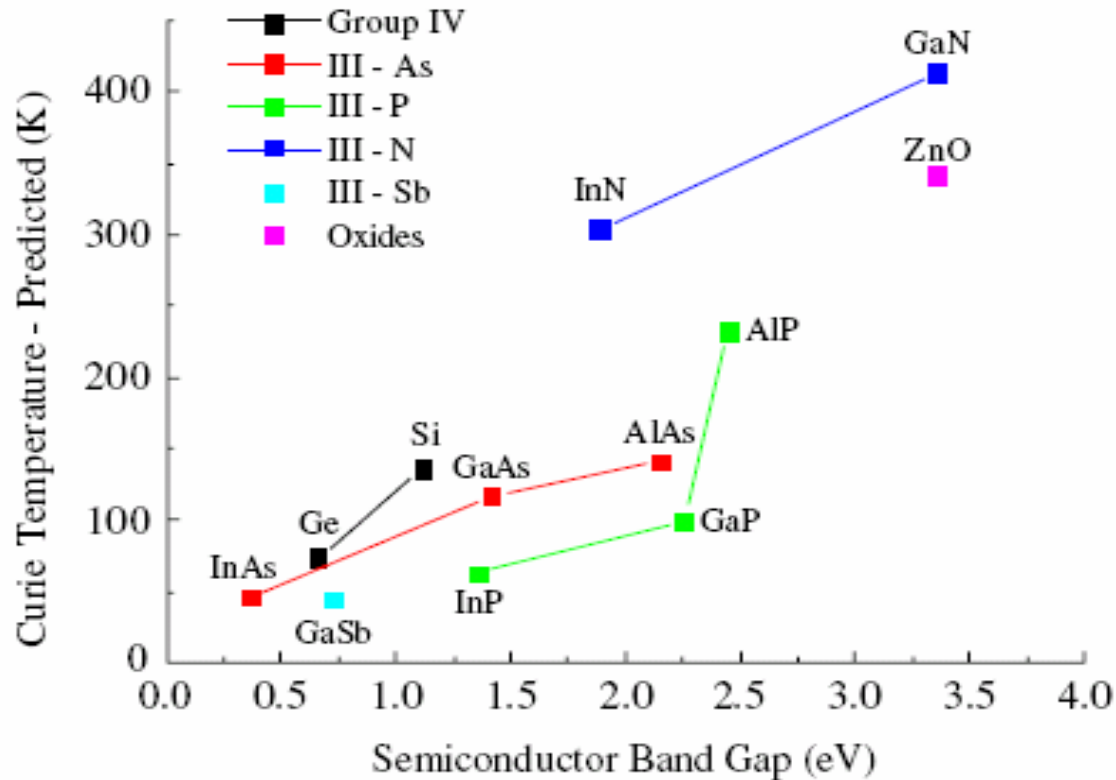
## *Semiconductor spintronics*



Improving existing functionality  
spin based devices i.e. spin transistors

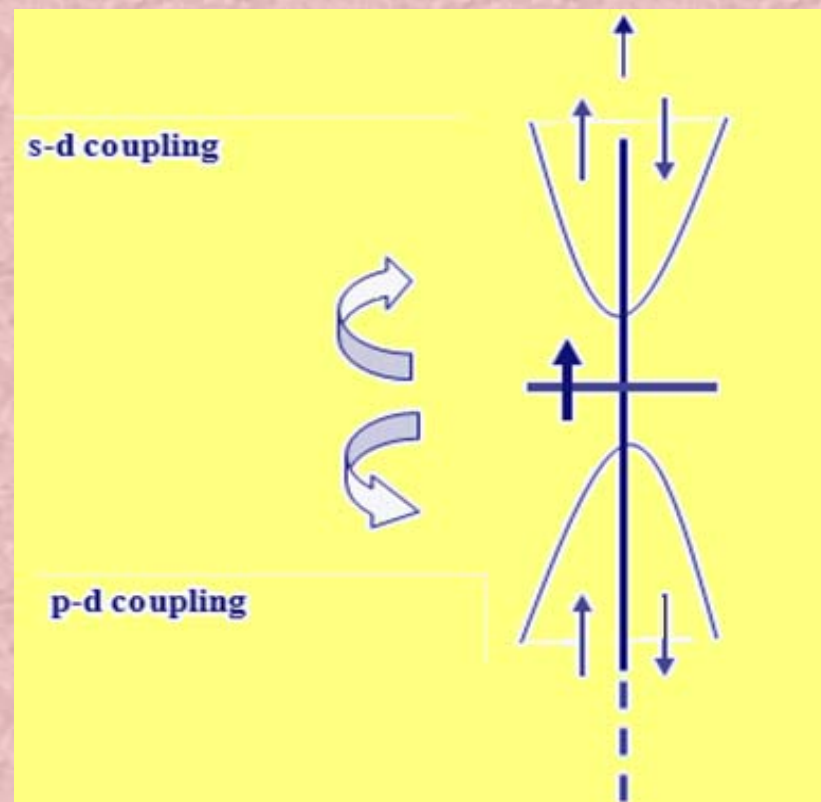
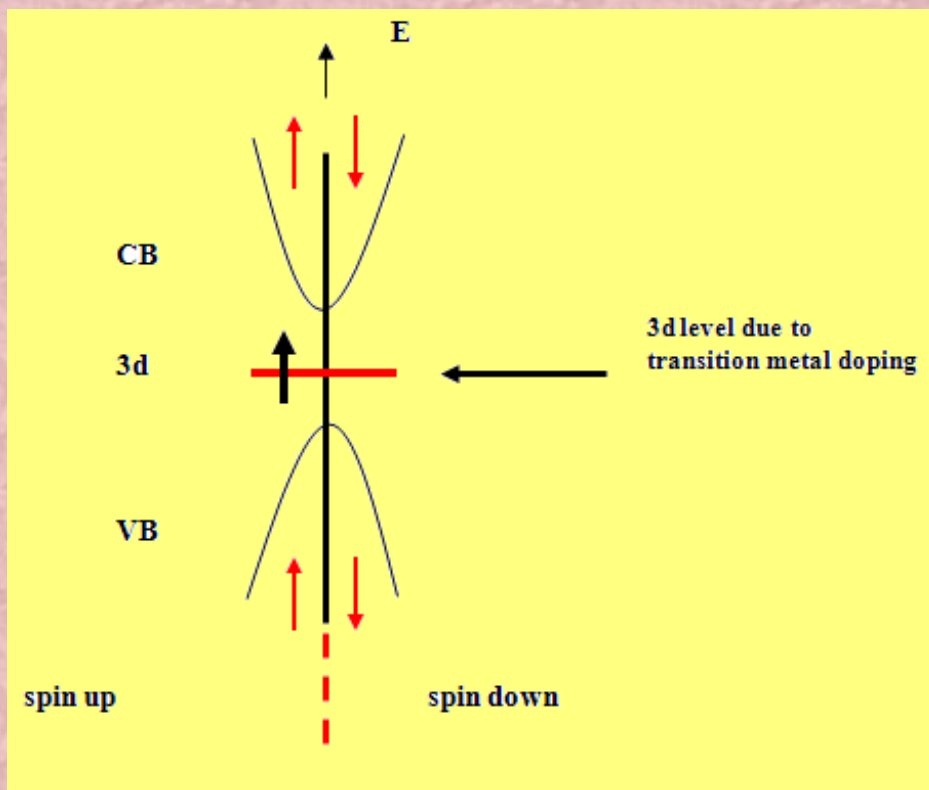


*Theoretically Predicted Curie temperatures in  
semiconductors*





## *Recipe for a diluted magnetic semiconductor*







## *Our earlier work (2005-2007)*

M. Naeem et al, Nanotechnology 17 (2007) 2675-2680 ;  
J. Phys. Cond. Matt.20 (2008) 025210

## *Room temperature FM in doped $Zn_{1-x}Co_xO$ nanoparticles*

- ✓ *Effects of reducing atmosphere (oxygen vacancies).*
- ✓ *Effects of size on the Nanoparticle band gap.*
- ✓ *Effects of co-dopants e.g. Cu and Al on the magnetic, optical and transport properties.*



## *Current work: (2007 onwards)*

***Thin films of ZnO prepared by different routes***

- ***Doped with magnetic dopant Co:  $Zn_{1-x}Co_xO$ .***
- ***Search for Ferromagnetism in ZnO films with non-magnetic dopant i.e. Carbon***
- ***Structural, Magnetic, transport and optical studies.***



## *Studies*

- *Preparation.*
- *XRD; XPS.*
- *Magnetization ( $M(H)$ ;  $M(T)$ )*
- *Electrical resistivity, Hall Effect.*
- *Optical studies (band gap studies and other excitations in UV-Vis range).*



## *Contributors:*

- *Mr. M. Naeem (nanoparticle work.)*
- *Ms. Sadaf Akbar (thin film work)*
- *Mr. Manzar Abbas (CIIT)*
- *Dr. Arif Mumtaz (QAU)*

## *Collaborators:*

- *Dr. Sadan Ozcan University of Hacettepe, Ankara, Turkey.*
- *Dr. Ismat Shah, University of Delaware, USA.*



## *Carbon Doped Dilute Magnetic Semiconductor*

### *Importance and Inspiration*

- \* Producing DMS with non-metal doping.*
- \* TM dopants in ZnO form clusters or secondary phases, which are detrimental to applications of DMS. This promoted search for DMS based on alternative dopants.*
- \* If non-TM dopants can be incorporated into ZnO and induce magnetism, DMS thus produced would not suffer from problems related to precipitates of dopants since they do not contribute to ferromagnetism, directly.*

***This promoted the search for DMS based on alternative dopants***



Magnetism & Superconductivity Group (MSG)  
Department of Physics  
Quaid-i-Azam University, Islamabad  
skhasanain@qau.edu.pk



## *Carbon Doped Dilute Magnetic Semiconductor*

[Physicsworld.com](http://Physicsworld.com)  
**NEWS**

**Oct 3, 2007**

✳ *Researchers in Singapore have created a room-temperature permanent magnet by mixing small amounts of carbon with the semiconductor zinc oxide. Although similar room-temperature dilute magnetic semiconductors (DMSs) have been made before, they were all semiconductors doped with copper. This new carbon-doped DMS is interesting because it could someday allow semiconductor manufacturing processes to be used to create spintronic circuits that process and store information using both the charge and spin of the electron. Room-Temperature Ferromagnetism in Carbon-Doped ZnO (Phys. Rev. Lett. 99 127201)*



## *Preparation of Carbon Doped ZnO Thin Films*

- We have prepared C-doped ZnO films using
  - **A: *Electron Beam Evaporation Technique***
  - ZnO/C<sub>x</sub> targets with carbon atomic concentrations, x = 1,3,5 % were prepared by mixing ZnO and Graphite
  - Deposited the C-doped ZnO on three different substrates
    - ⊙ 7059 Corning glass slide
    - ⊙ 0120 Corning glass slide
    - ⊙ Microscope glass slide (soda lime)
  - The base pressure was  $< 2 \times 10^{-6}$  mbar.
  - Rate of deposition was kept constant for all films at 5Å<sup>0</sup>/sec
  - All film thickness were set for 200 nm.



## *Cleansing of Substrates Before Evaporation*

➤ We have cleaned the substrate with IPA (isopropanol alcohol) in ultrasonic bath for 30min. Further cleaned with ion exchanged distilled water, acetone and ethanol successively and then dried with nitrogen gas.

## *Annealing of substrates after Evaporation*

➤ All substrates are amorphous black in color before annealing. Annealed at 500°C for 1 hour; they turned to white color.

➤ These films are smooth and continuous as seen by AFM





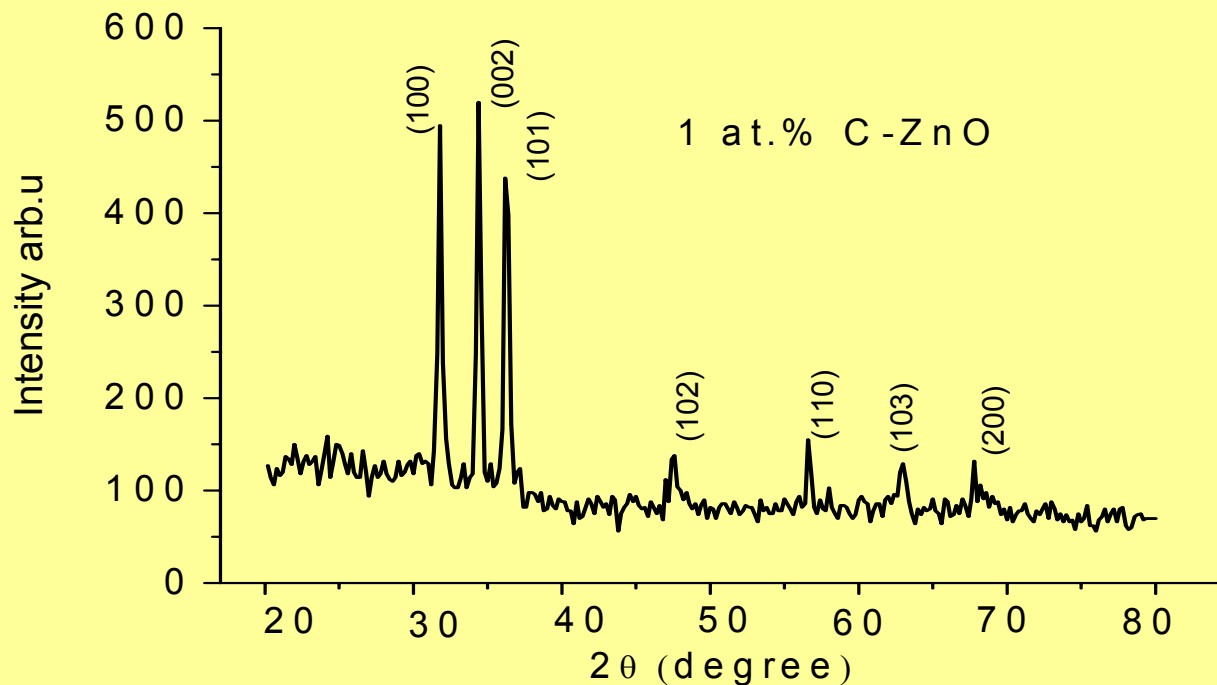
## *Second Method of Preparation of Carbon Doped ZnO*

- *Firstly we grew undoped ZnO film on the substrate by Electron Beam*
- *Next deposited a thin layer of carbon on it. Using pulse discharge C is sputtered from graphite anodes by energetic ion beam (Ne). Expect the diffusion of C atoms into the ZnO films. (Annealed at 550C, 1 hour).*
- *Deposition of C layer at PINSTECH, Accelerator Group of Dr. Shoaib Ahmed.*

❑ *Aluminum Ohmic Contacts grown by thermal evaporation*

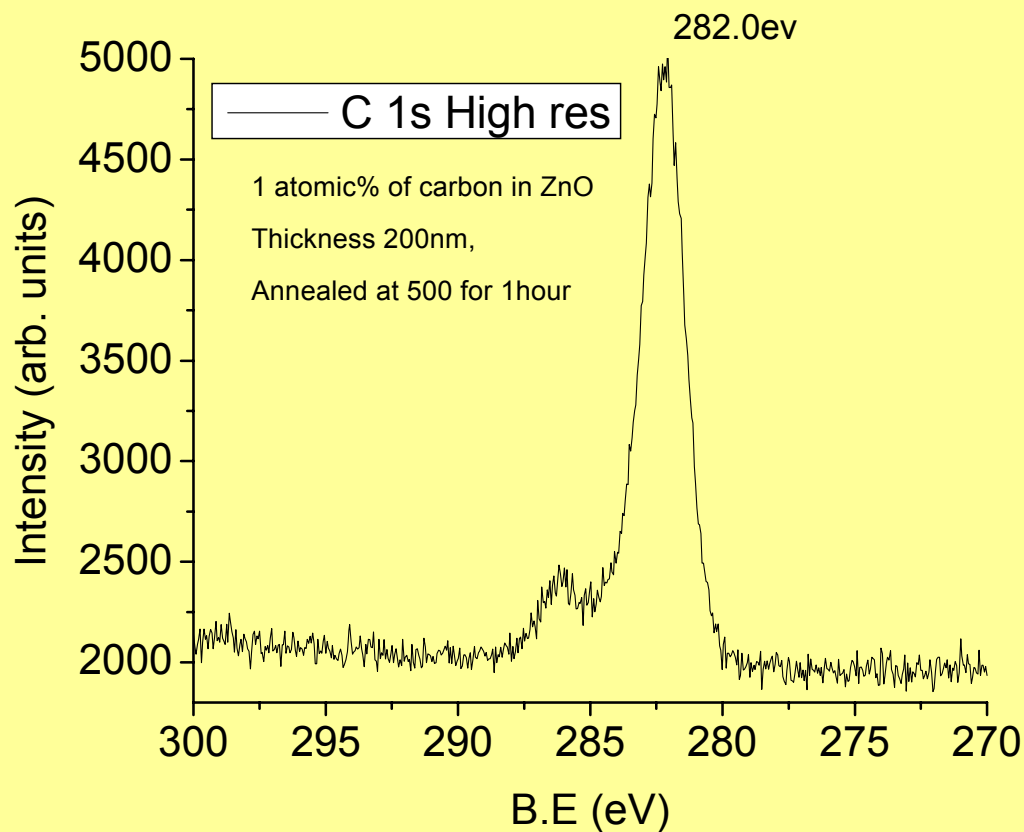


*XRD Pattern for C-doped ZnO film grown by  
e-beam evaporation (200 nm)*



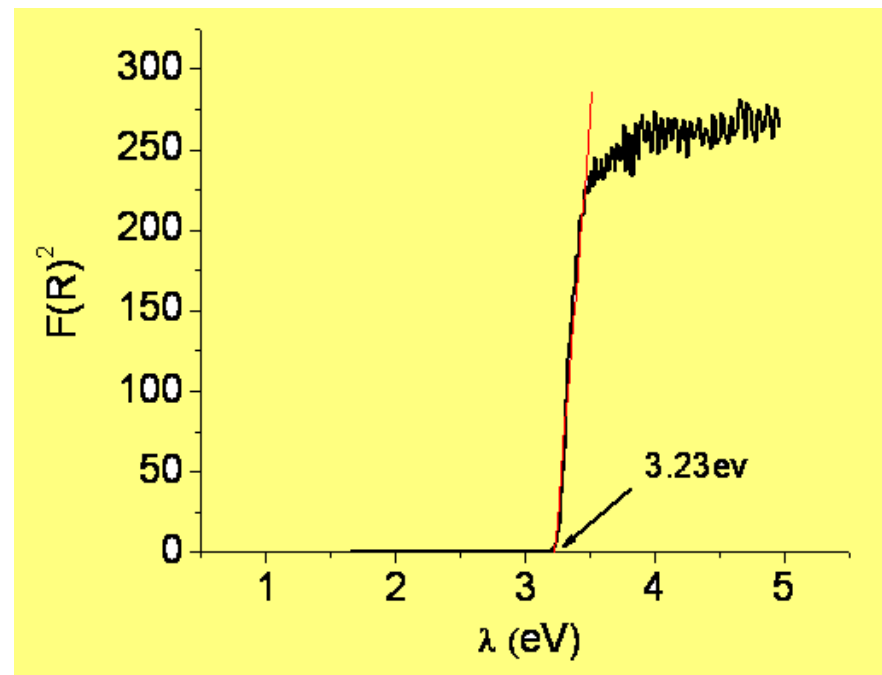
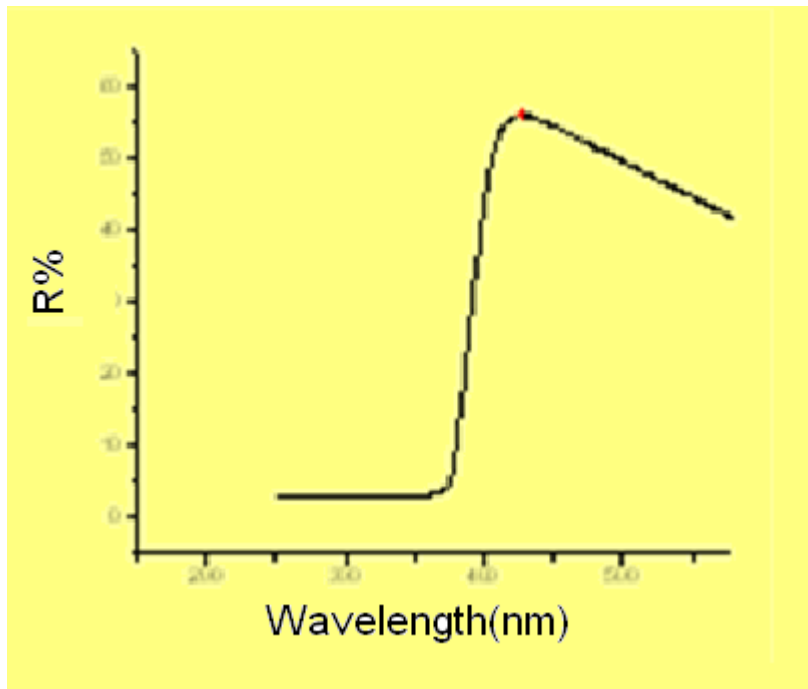


## *XPS Scan For C-Doped ZnO*





## *Band gap for C-doped ZnO*

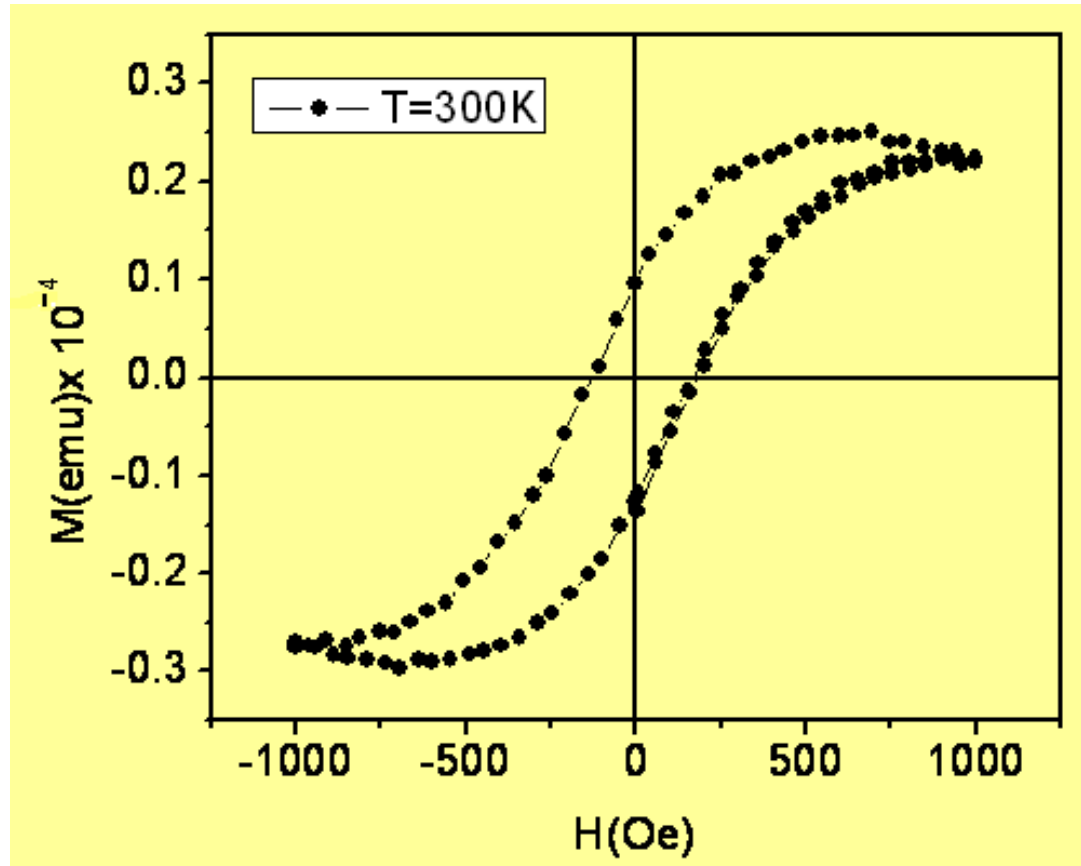


Kubelka-Munk function  $F(R)$

$$F(R) = \frac{(1 - R)^2}{2R}$$

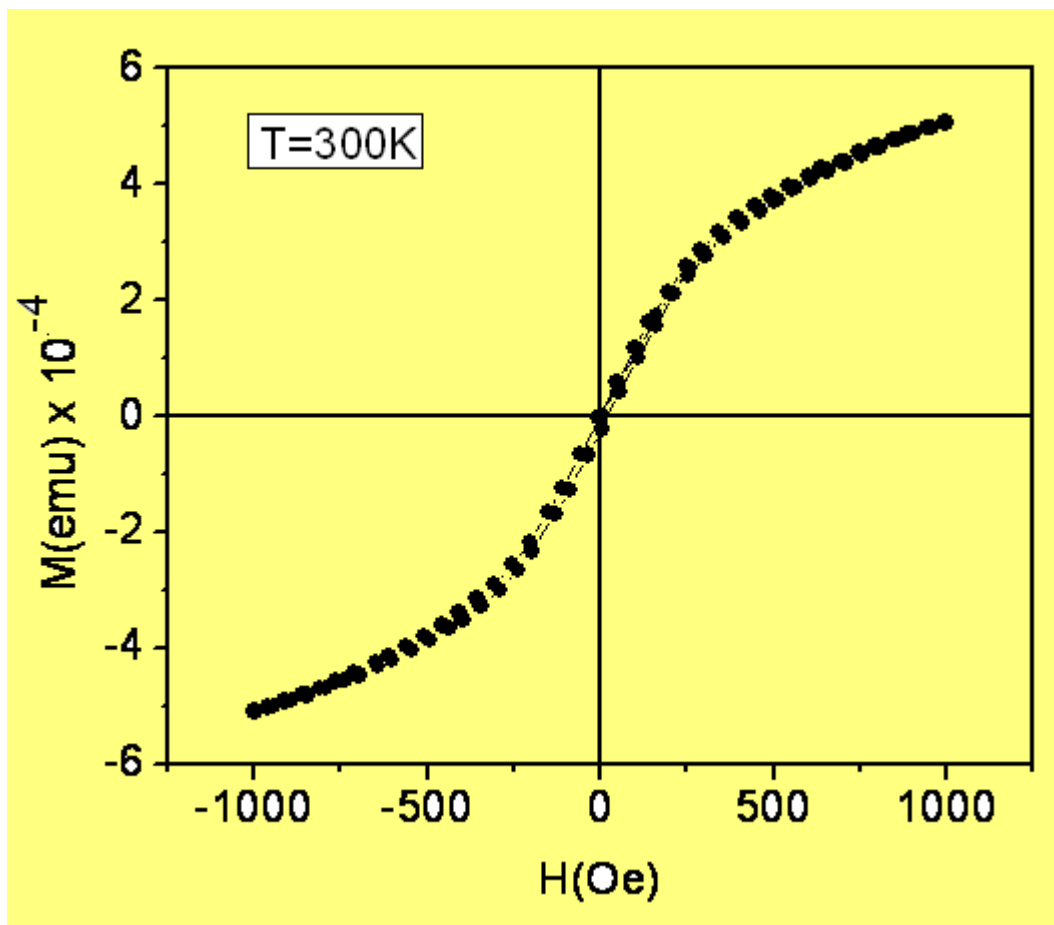


*Magnetization vs Field for 3 at.% C-Doped ZnO Thin film at 300k*



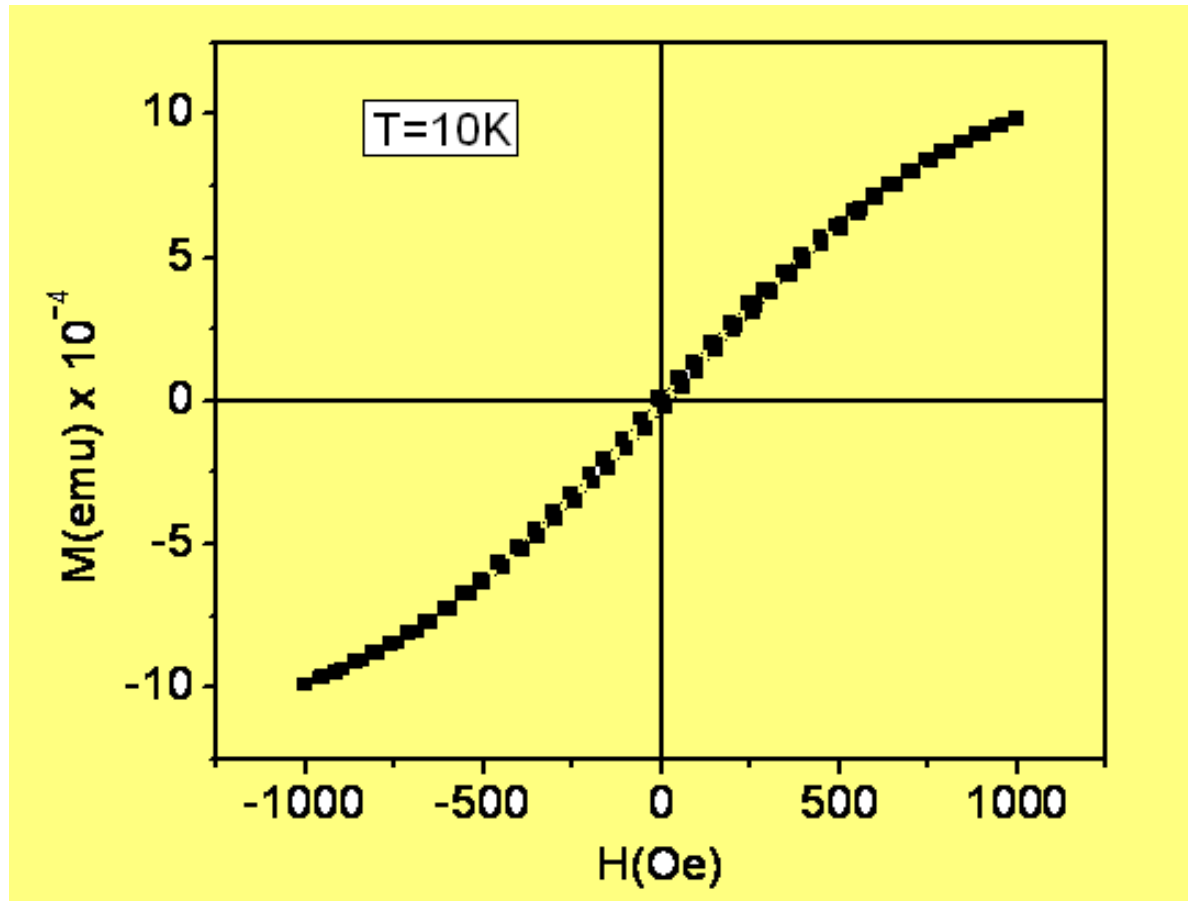


*Magnetization vs Field for 1 at.% C-Doped ZnO Thin film at 300 K*



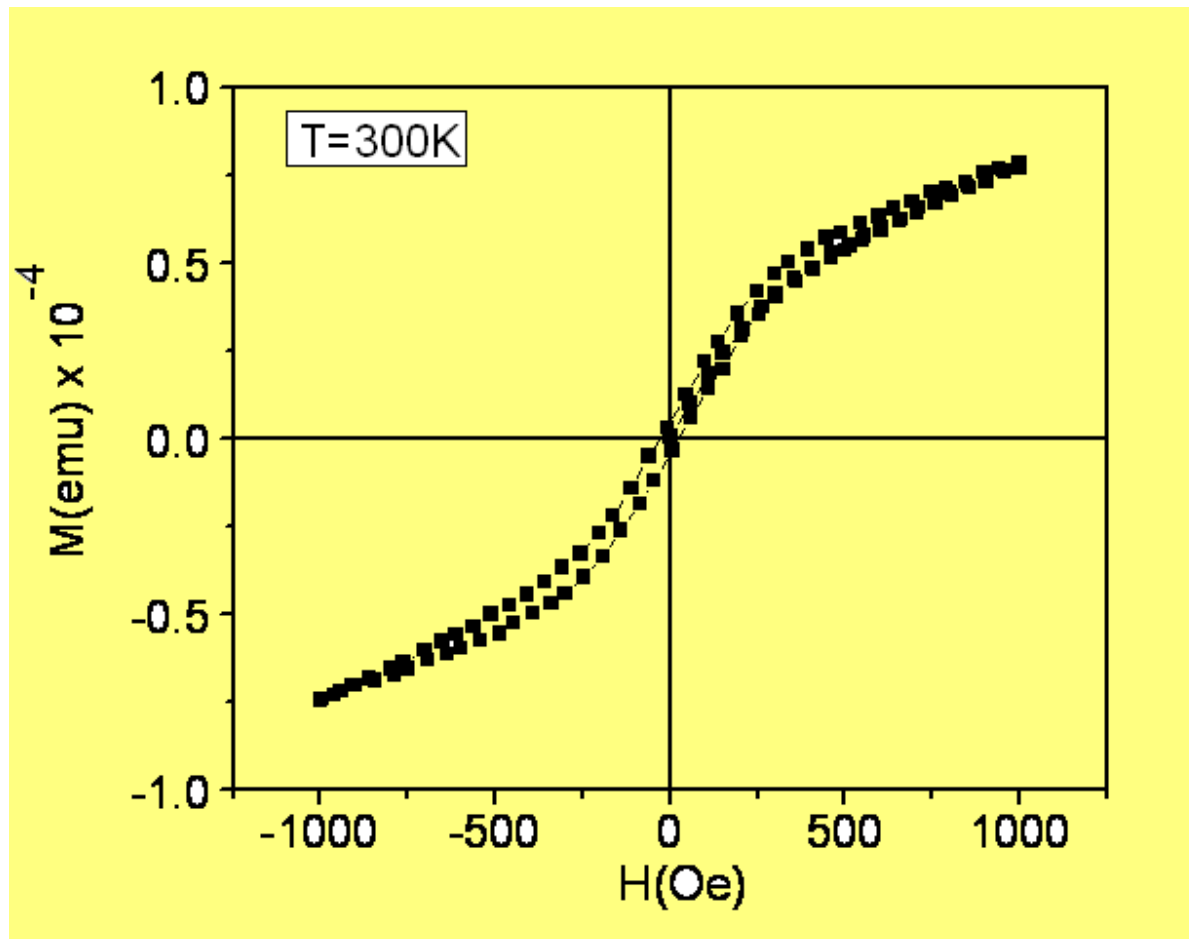


*Magnetization vs Field for 1 at.% C-Doped ZnO Thin film at 10 K*





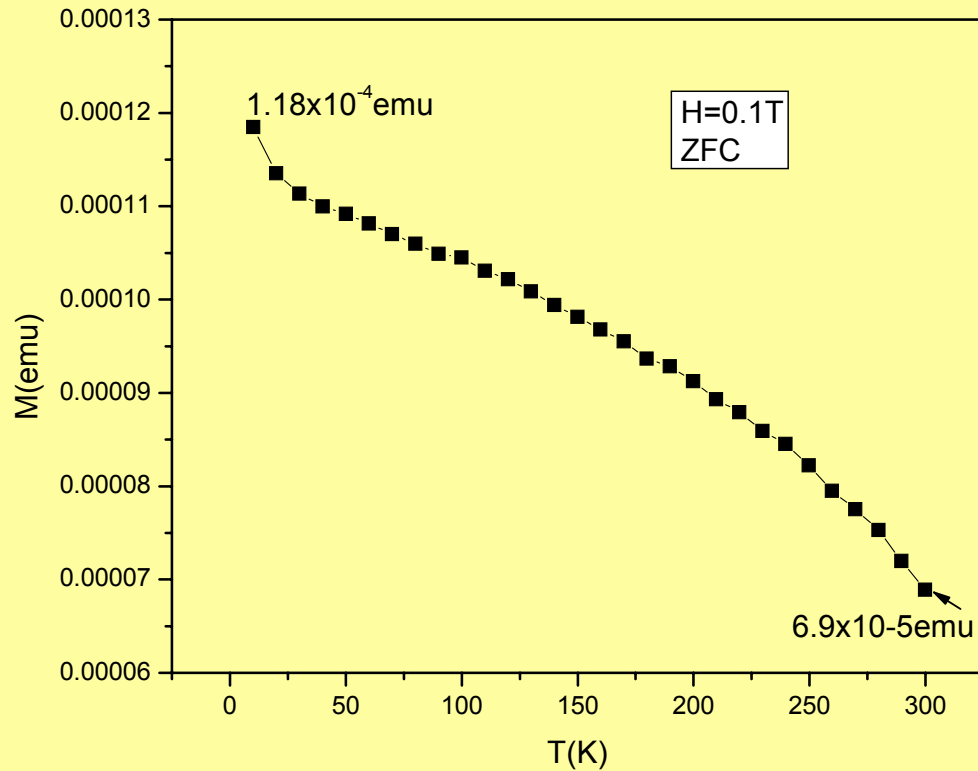
*Magnetization vs Field for Carbon Layer on ZnO Thin film at 300 K*







## *M(T) for Carbon Layer-ZnO Thin Film*



*Comparison of Magnetization for different Carbon doped thin films (T=300, 10K)*

* Composition of Films	Magnetization at 300K For H=1KOe (emu)	Magnetization at 10K For H=1KOe (emu)
1 at.% C in ZnO (Micro. Glass Slide)	$5.0 \times 10^{-4}$	$1.0 \times 10^{-3}$
3 at.% C in ZnO (Micro. Glass Slide)	$2.2 \times 10^{-5}$	$2.2 \times 10^{-4}$
Carbon Layer on ZnO (Corning glass 0120)	$7.8 \times 10^{-5}$	$1.4 \times 10^{-4}$



- **Three of the C doped ZnO films show Ferromagnetism at room temperature!!**
- The room temperature moment is typically in the range of  $10^{-5}$  to  $10^{-4}$  emu for 200nm films.
- M increases smoothly with cooling down. In one case a sharp transition is seen at low T ( $T < 50\text{K}$ )
- Low hysteresis in general.
- Interestingly, the carbon film prepared via the discharge technique also appears to yield a ferromagnetic specimen, i.e. C doped ZnO.



## *Hall Measurements for Carbon-doped ZnO*

Composition of Films	Carrier Concentration (/cm <sup>3</sup> )	Mobility (cm <sup>2</sup> /V.s)	Resistivity Ω cm
ZnO	-5.7X10 <sup>16</sup>	1.8	5.8X10 <sup>1</sup>
3at% C-ZnO	-1.7X10 <sup>17</sup>	1.6	2.3X10 <sup>1</sup>



## *Hall effect measurement shows:*

- *n-type conductivity as expected.*
- *Carrier concentration  $10^{16}$  to  $10^{17}$  /cc.*
- *Carrier concentration increases significantly with C doping.*
- *The low resistivity values confirm high quality of inter-grain contact in the thin films.*

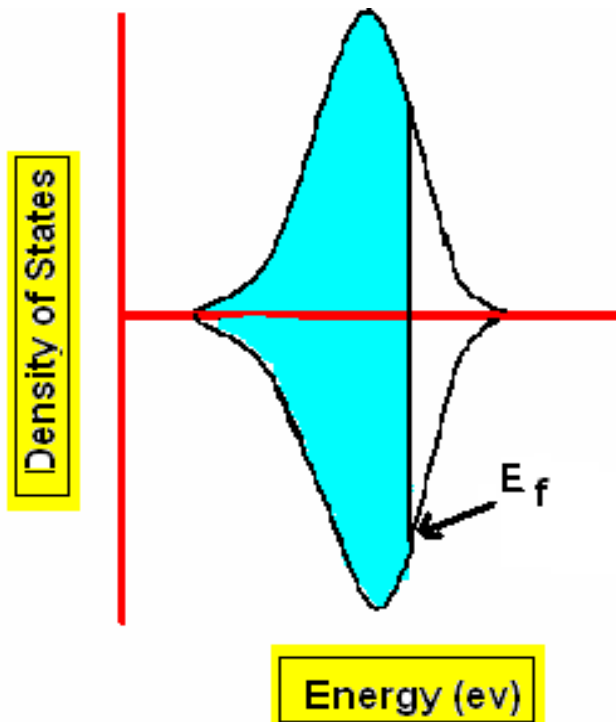


## *How Carbon (a non metal) makes ZnO Ferromagnetic?*

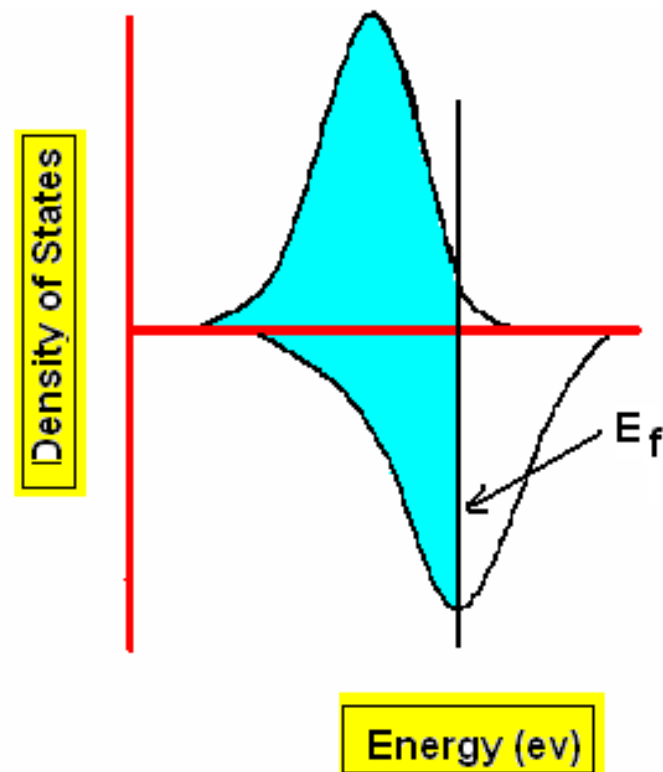
- **Local density of states (LDOS) calculations (H.Pan et al 2007) predicted magnetism in carbon doped ZnO if carbon can substitute for oxygen.**
- **Their simulations show overlap between the carbon *s* and *p* orbitals and the *s* orbital of Zn, respectively. (i.e. same energy for the different orbitals)**
- **Results in Strong coupling between these states (mixing, hybridization).**
- **This interaction (mixing) causes the carbon *2s* orbital around  $-9$  eV and the carbon *2p* orbital near  $2.3$  eV to split. (i.e. spin up and spin down sub-bands are split).**

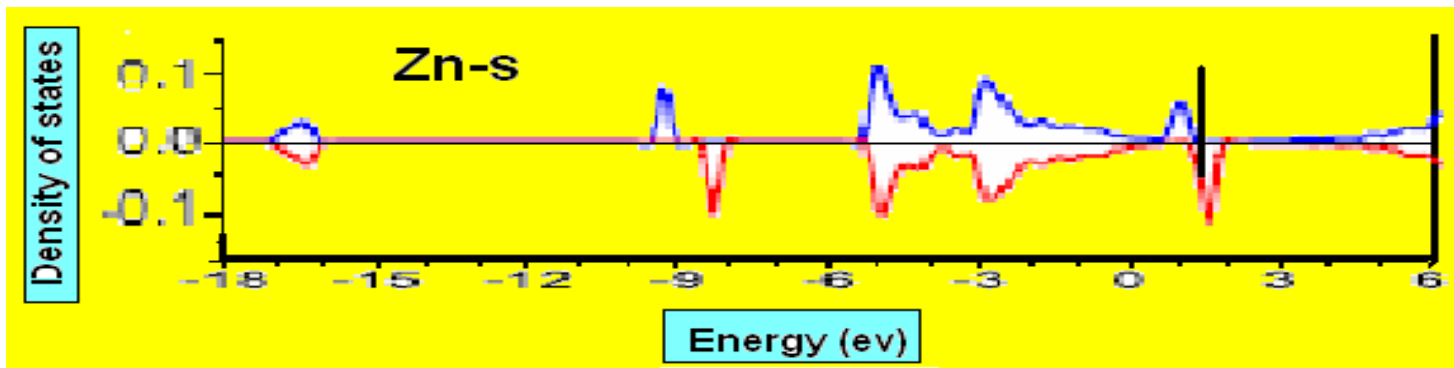
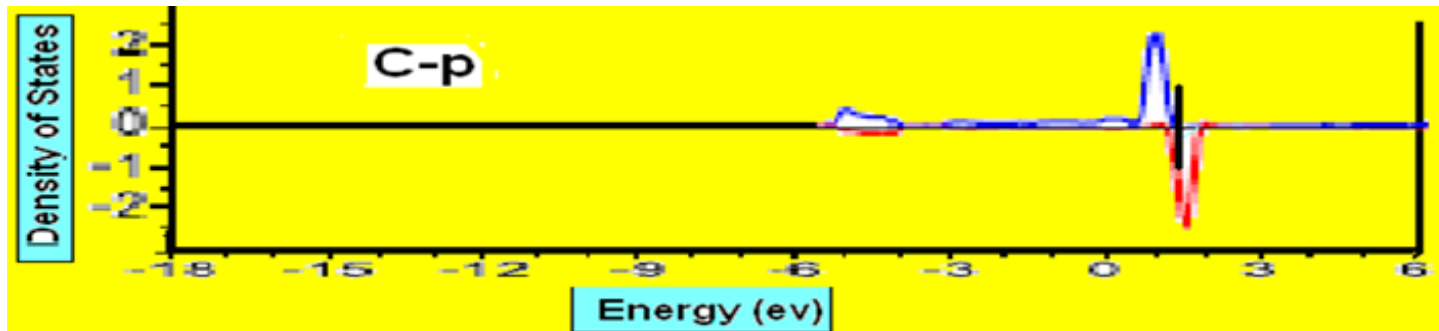
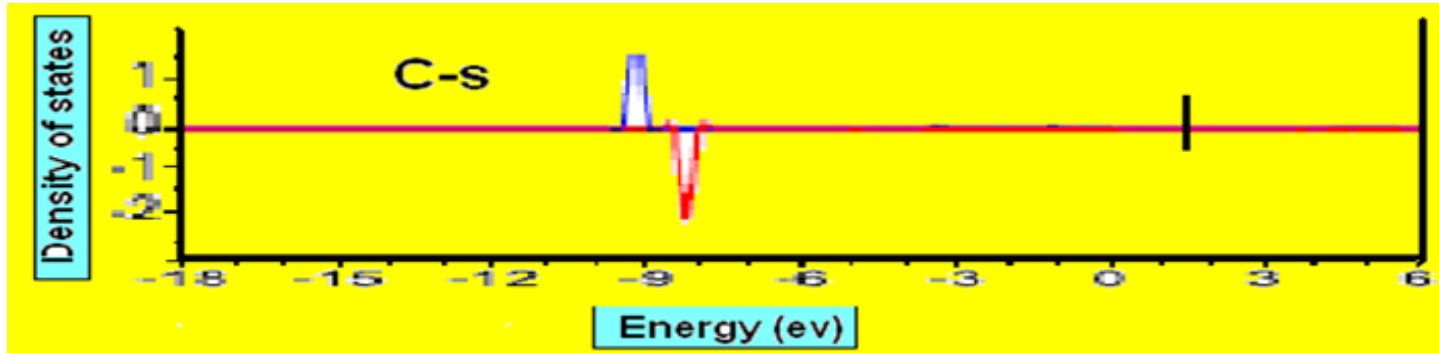
*How Carbon (a non metal) makes ZnO Ferromagnetic?*

$n_{\downarrow} = n_{\uparrow} \Rightarrow m = 0$



$n_{\downarrow} \neq n_{\uparrow} \Rightarrow m \neq 0$

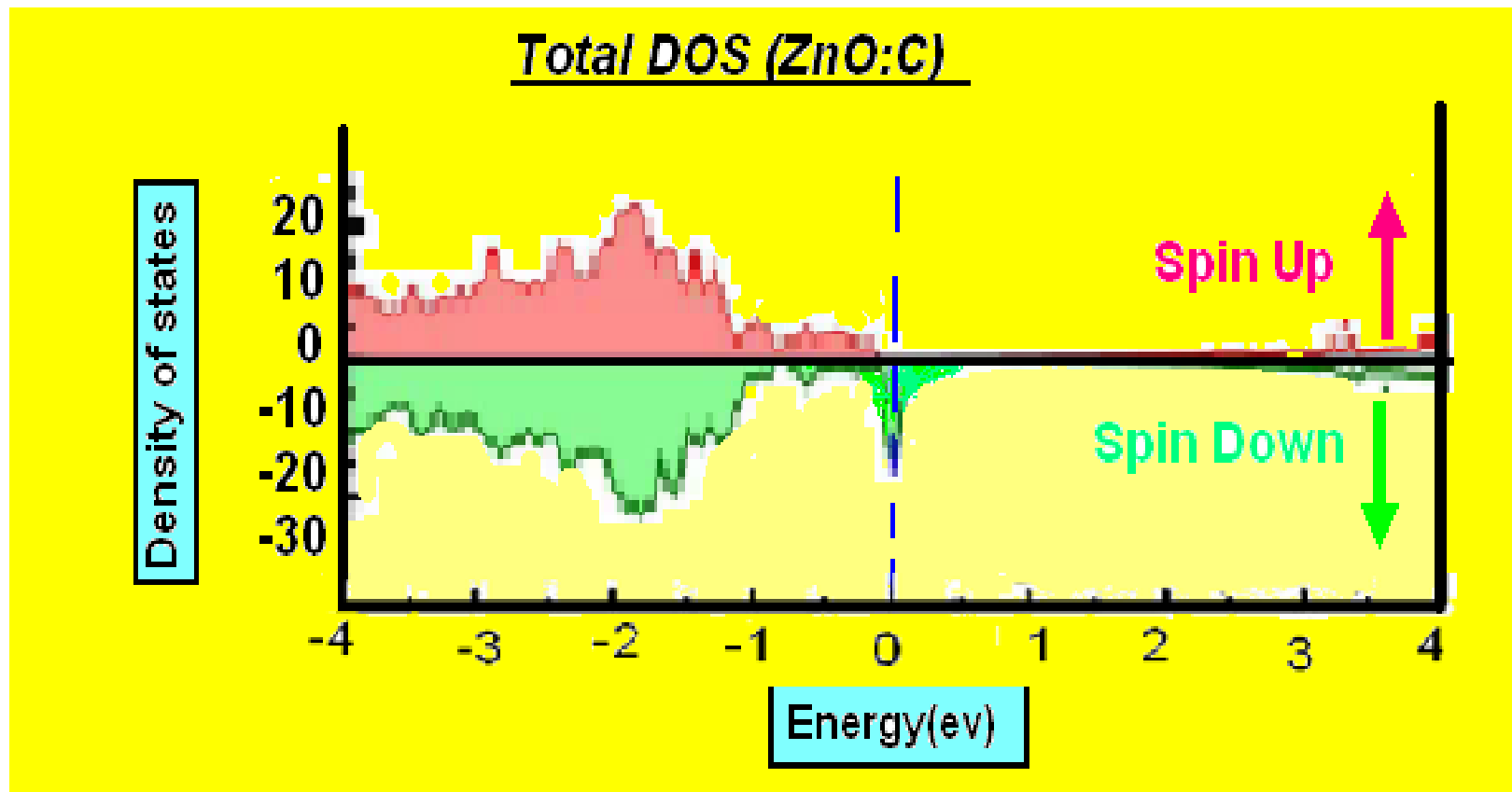








*How Carbon (a non metal) makes ZnO Ferromagnetic?*



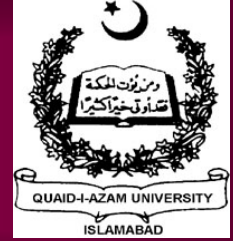


Magnetism & Superconductivity Group (MSG)

Department of Physics

Quaid-i-Azam University, Islamabad

skhasanain@qau.edu.pk



## *How Carbon (a non metal) makes ZnO Ferromagnetic?*

- *The spin-up bands are fully occupied while the spin-down bands are partially filled, resulting in a magnetic moment of **1.78  $\mu\text{B}$**  per carbon dopant. The magnetic moment is mainly contributed by the carbon **p** orbitals (**0.80  $\mu\text{B}$** ), while each of the neighboring **Zn** atoms and second nearest neighboring oxygen atoms also contribute a small part (**0.1  $\mu\text{B}$** ) and **0.04  $\mu\text{B}$** , respectively).*
- *The estimated formation energy of the **Co** defect is **5.3 eV**. Similar calculations on carbon substitution for **Zn** and interstitial carbon showed that they do not result in magnetism.*



## ***ZnO & Cobalt-doped ZnO Thin Films***

### **➤ *Method of Preparation***

- ***We prepared Co-doped ZnO Thin Films by Heat Resistive Evaporation Method***
- ***Thin films made from pellets of  $Zn_{1-x}Co_xO$  nanoparticles (synthesized in our Lab. by sol-gel method)***
- ***Corning glass slides 0120 were used after cleansing***
- ***The films are deposited at 533K temperature.***
- ***The base pressure was better than  $10^{-6}$  mbarr***



## ***ZnO & Cobalt-doped ZnO Thin Films***

- ***Rate of deposition was  $5\text{Å}^0$  /sec.***
- ***Thickness of films were kept constant for all films (160 nm).***
- ***Nanoparticles were annealed in forming gas at  $600\text{c}^0$  for 8hours. No annealing of films after deposition.***
- ***Aluminum four (square) contacts were grown on each film for Hall measurements.***



## ***Some Highlights of Target Material*** ***(Co doped ZnO nanoparticles)***

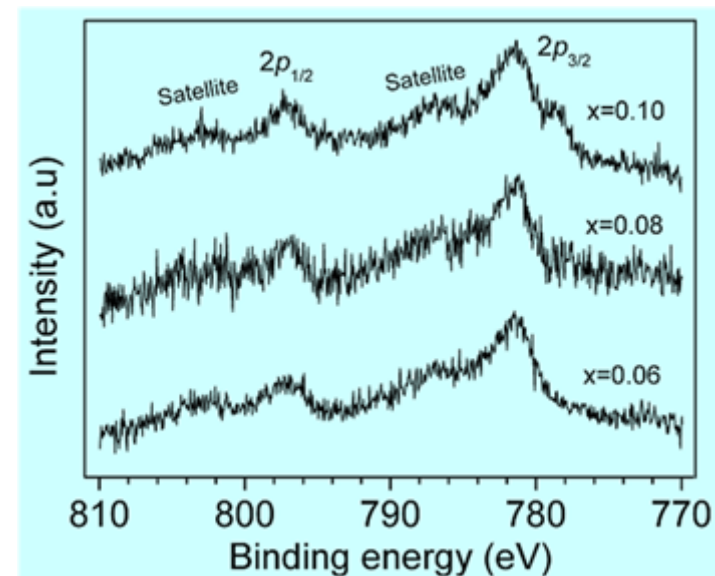
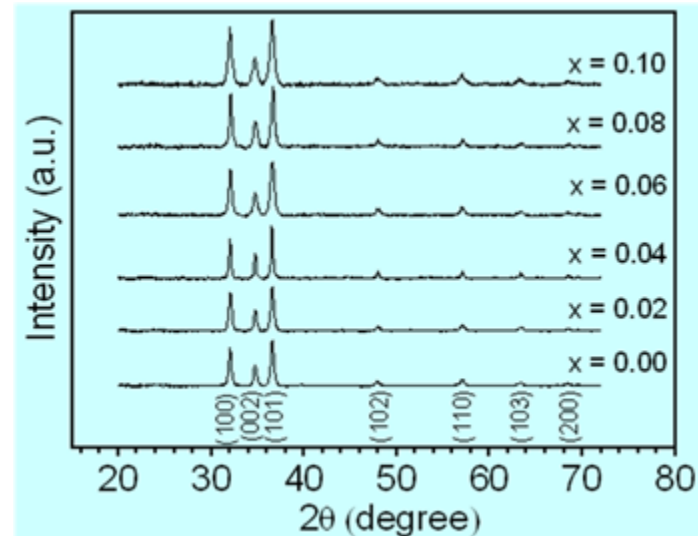
- ❑ ***Co -doped ZnO nanoparticles were synthesized via sol- gel route.***
- ❑ ***The end products depend crucially on the annealing atmosphere:***
  - ***Samples Annealed at: 600°C***
  - ***Samples annealed in open air: Structurally OK. (Wurtzite Hexagonal with correct lattice constants is obtained).***
  - ***However completely non-magnetic down to lowest T investigated (10K).***
  - ***Samples Annealed in a reducing atmosphere: (95% Ar-5% H)***  
***Correct structure for all***
    - $x=0 \Rightarrow$  nonmagnetic.***
    - $x>0 \Rightarrow$  all compositions are ferromagnetic at room temperature.***



➤ **XRD Diffraction spectra of Zn<sub>1-x</sub>Co<sub>x</sub>O Nanoparticles ( $0.00 \leq x \leq 0.10$ )**

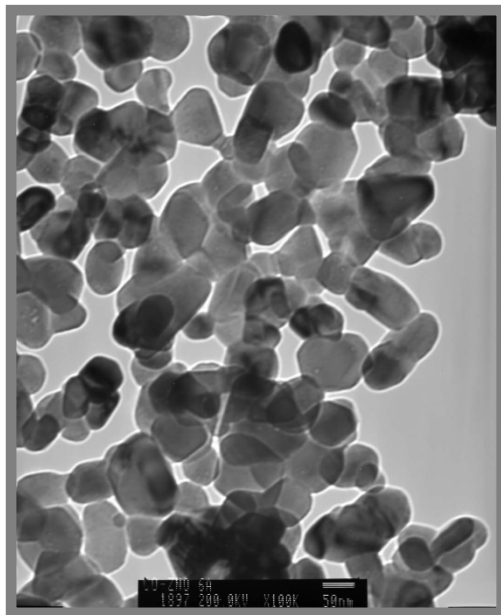
➤ **XPS spectra of Co 2p core levels as a function of Co concentration ( $x = 0.06, 0.08, 0.10$ ) recorded at room temperature.**

➤ **X-ray Photoemission spectra suggested that Co is incorporated well at the Zn site in ZnO lattice.**

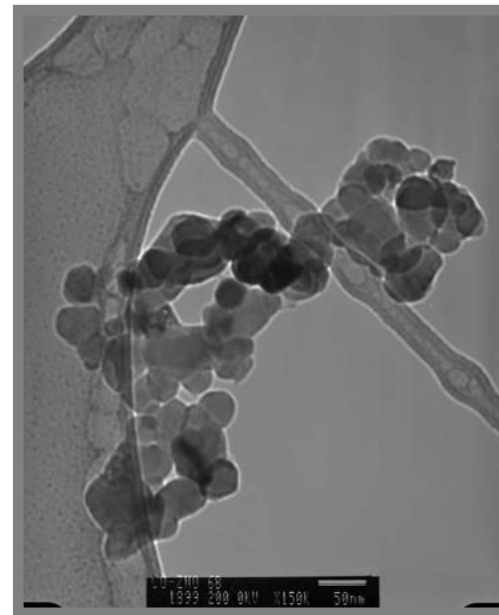




## *Transmission Electron Micrograph*



$\text{Zn}_{0.94}\text{Co}_{0.06}\text{O}$  annealed in  
forming gas



$\text{Zn}_{0.94}\text{Co}_{0.06}\text{O}$  annealed in  
air

❖ *Estimated particle size: 20-40nm*

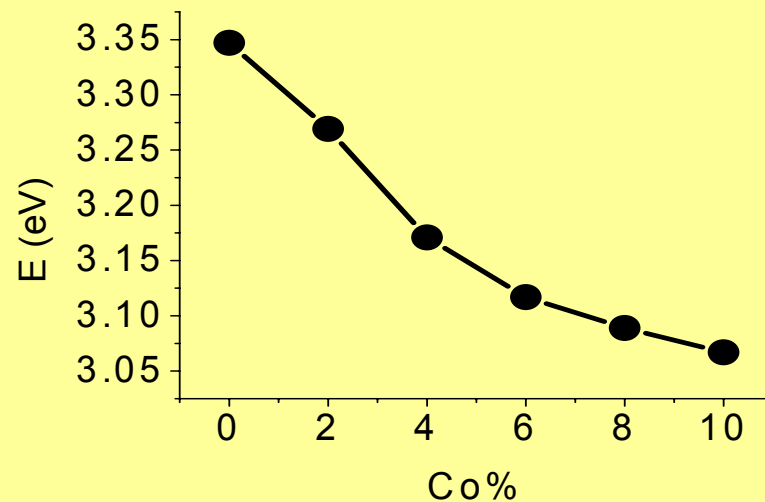
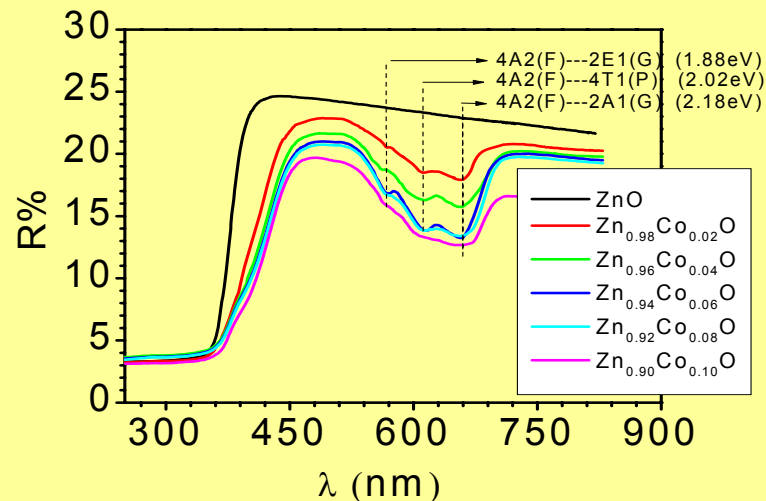


## Diffuse Reflectance Spectra

➤ The reflectance peaks in spectra correspond to Co<sup>2+</sup> d-d (tetrahedral symmetry) crystal field transitions.

➤ The bandgap energy of the Zn<sub>1-x</sub>Co<sub>x</sub>O nanoparticles were calculated from diffuse reflectance spectra by the Kubelka-Munk function

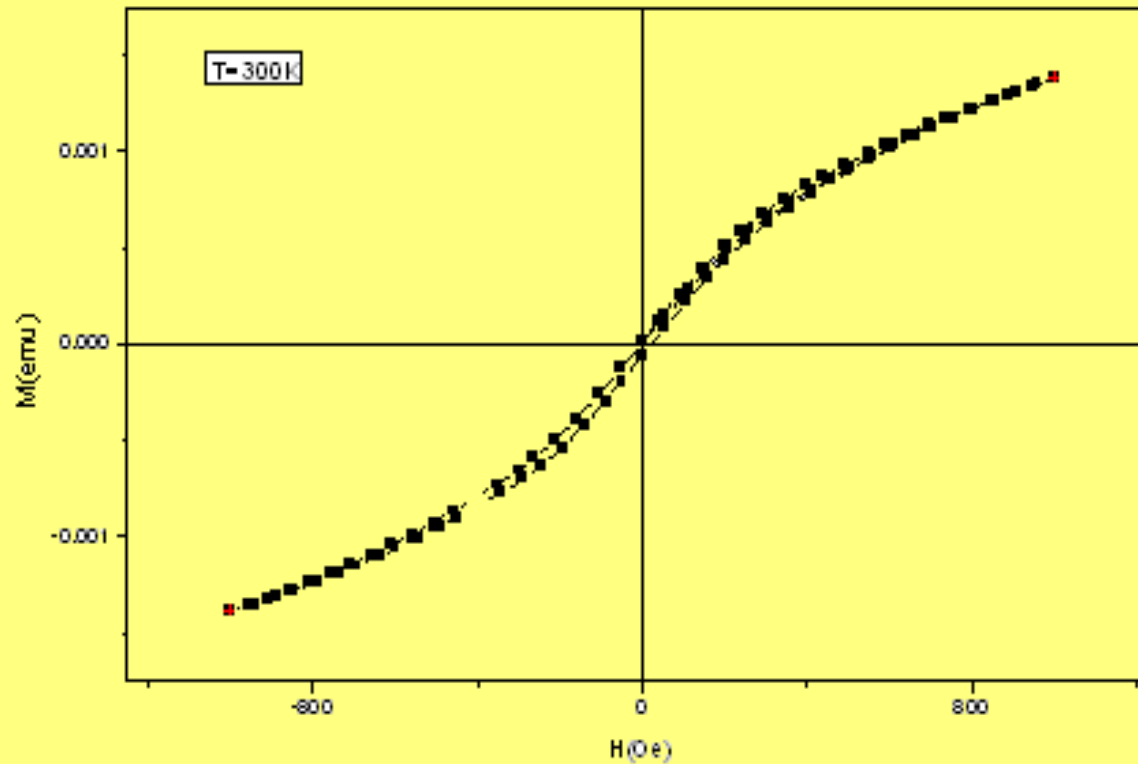
$$F(R) = (1-R)^2/2R$$







*Magnetization vs Field for Cobalt-doped ZnO Thin film at 300 K*





*Hall Measurements for ZnO & Cobalt-doped ZnO  
Thin films*

Name of Films	Carrier Concentration (/cm <sup>3</sup> )	Mobility (cm <sup>2</sup> / Vs)	Resistivity Ω cm
<b>ZnO</b> (Corning glass slide 0120)	-2.0x10 <sup>16</sup>	1.6x10 <sup>1</sup>	2.0x10 <sup>1</sup>
<b>Cobalt-doped ZnO</b> (Corning glass slide 0120)	-6.4x10 <sup>16</sup>	1.0x10 <sup>1</sup>	9.6



## *Conclusions*

I:

- *Thin films of ZnO can be grown by e-beam or thermal evaporation Evaporation.*
- *Co doped films show room temperature ferromagnetism.*
- *The behavior of component particles depends crucially on the annealing atmosphere.*

II:

- *C doped thin films grown by different techniques also show room temperature Ferromagnetism with a small moment.*
- *The potential for the C doped films is very exciting for applications in spintronic applications.*
- *The optimization of C content; control and correlation of the resistive and magnetic behaviour; needs to be worked on.*

*How general is this trend? i.e. magnetism via the doping of non-magnetic elements. Not clear yet.*

**Magnetism & Superconductivity Group (MSG)**  
**Department of Physics**  
**Quaid-i-Azam University, Islamabad**  
**skhasanain@qau.edu.pk**

**Thanks**