Applications of Synchrotron Radiation in Transition Metal Oxide Nanomaterials

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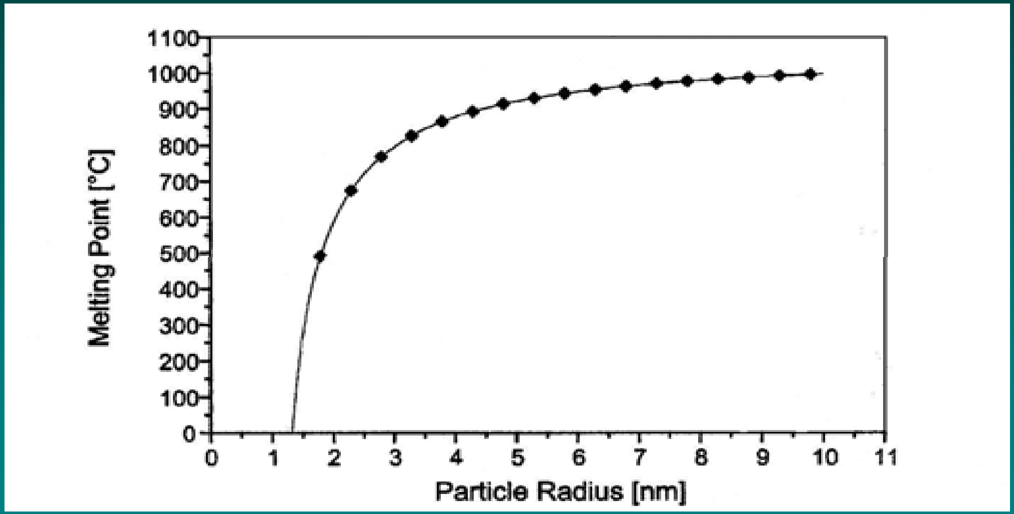
Outline

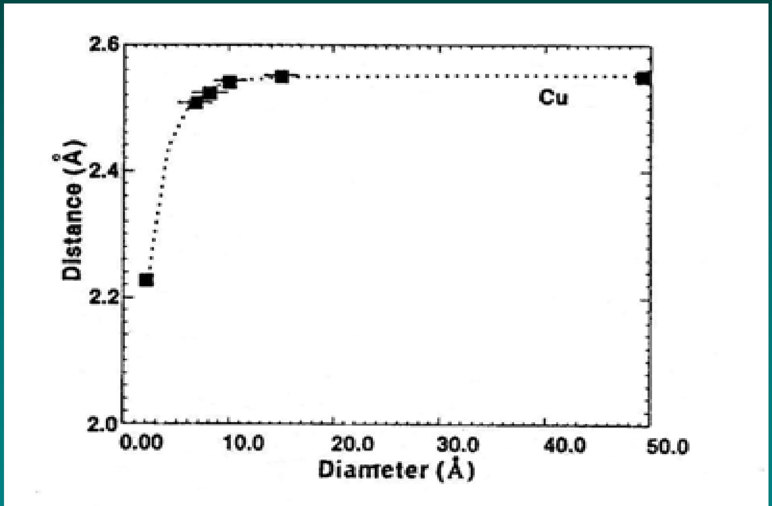
- **Electronic Structure of ZnO Nanorods**

- **Electronic and Ferromagnetic Properties of $Zn_{1-x}Mg_xO$** and **$Zn_{1-x}Co_xO$ Nanorods**

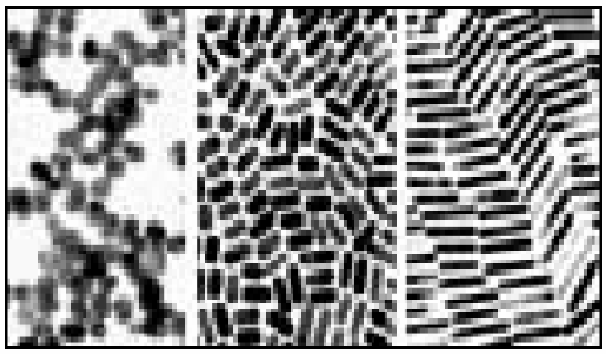
Physical properties of nano-materials



Various Au particles and melting points



Cu-Cu distance with particle size



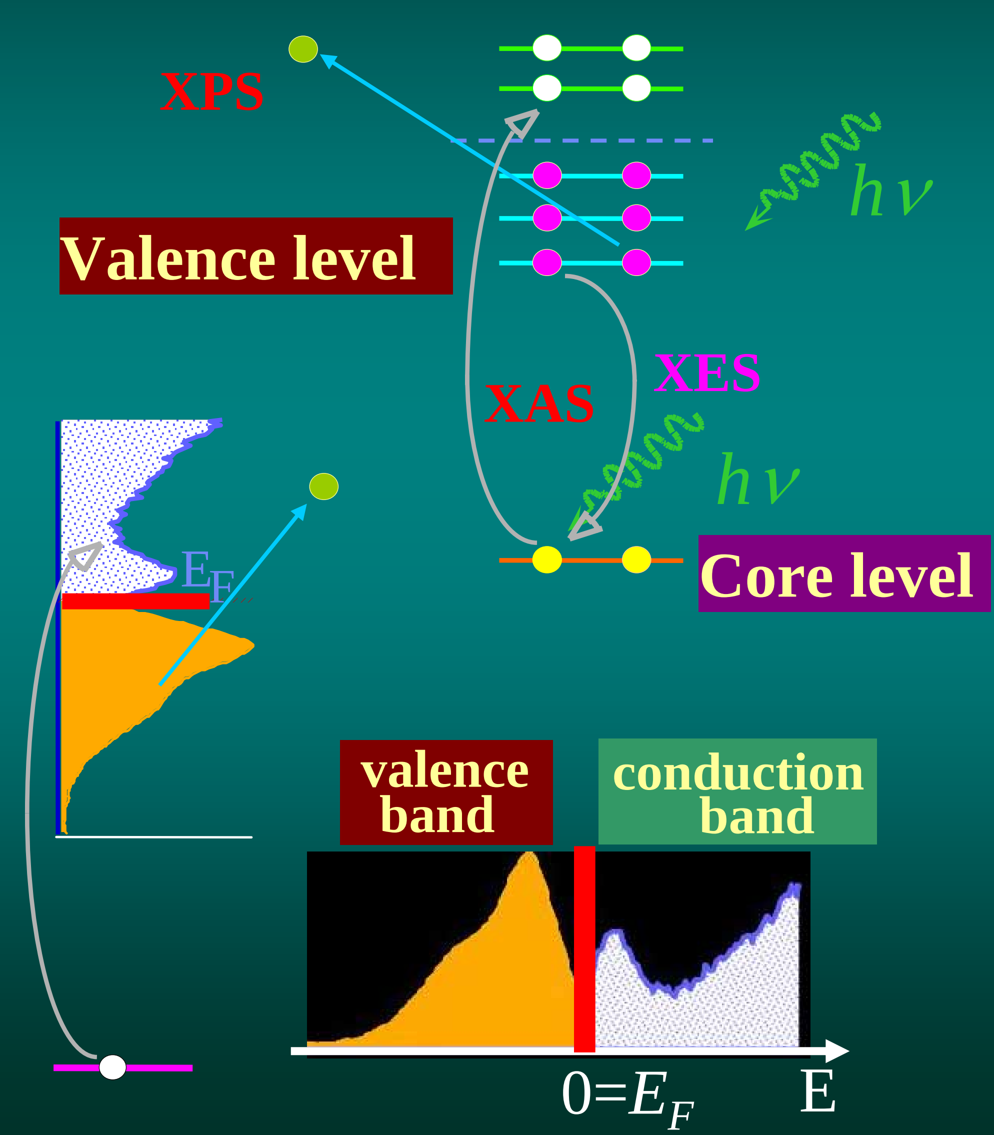
Different dimension of Au particles and its color

Generate different color (CdSe nanoparticles 2.1~3.5 nm)

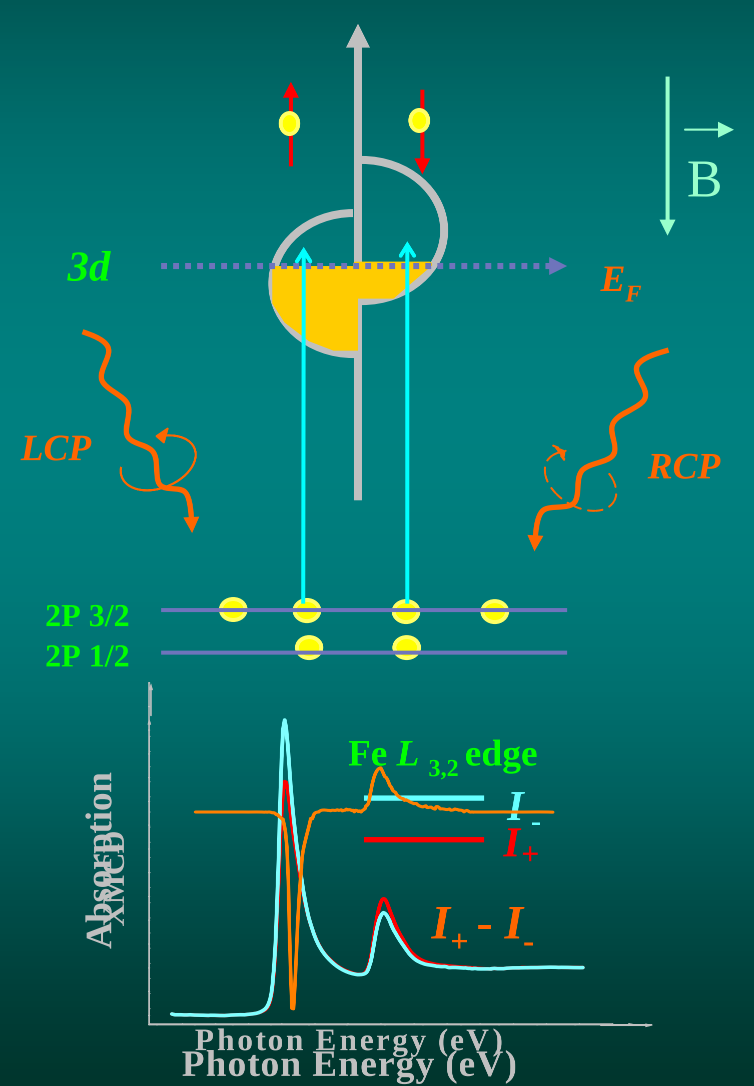
T. Castro, R. Reifenberger et al., Phys. Rev. B 1990
P. A. Montano et al., Phys. Rev. Lett. 1986

Experimental

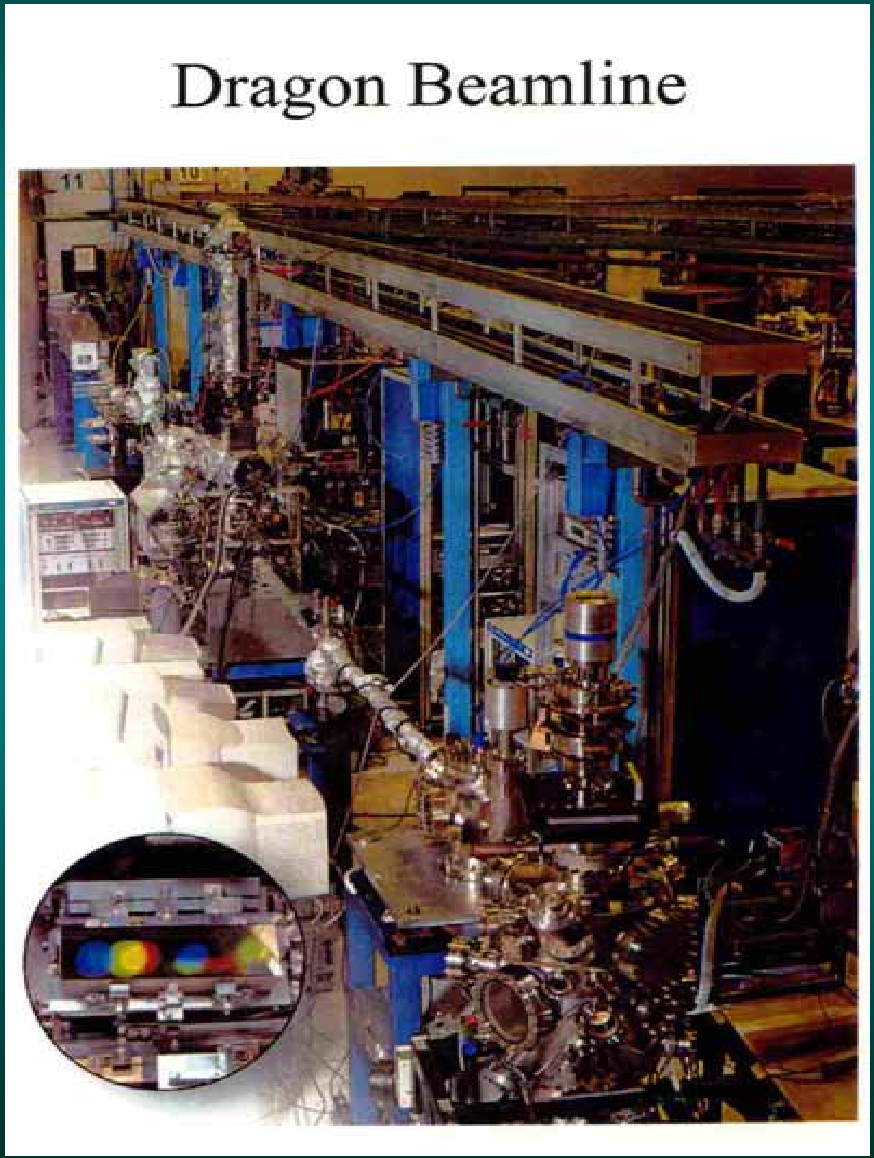
XAS, XES & XPS Measurements

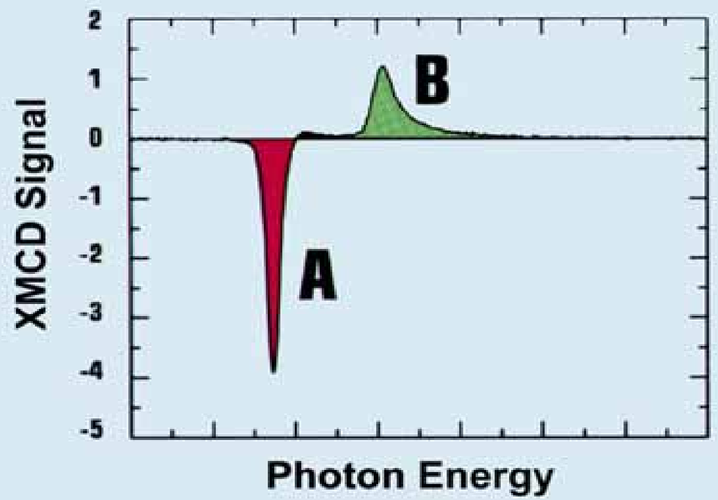


XMCD Measurement



XMCD Sum Rules



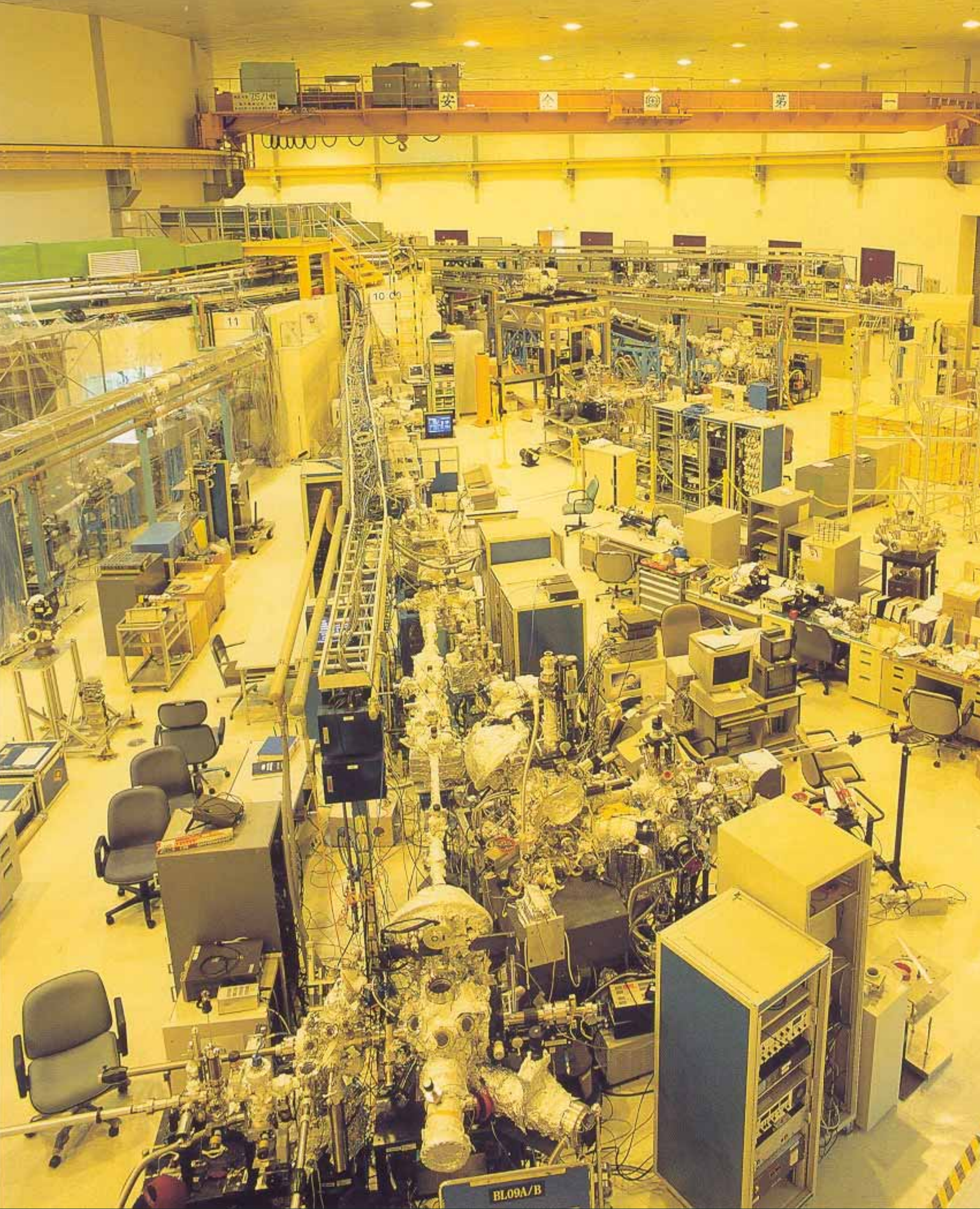


- **Orbital Magnetic Moment**

  $m_{orb} \propto (A+B)$

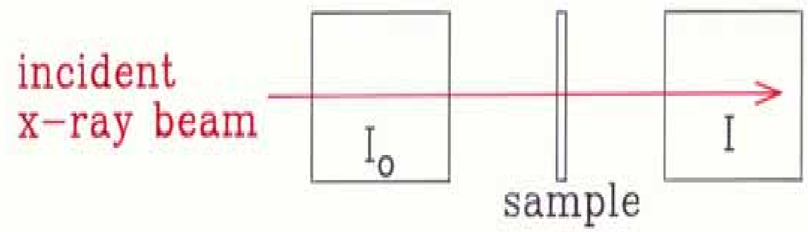
- **Spin Magnetic Moment**

  $m_{spin} + m_D \propto (A-2B)$



Experimental Techniques:

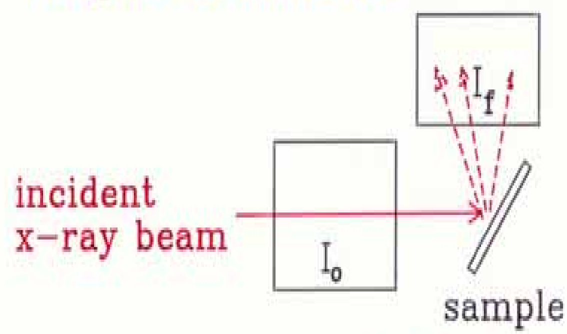
Transmission:



measure absorption as function of incident energy

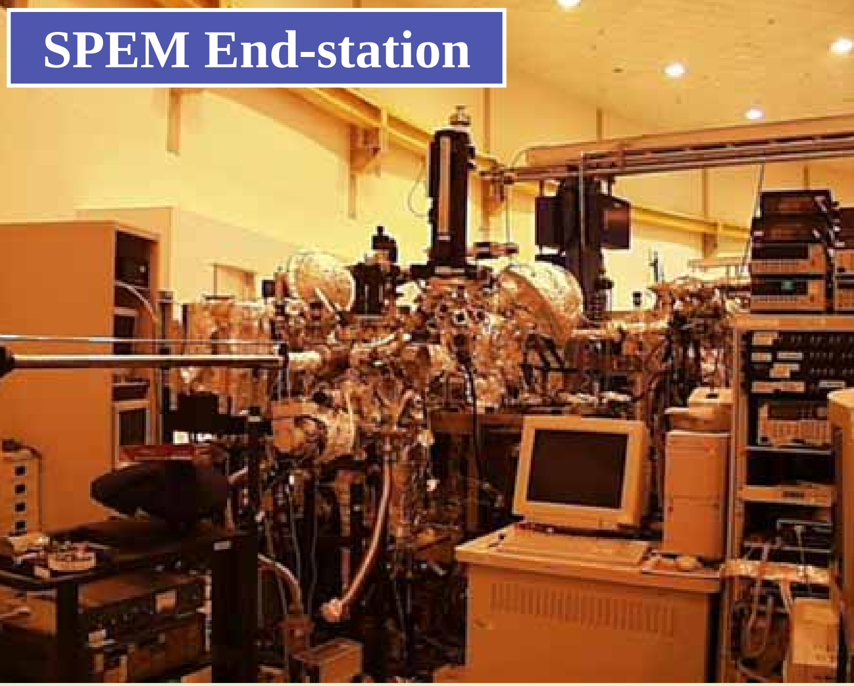
Detection of Secondary Particles:

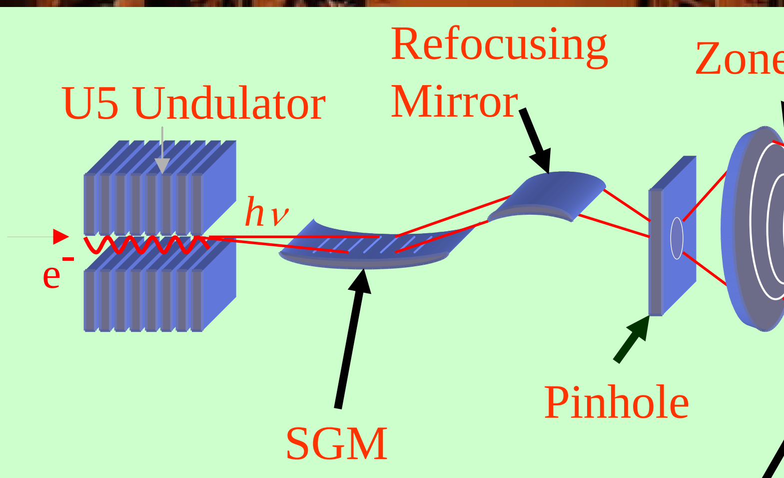
- o Fluorescence X-Rays
- o Electrons: (photoelectrons
  secondary electrons
  Auger electrons)
- o Optical Luminescence

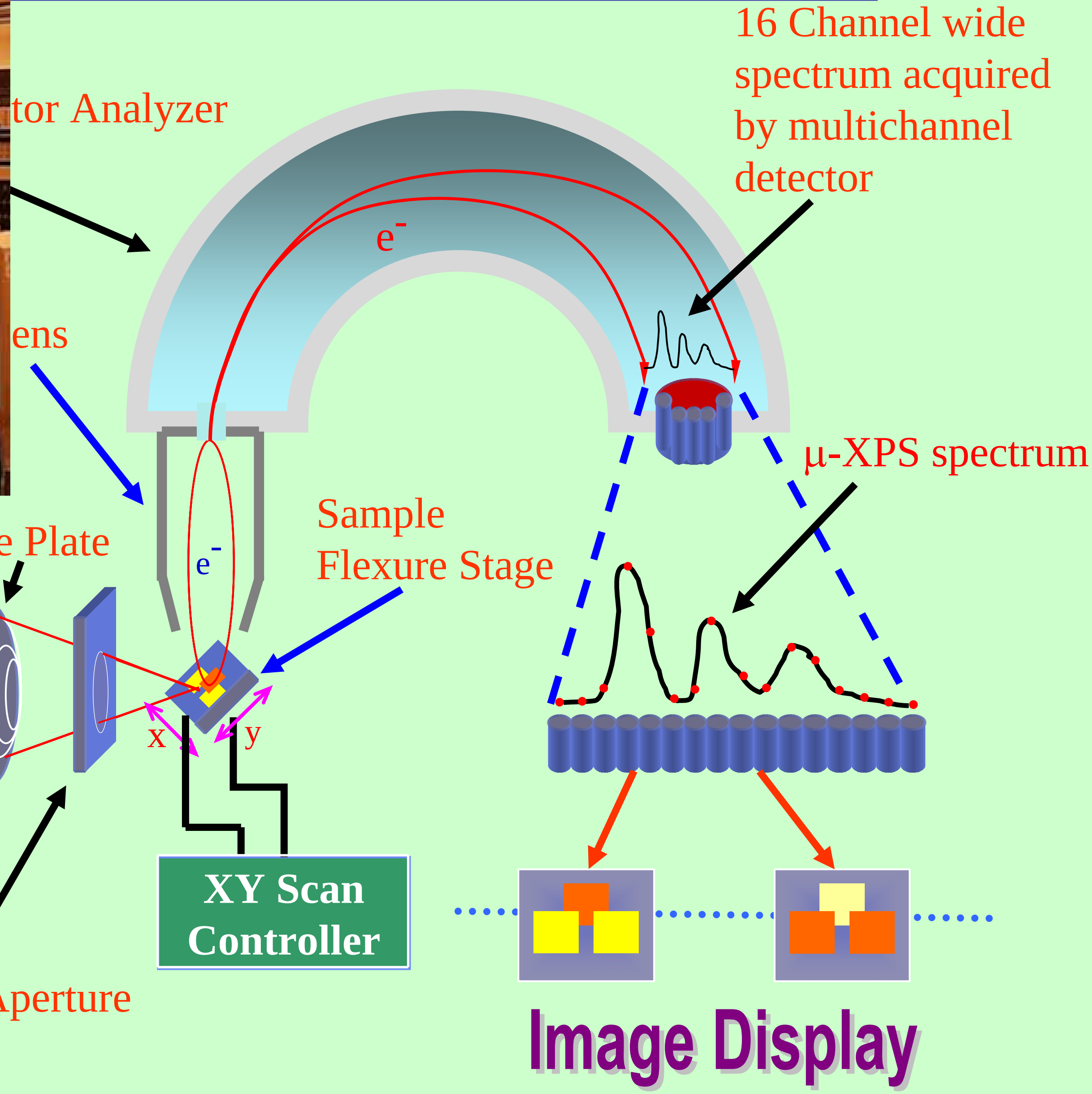


measure I_f as function of incident energy

-SPEM system at NSRRC

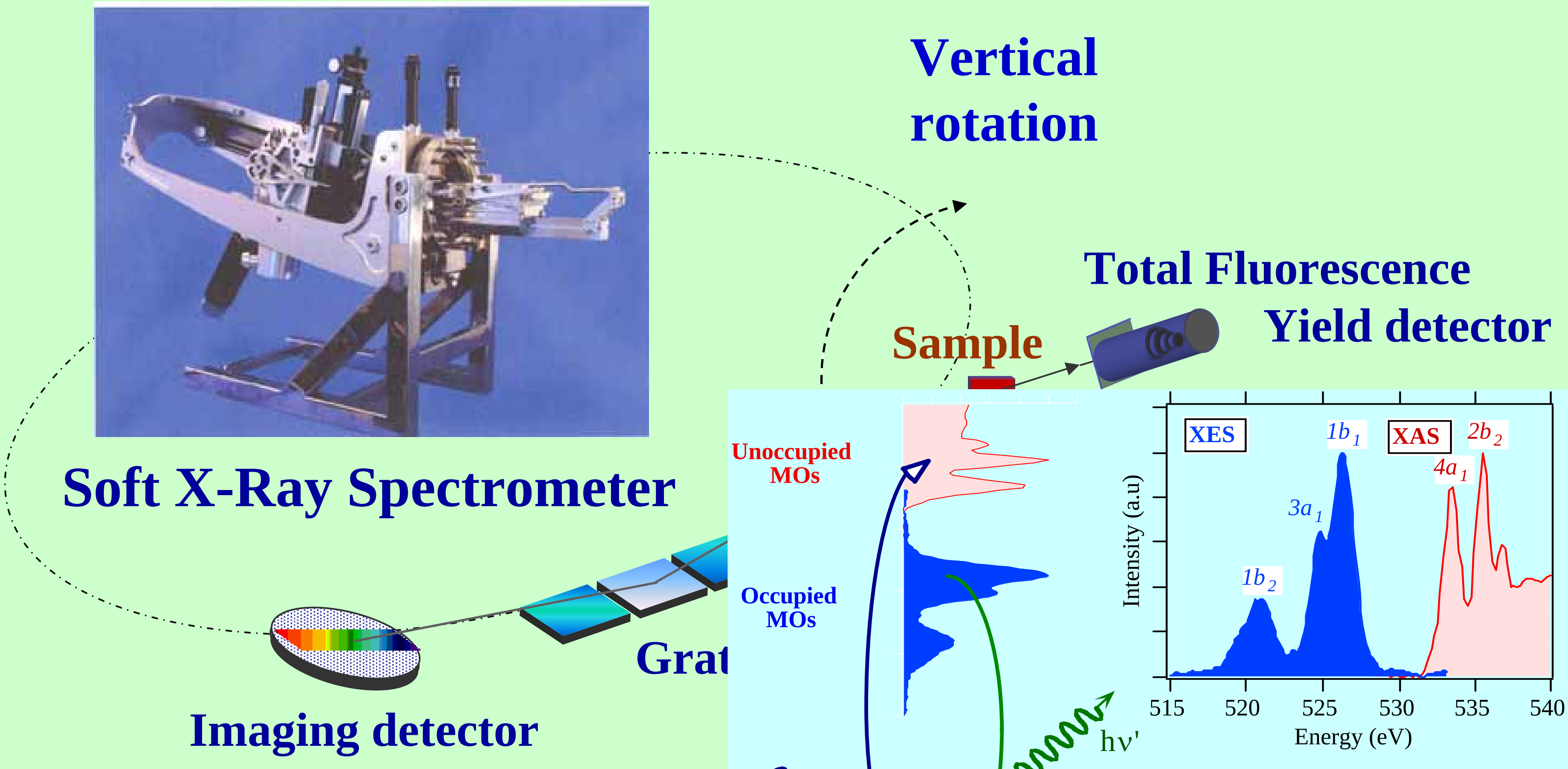






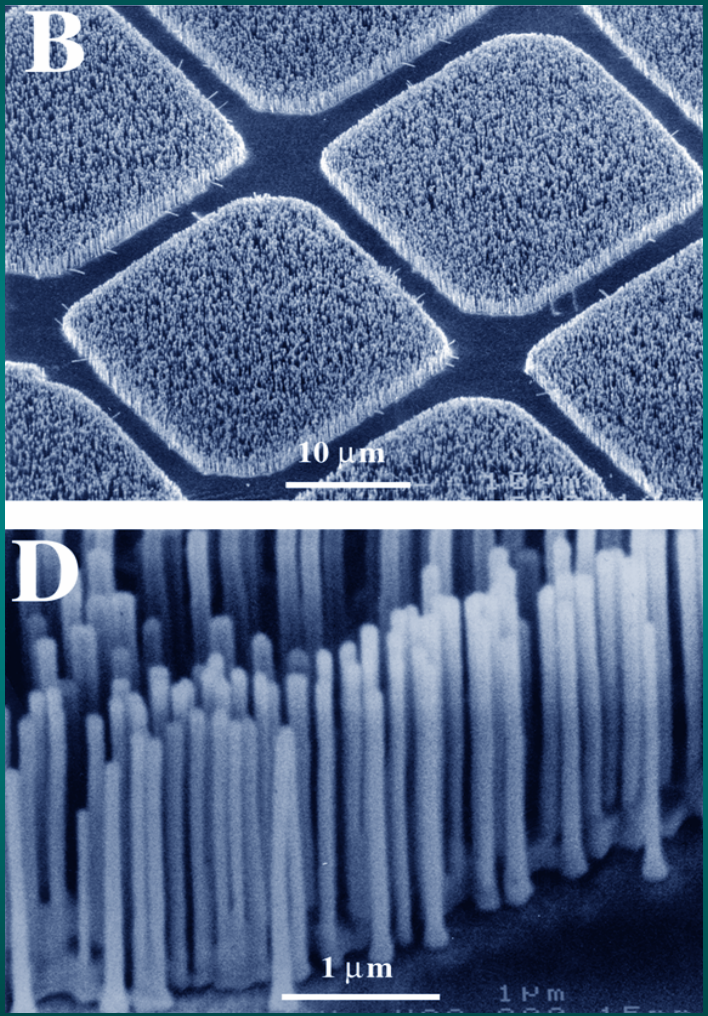
I-H Hong *et al.*, Nucl. Instru. & Meth Phys. Res. A467-468, 905 (2001).

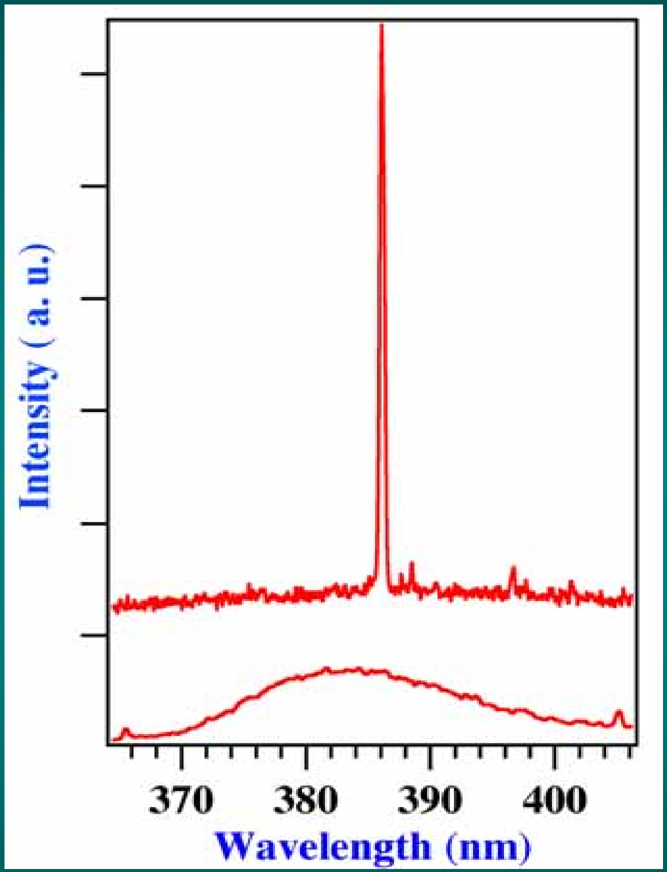
Schematic of BL7.0.1-XES system at ALS



- ✓ *Element selective*
- ✓ *Chemical state sensitive*
- ✓ *Symmetry selective*

Laser from aligned ZnO nanowires



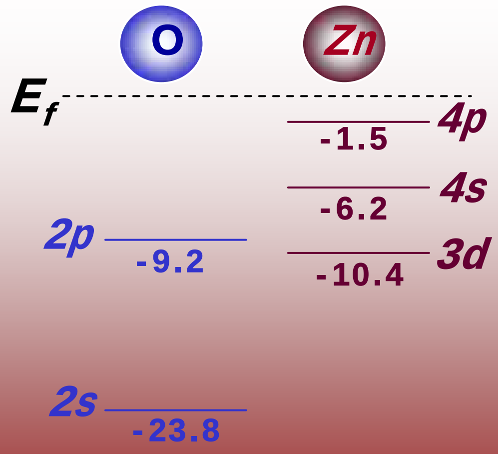


Huang *et al*., Science 292, 1897 (2001)

ZnO nanoparticles and defect-rich nanorods

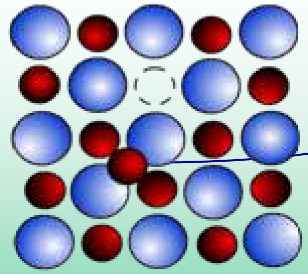
ZnO, wide band gap semiconductor, has received intensive attention due to potential technological applications:

- ✓ **Photocatalysts**
- ✓ **Light emitting diodes (LED)**
- ✓ **Tunable band gap from 2.8 to 4 eV by alloying with Cd or Mg**
- ✓ ……….

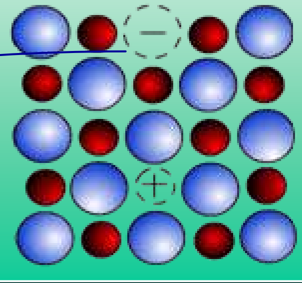


LDA energy levels (eV)

Two common defects in ZnO



Frenkel defect : an ion moves to an interstitial site. (Interstitial)

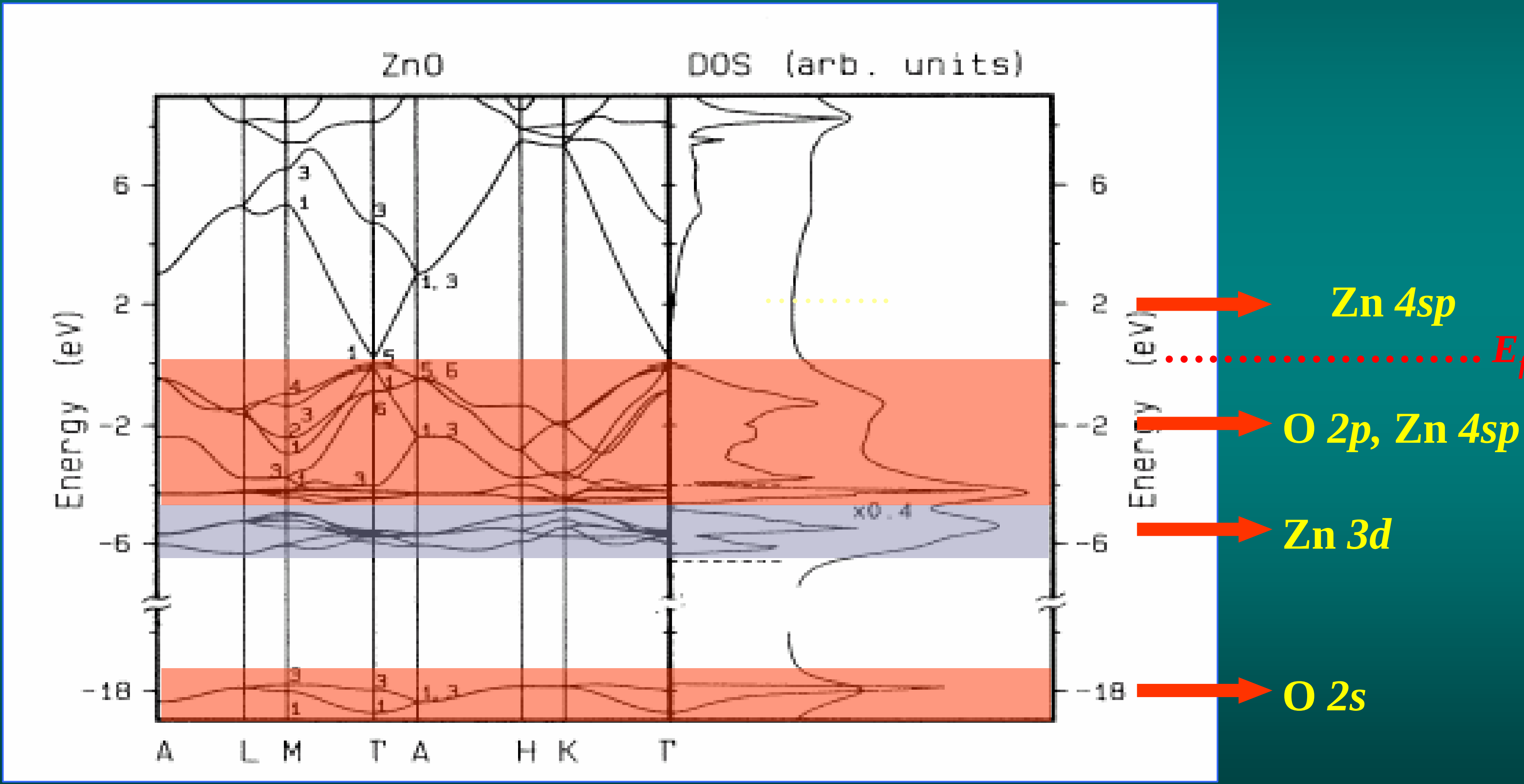


Schottky defect : absence of an ion from a site. (Vacancy)

PHYSICAL REVIEW B VOLUME 47, NUMBER 12 15 MARCH 1993-II

First-principles calculation of the electronic structure of the wurtzite semiconductors ZnO and ZnS

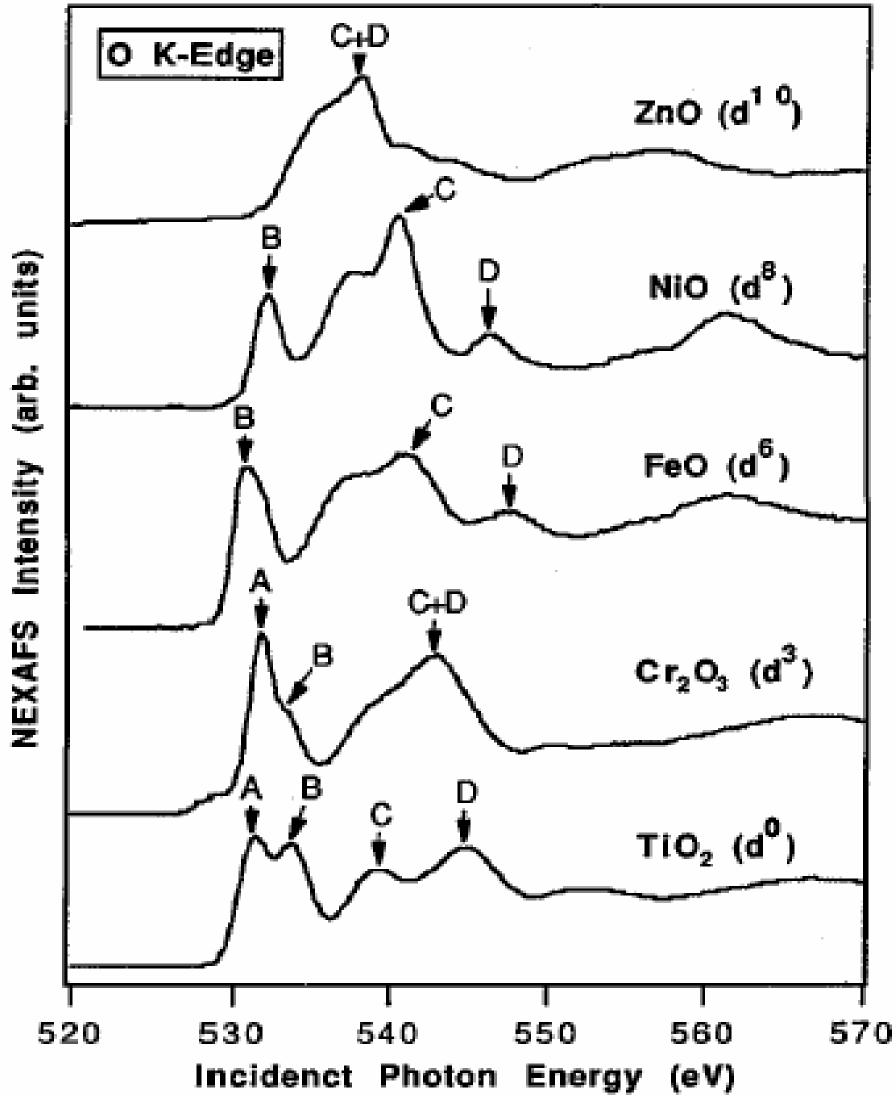
Peter Schröer, Peter Krüger, and Johannes Pollmann



Near-edge x-ray absorption fine structure characterization of compositions and reactivities of transition metal oxides

J. G. Chen,[a)] B. Frühberger, and M. L. Colaianni
Corporate Research Laboratories, Exxon Research and Engineering Company, Annandale, New Jersey 08801

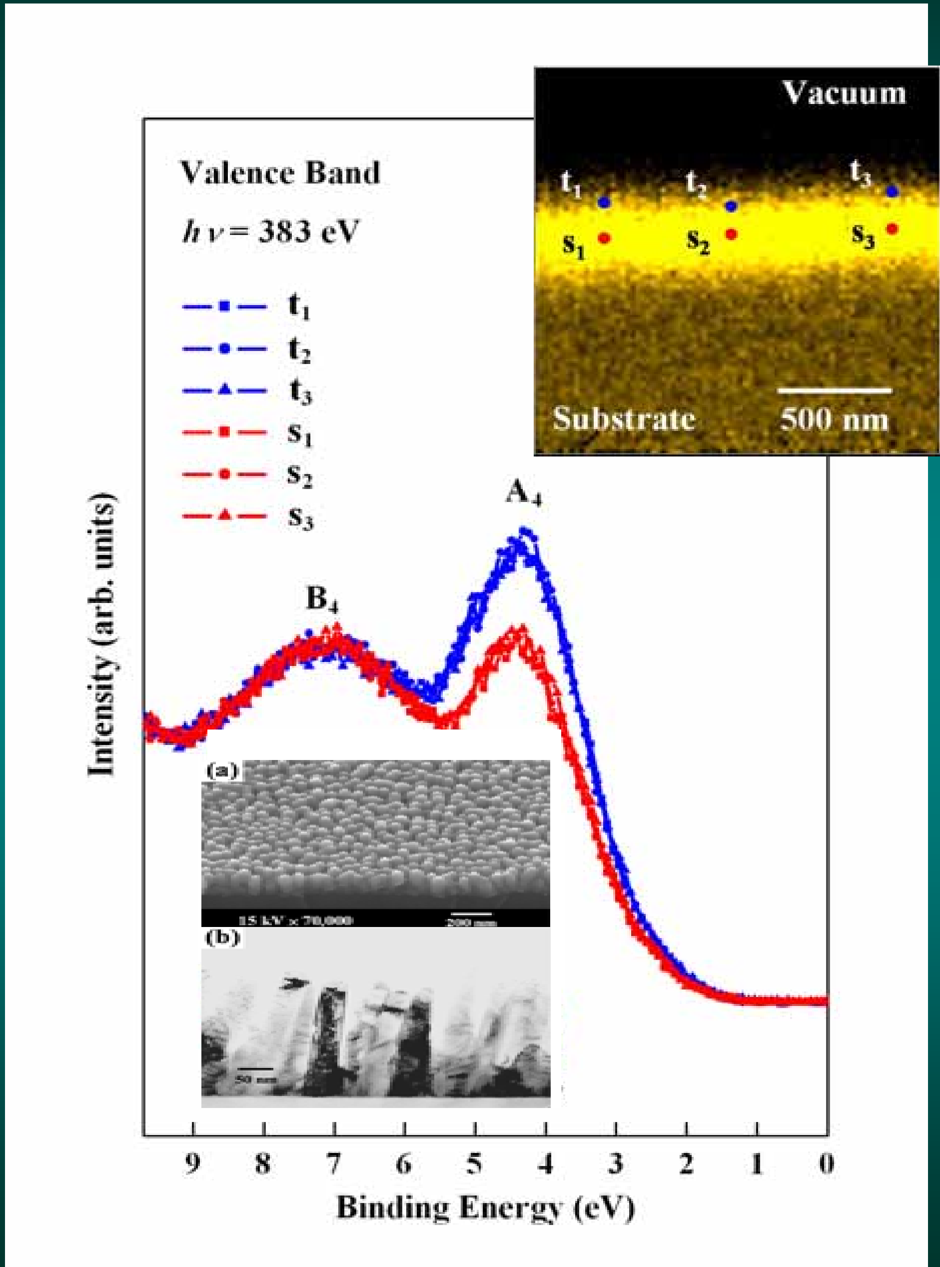
J. G. Chen. *et al.*, J. Appl. Phys. 79, 7983 (1996)



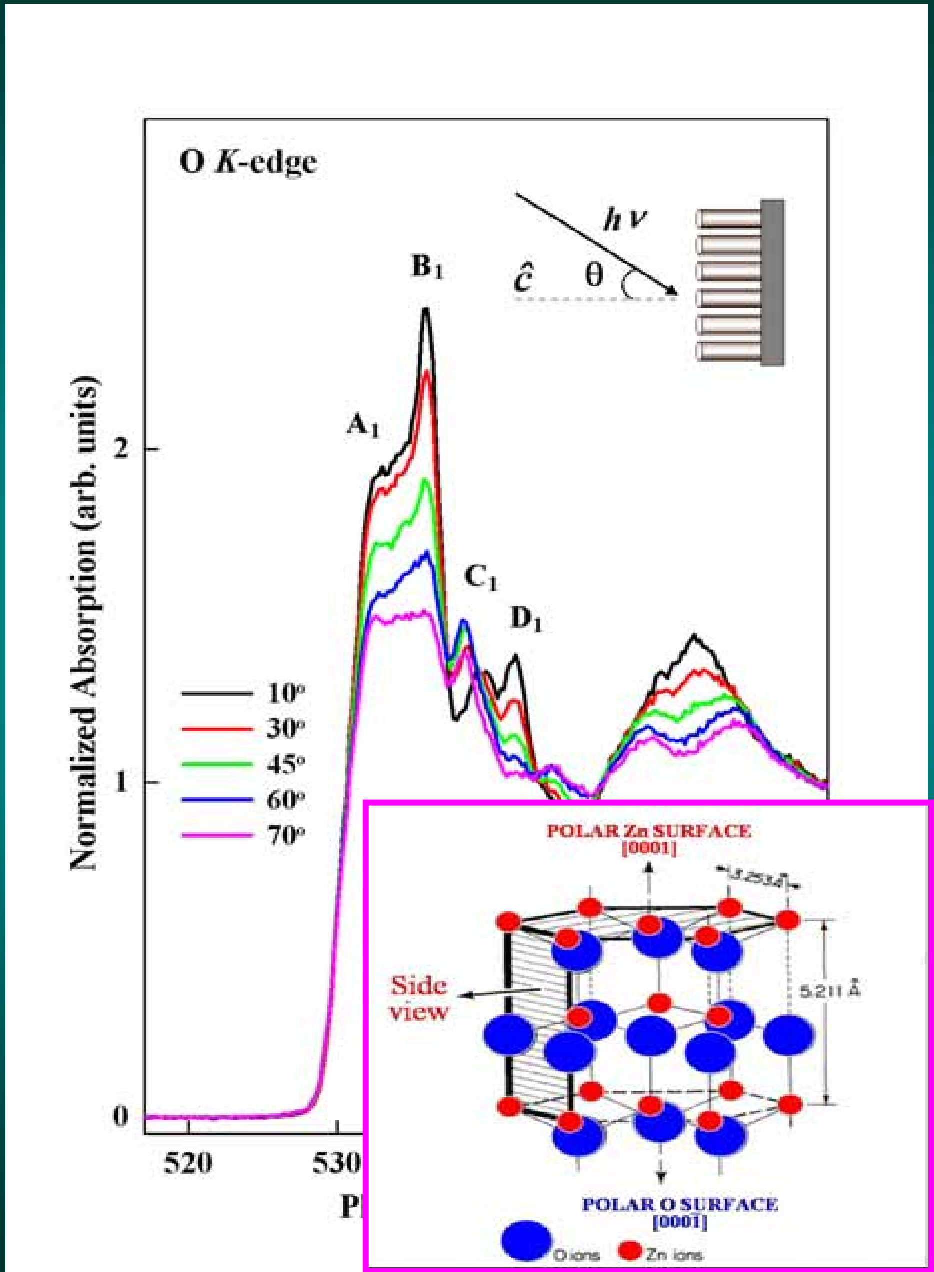
TB-calculation

t_{2g} (TM 3d; O 2pπ)	**A**
e_g (TM 3d; O 2pσ)	**B**
a_{1g} (TM 4s; O 2pσ)	**C**
t_{1u} (TM 4p; O 2pπ)	**D**

Aligned ZnO Nanowires

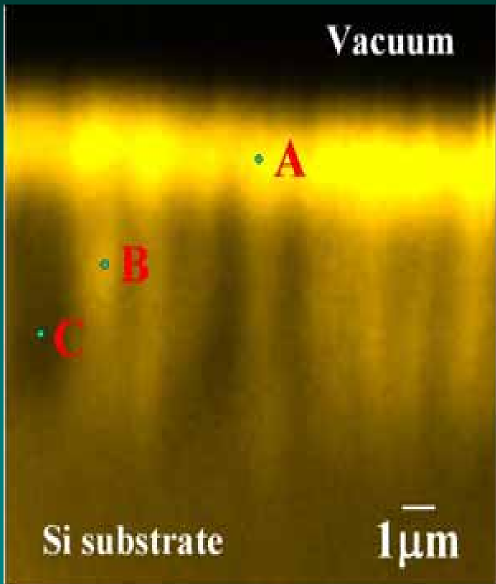


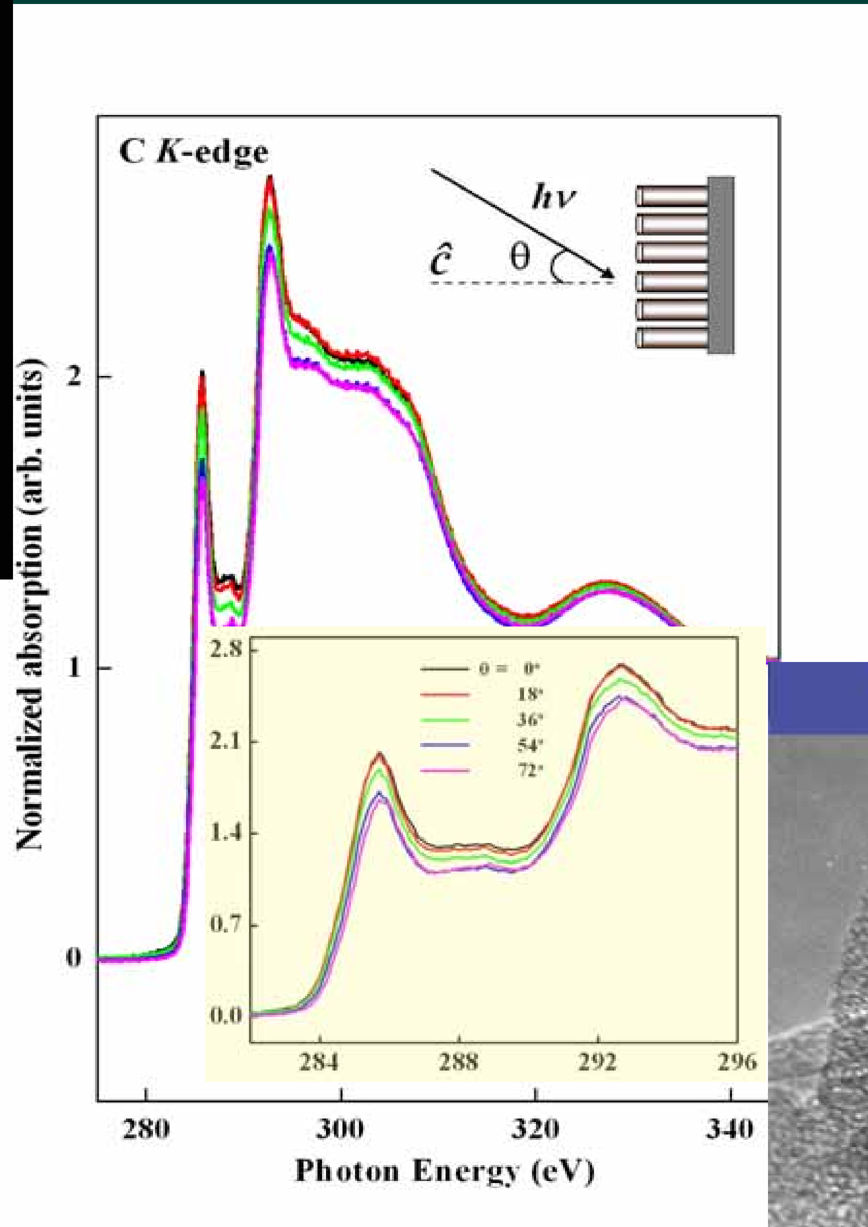
J. W. Chiou *et. al.*, Appl. Phys. Lett. 84, 3462 (2004)

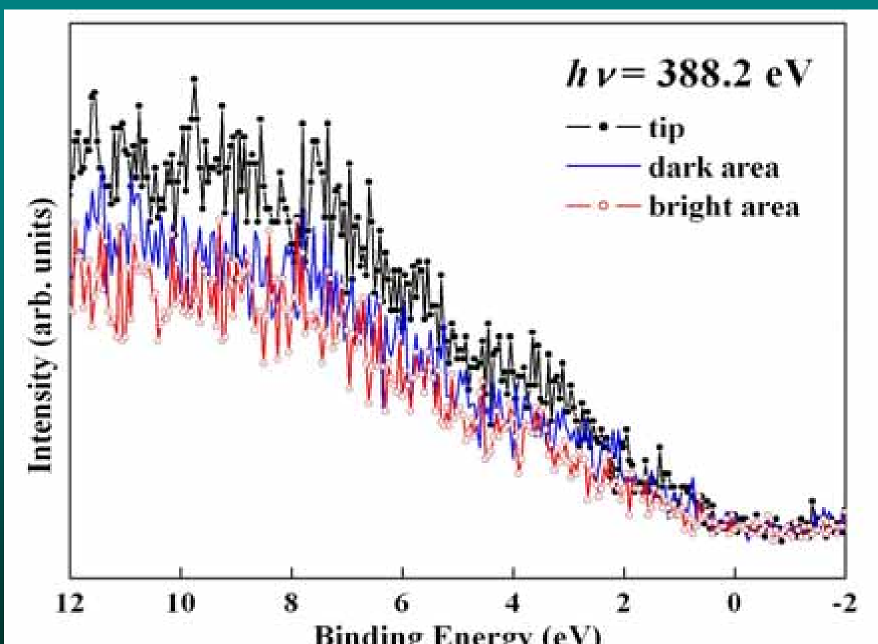


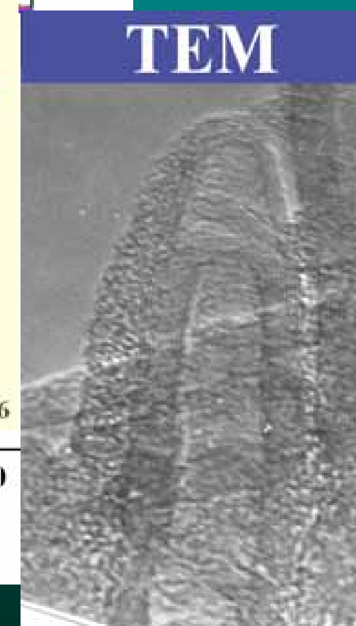
Y. X. Liu *et al.*, Solid State Commun. 121, 531 (2002).

Carbon Nanotubes



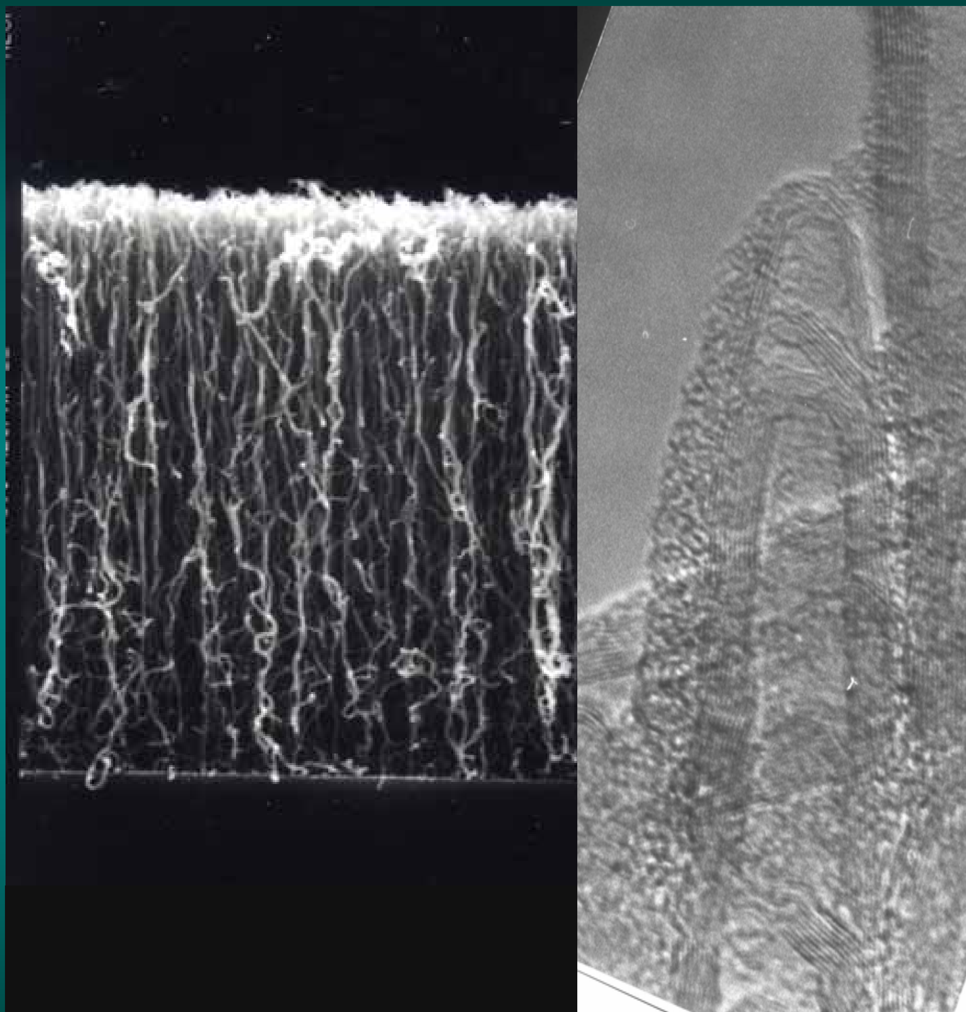




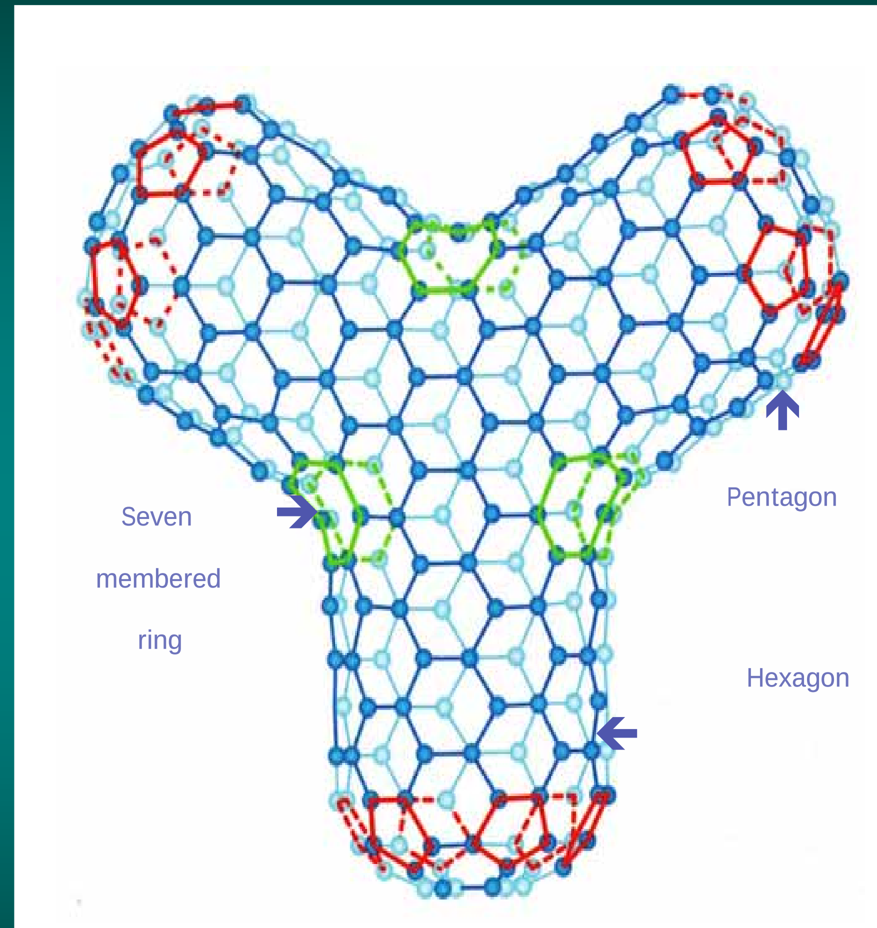


J. W. Chiou *et al.*, Appl. Phys. Lett. 81, 4189 (2002)

SEM & TEM Images



The TEM image shows that the radius of tip decreases gradually



Probably insertion of five- or seventh-membered rings and dangling bonds

⇒ the tip has a much larger curvature

Electronic Structure and Localized States at Carbon Nanotube Tips

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Max-Planck-Institut für Metallforschung, Seestraße 92, 70174 Stuttgart, Germany

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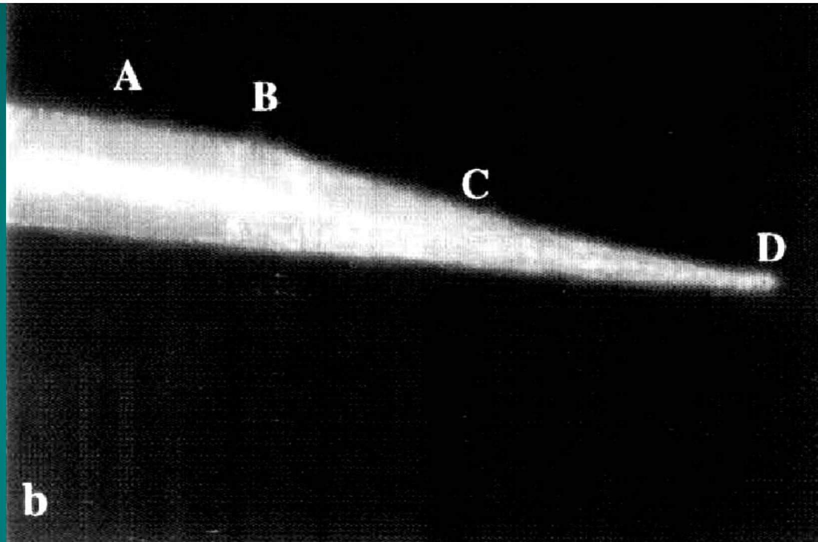
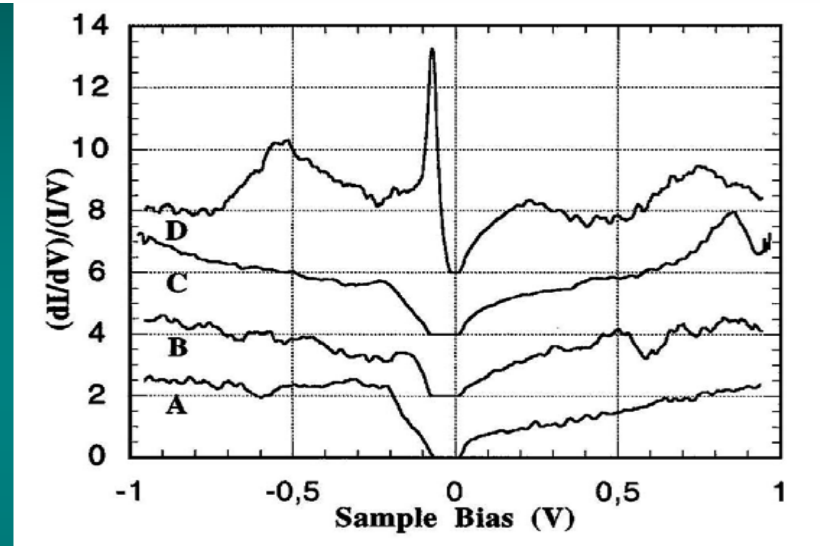
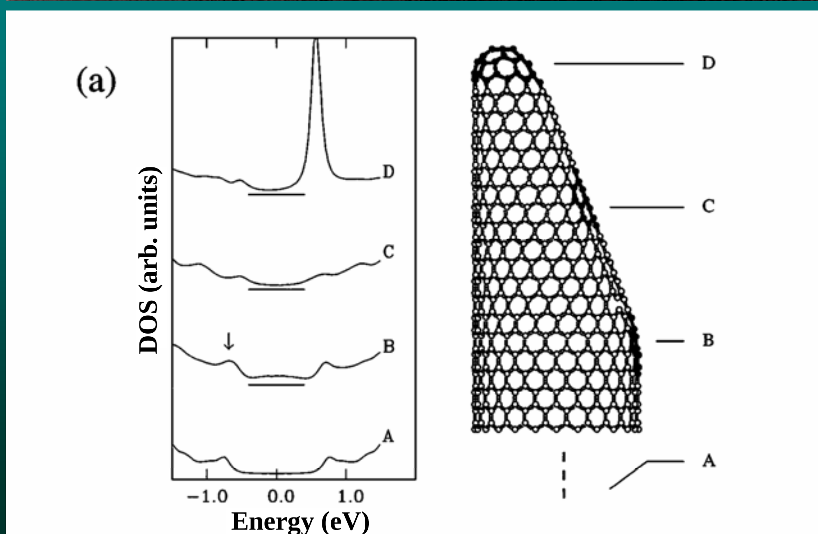
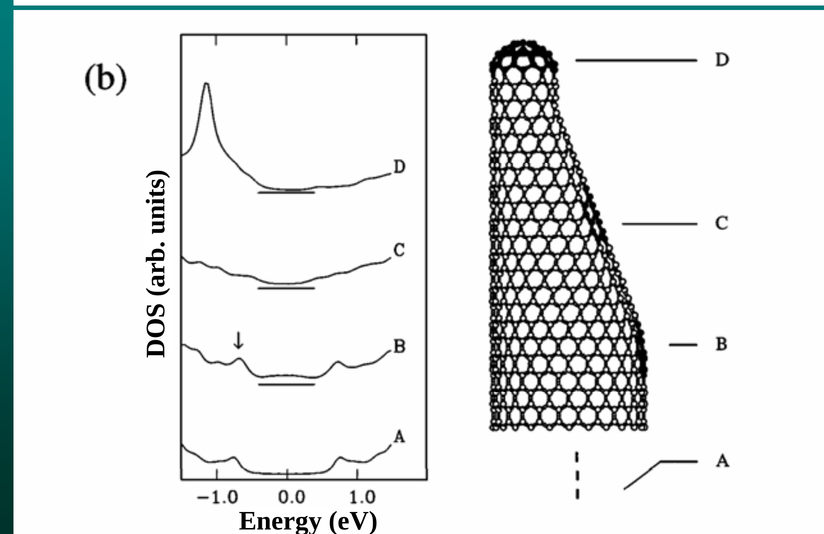
Institut Romand de Recherche Numerique en Physique des Materiaux IN-Ecublens, CH-1015 La
(Received 12 August 1996; revised manuscript received 25 November 1996

PRL 78, 2811 (1997)



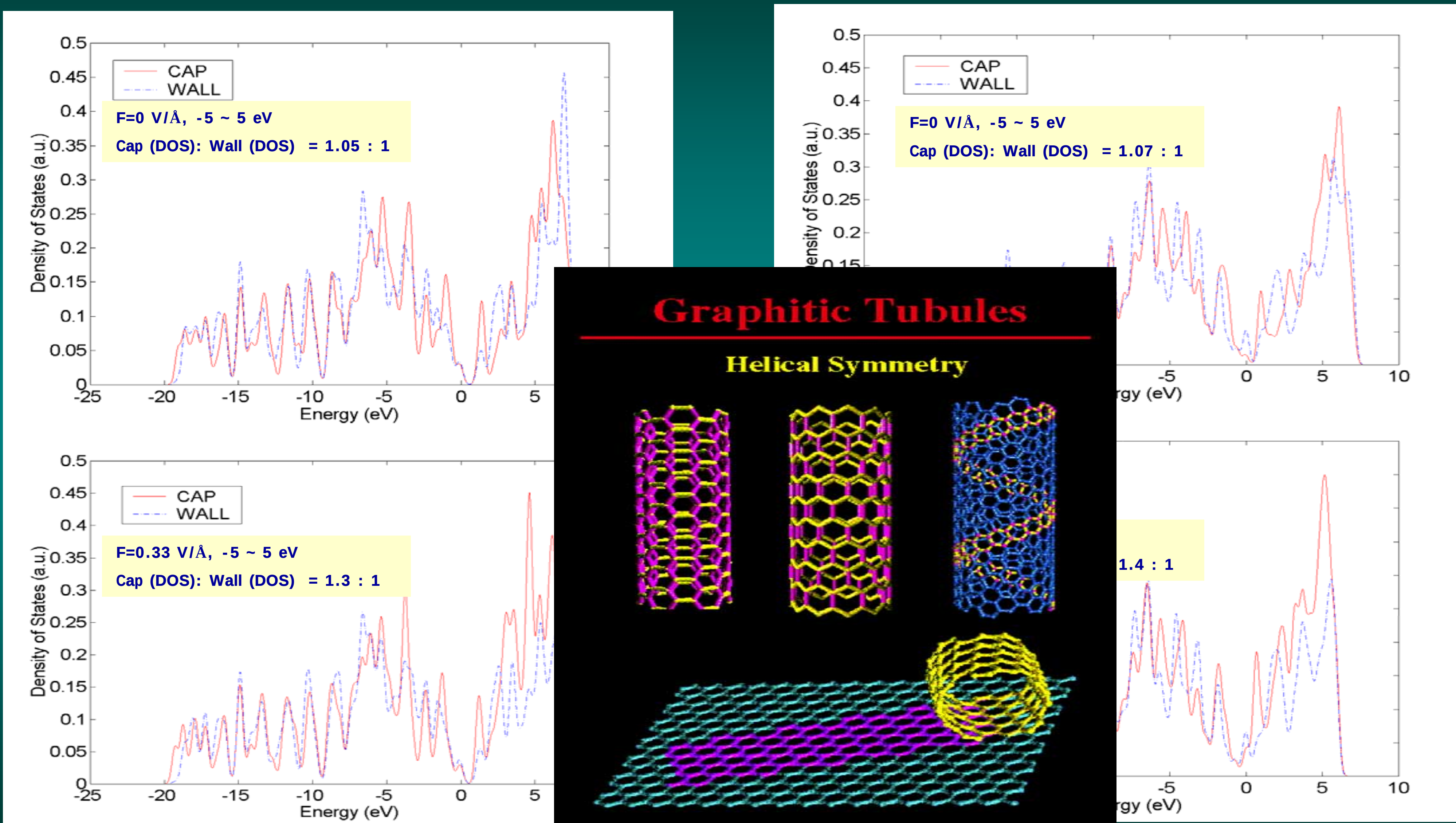






Field Enhancement of Localized DOSs at (5,5) CNT Tips

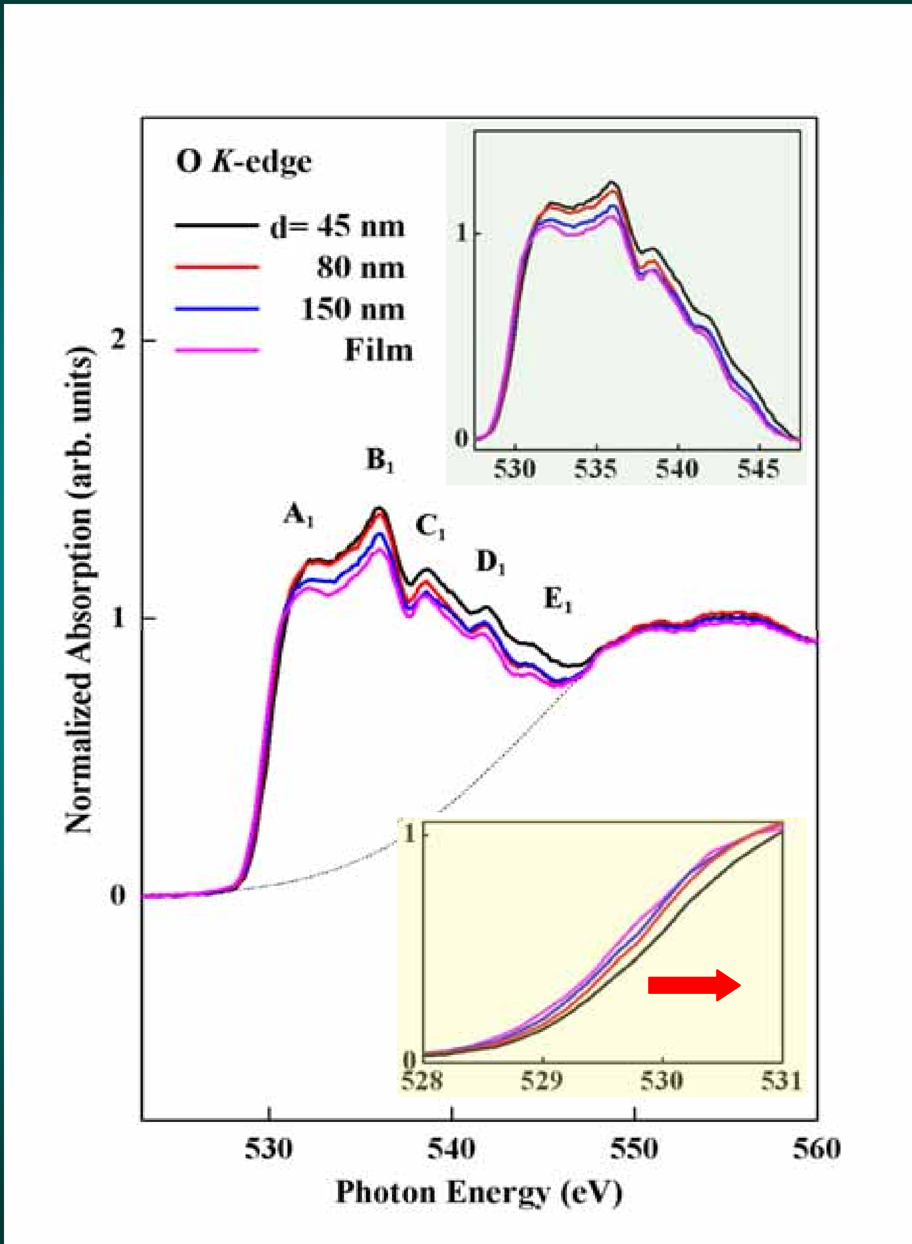
Field Enhancement of Localized DOSs at (9,0) CNT Tips

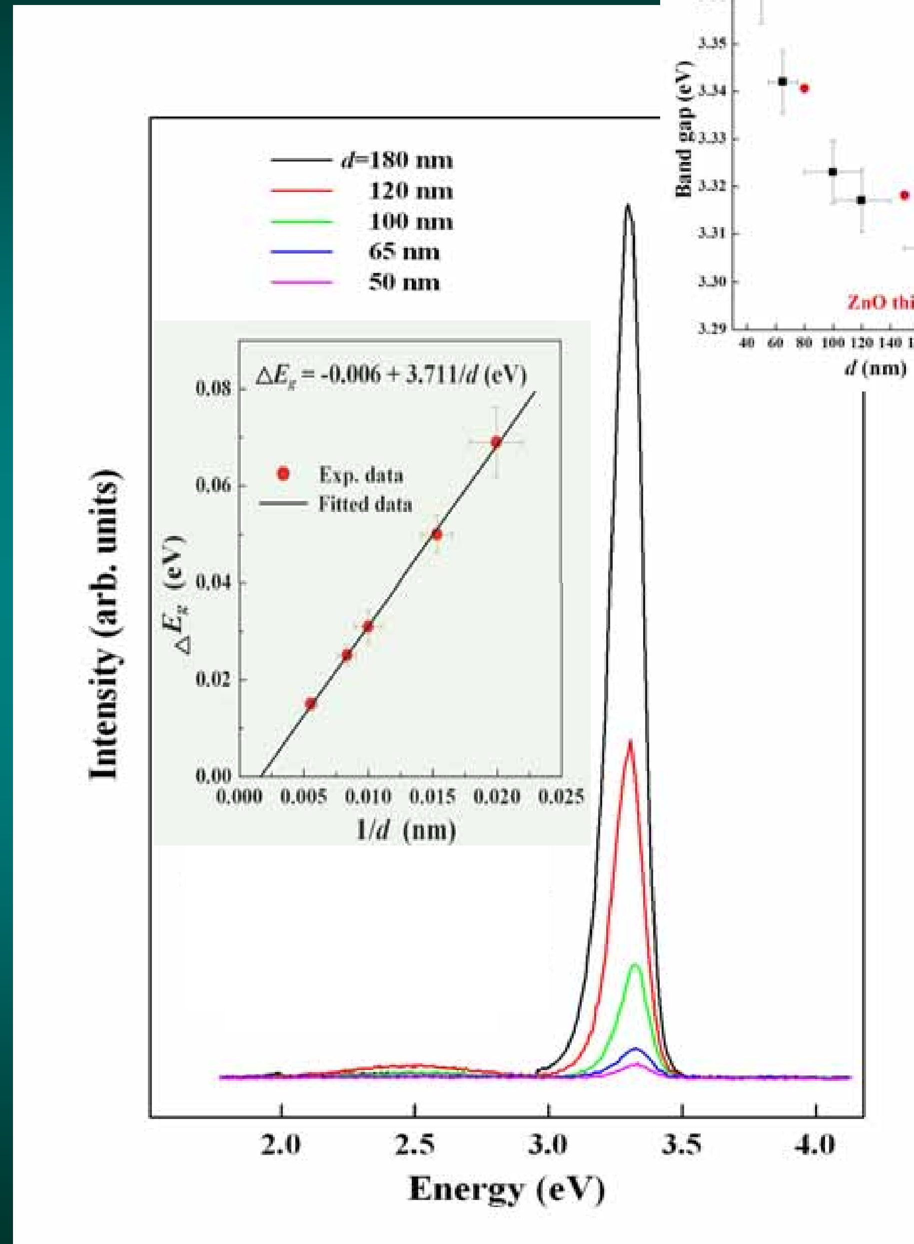


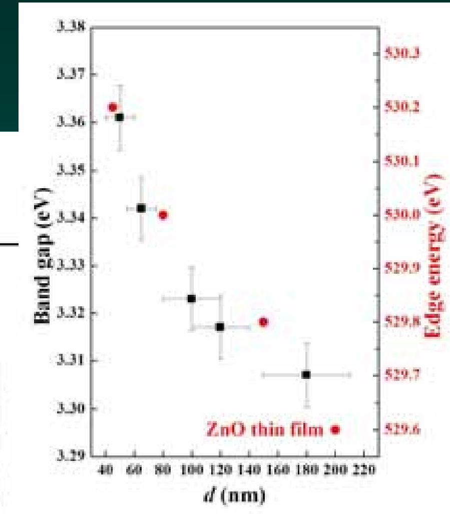
DOS is normalized to one atom

C. W. Chen *et al.*, Appl. Surf. Sci. 228, 143 (2004)

Diameter-dependent ZnO Nanorods



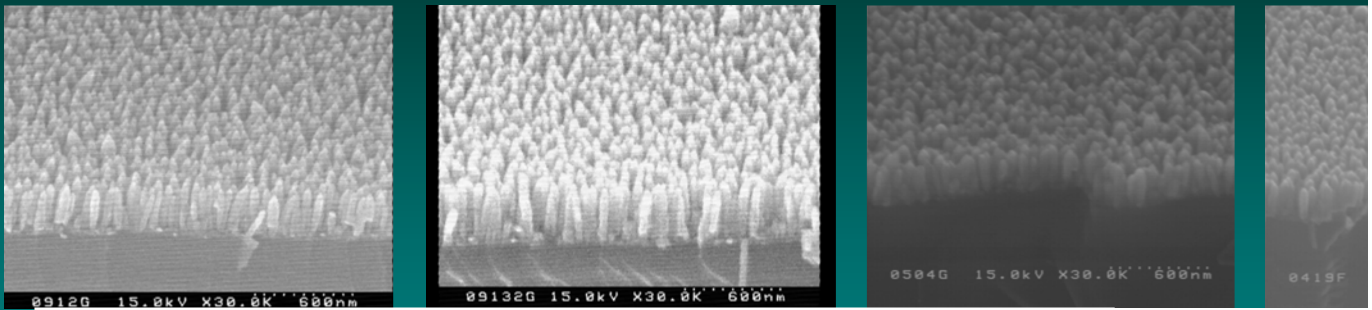


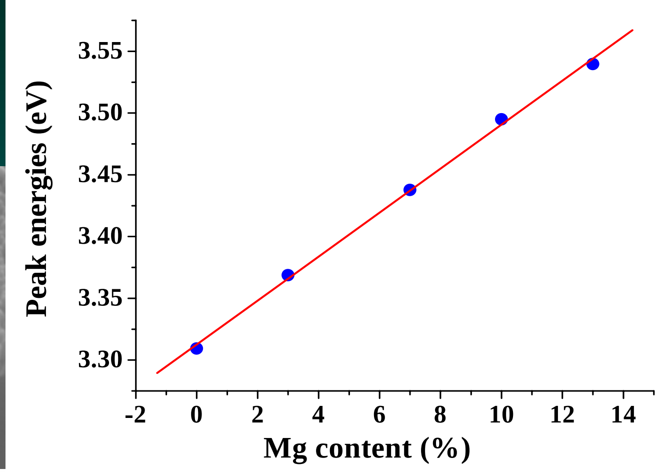


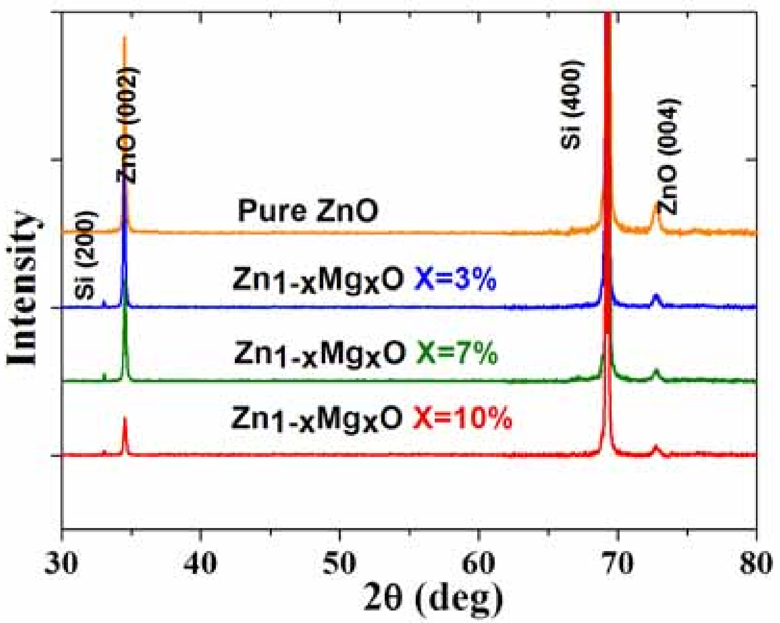
J. W. Chiou *et. al.*, Appl. Phys. Lett. 85, 3220 (2004)

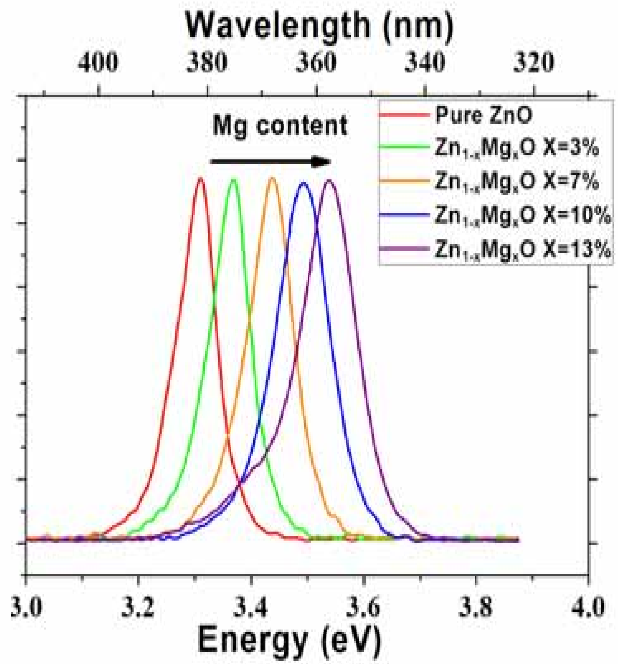
C. W. Chen *et. al.*, Appl. Phys. Lett. 88, 241905 (2006)

$Zn_{1-x}Mg_xO$ Nanorods







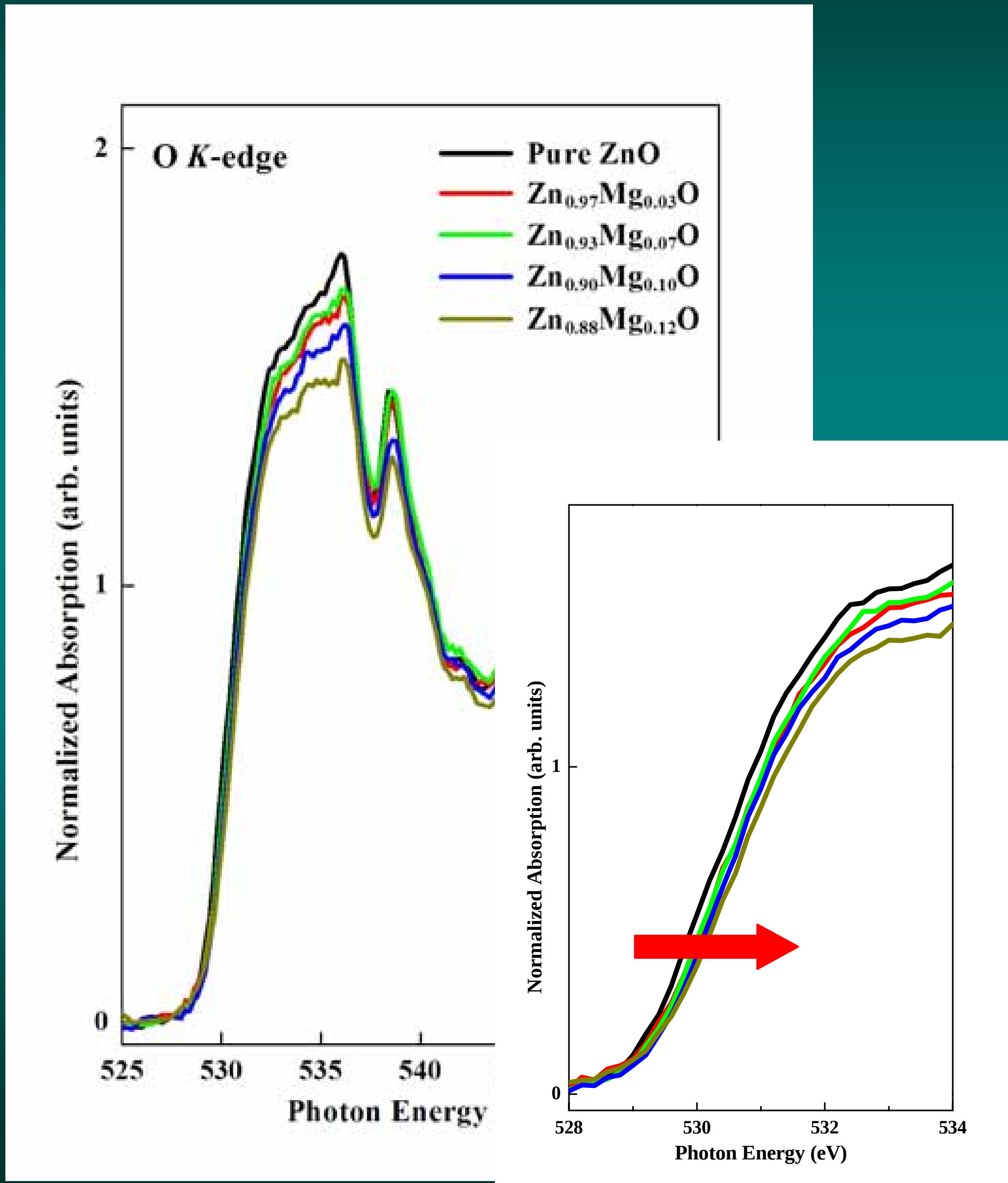


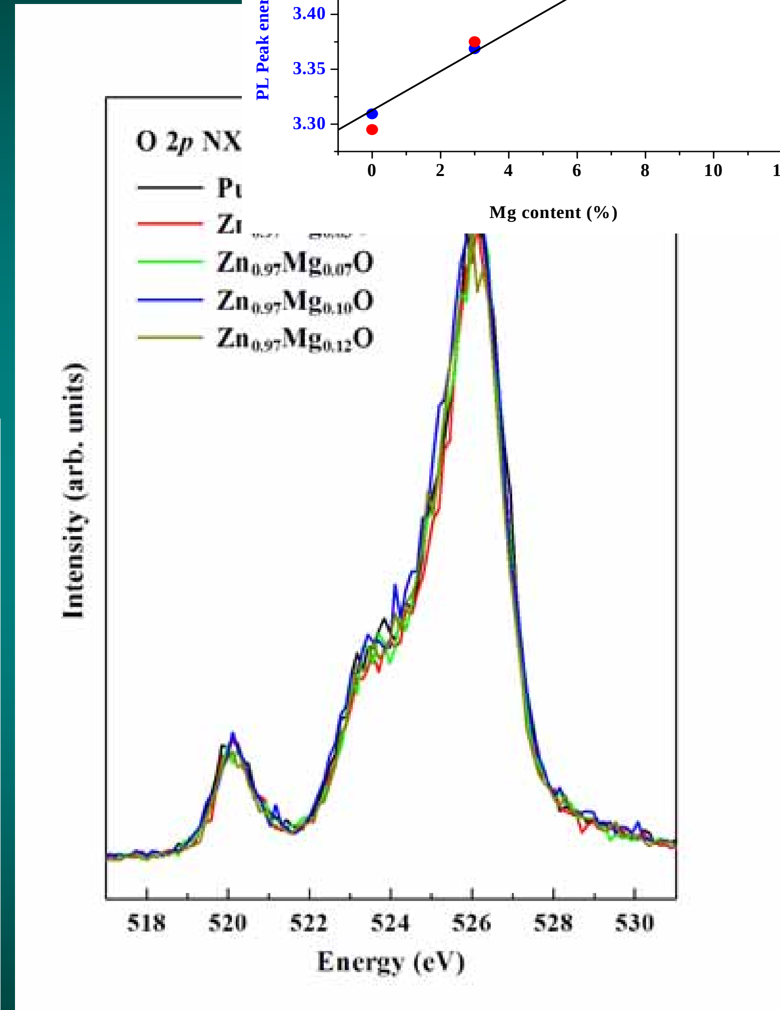
J. J. Wu *et al.*, Appl. Phys. Lett. 85, 1027 (2004)

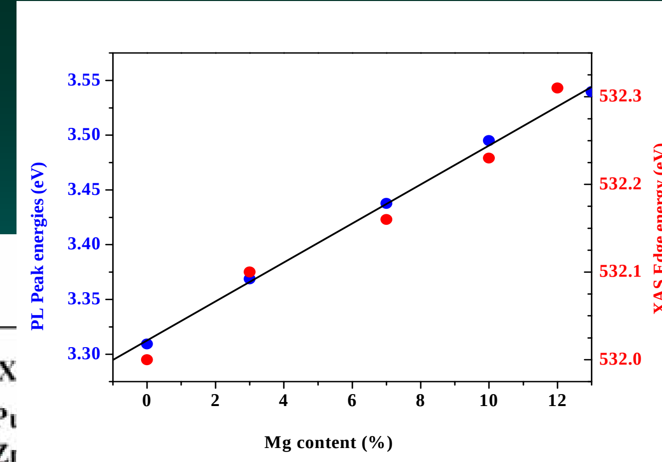
Mg ↑ emission energy ↑

Band gap increasing ↑ ?

$Zn_{1-x}Mg_xO$ Nanorods

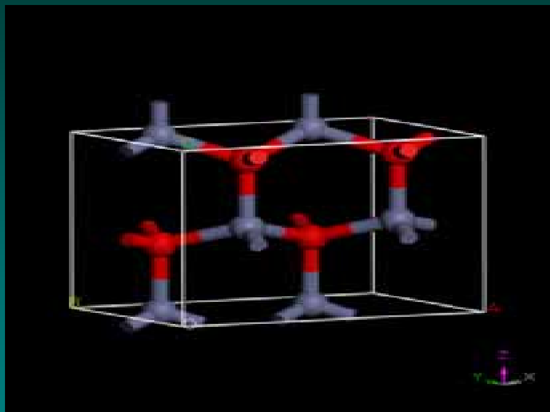




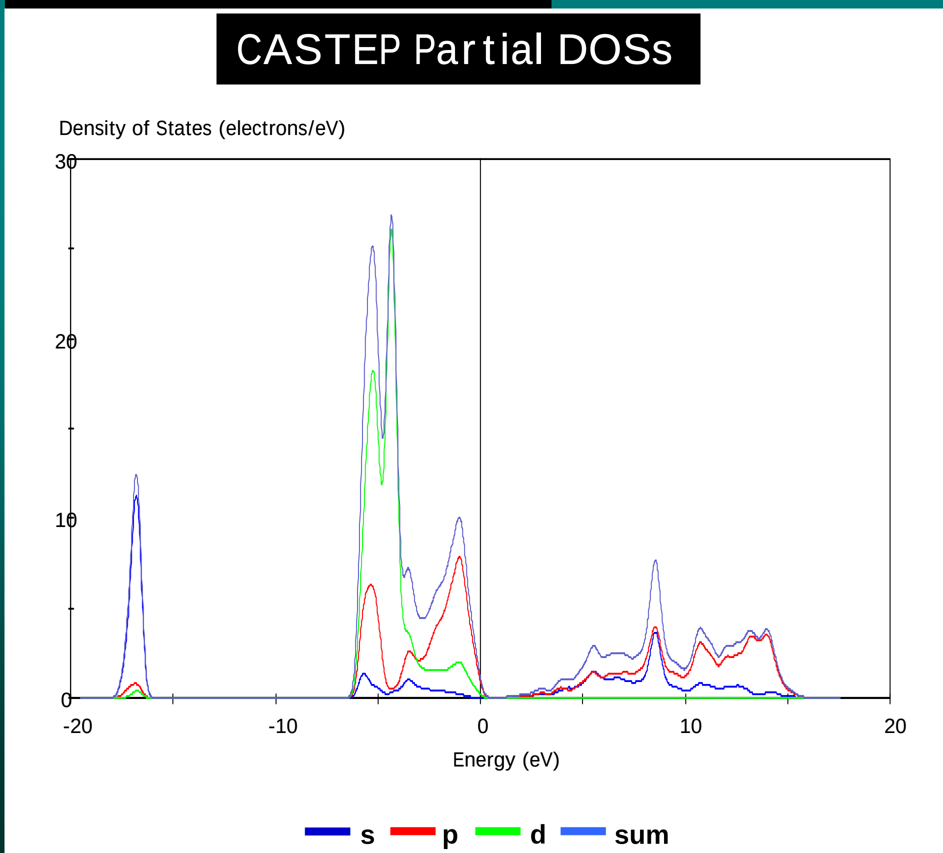


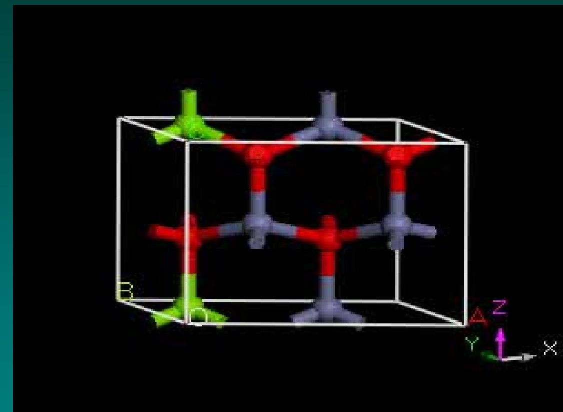
CBM/Band gap increasing with increasing Mg content

Density of States

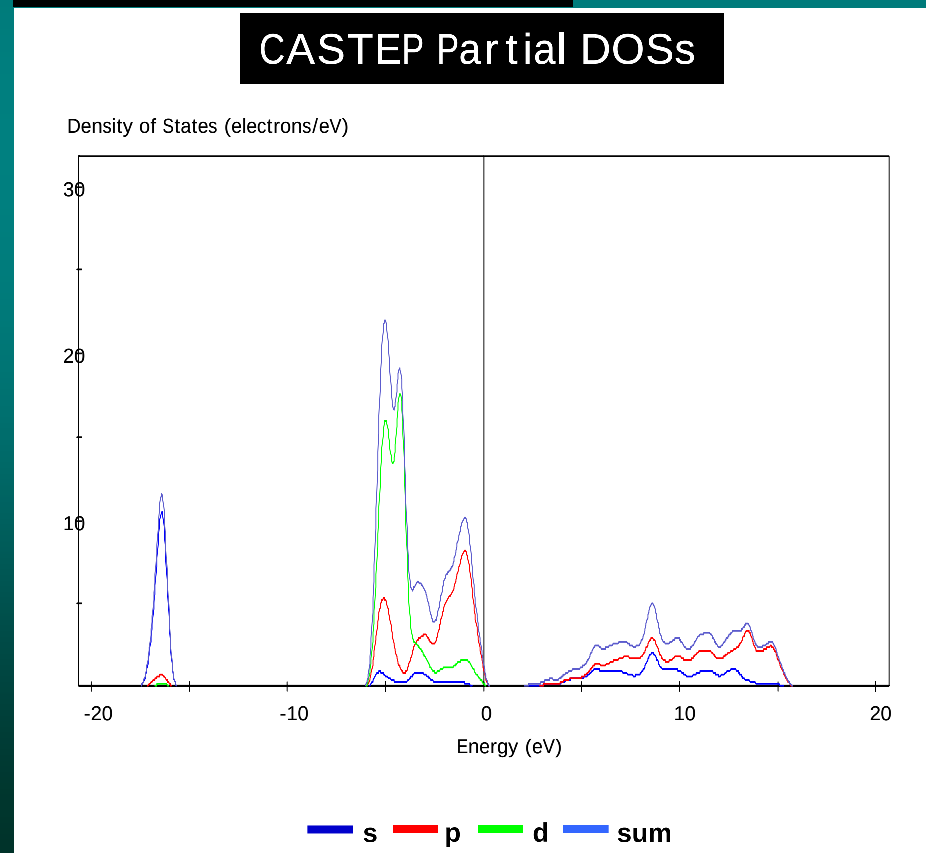


ZnO

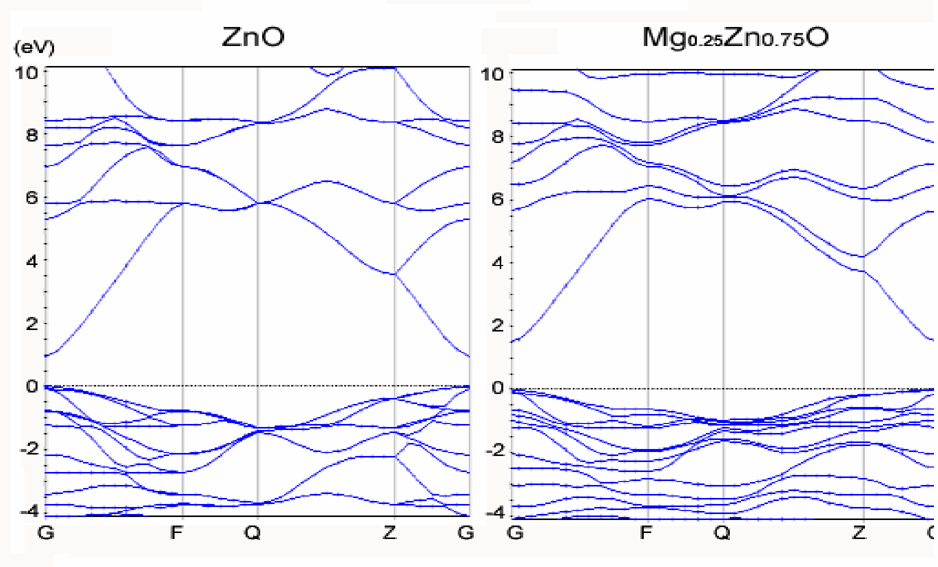


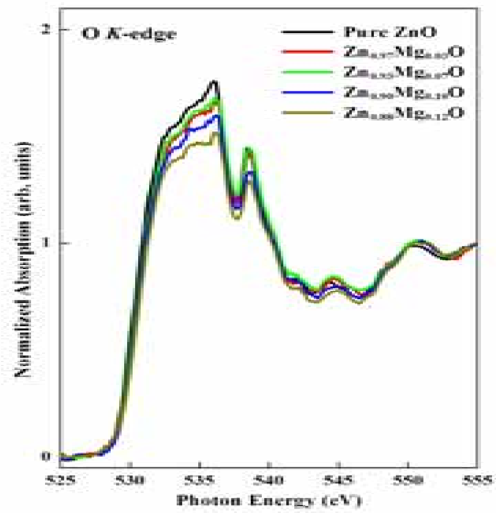


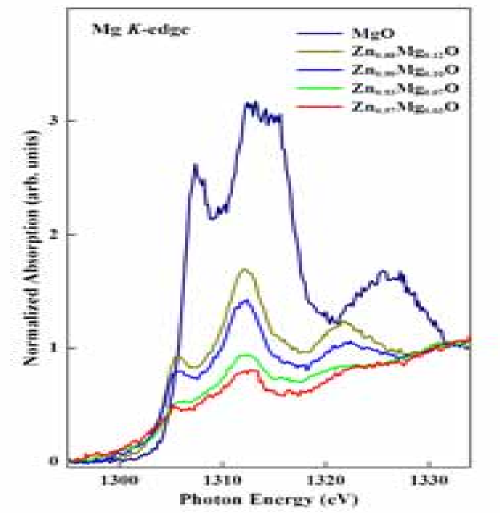
Mg: ZnO



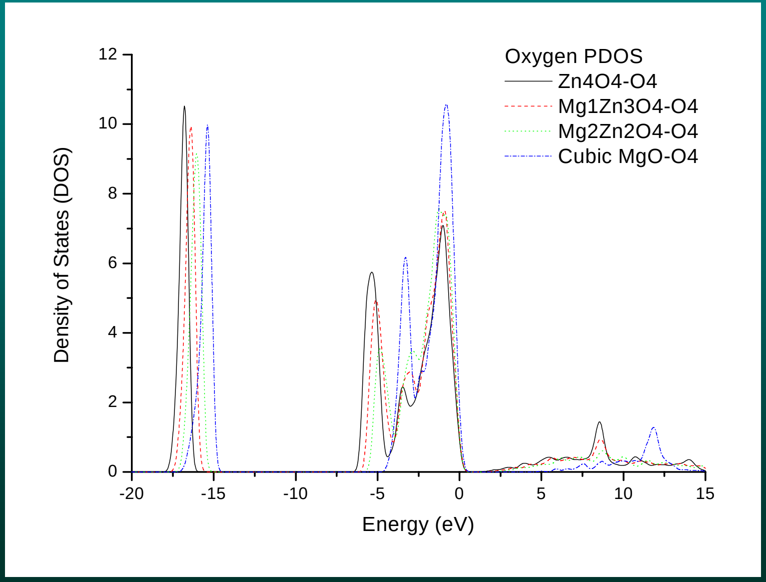
Band Structure



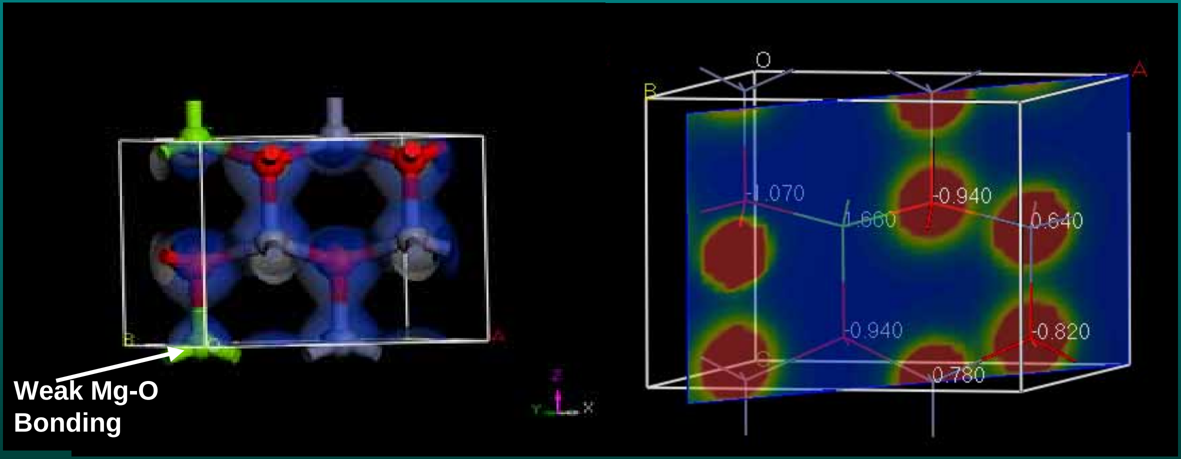




Density of States



Electron Density



Larger charge transfer from Mg → O

More localized O *p* orbital in the Mg addition

Dilute Magnetic Semiconductor (DMS)

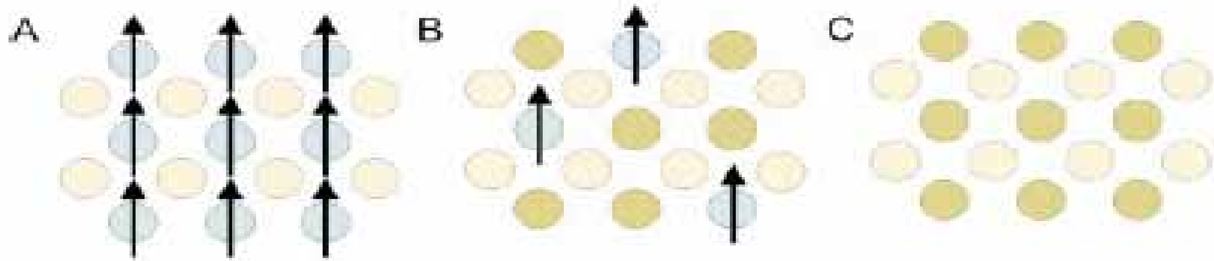


Fig. 1. Three types of semiconductors: (A) a magnetic semiconductor, in which a periodic array of magnetic element is present; (B) a diluted magnetic semiconductor, an alloy between nonmagnetic semiconductor and magnetic element; and (C) a nonmagnetic semiconductor, which contains no magnetic ions.

H. Ohno *et al*., Science 281, 951 (1998)

Theoretical Predication

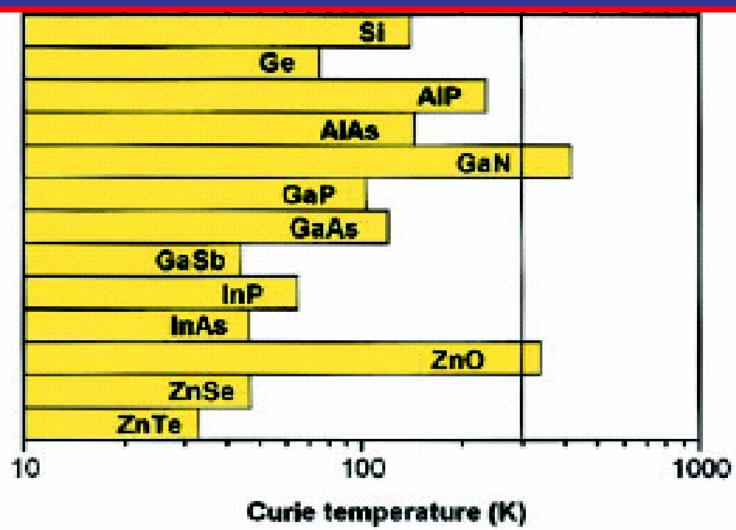


Fig. 3. Computed values of the Curie temperature T_C for various p-type semiconductors containing 5% of Mn and 3.5×10^{20} holes per cm^3.

Dietl *et al*., Science 287, 1019 (2000)

Experimental Results

- **$Zn_{1-x}Co_xO$ Film $T_c \approx 300$ K @ x=0.15**
  [K. Ueda *et al.*, Appl. Phys. Lett. 79, 988 (2001)]
- **$Ti_{1-x}Co_xO_2$ Film $T_c > 400$ K @ x=0.07**
  [Y. Matsumoto et al., Science 291, 854 (2001)]

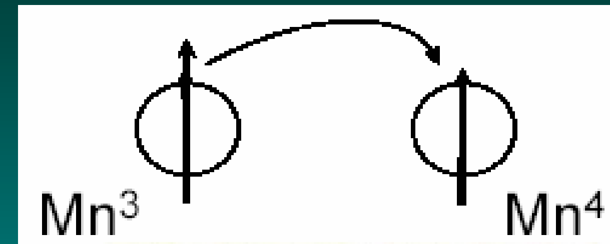
……

Controversy: ***High-temperature n-type ferromagnetic ordering arises originally from Co clusters/precipitates or DMS intrinsic properties ?***

Exchange Interactions

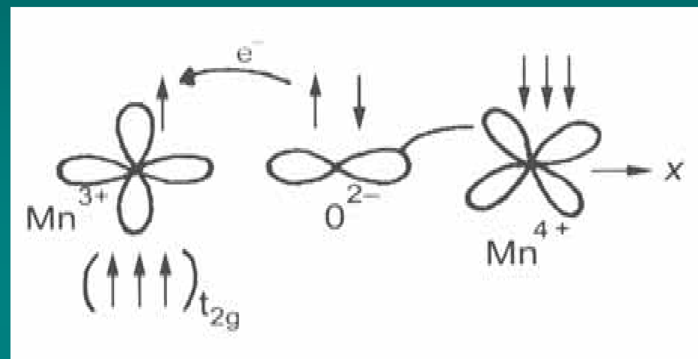
Direct exchange

Nearest-neighbor interaction, ferromagnetic, requires mixed cation valence for $3d^n$-$3d^{n+1}$ fluctuations.



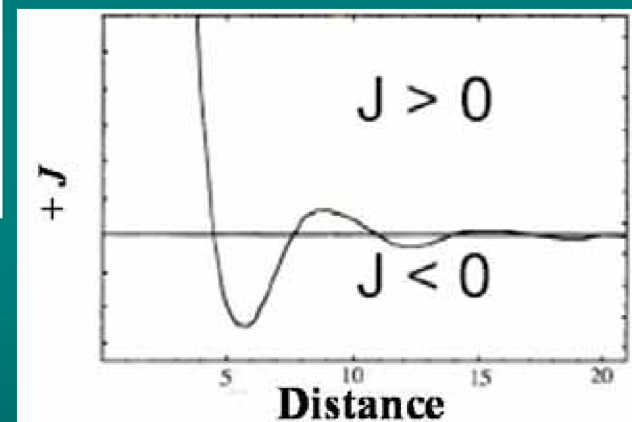
Superexchange

Nearest-neighbor interaction, usually antiferromagnetic.



RKKY interaction

Long-range oscillatory interaction.

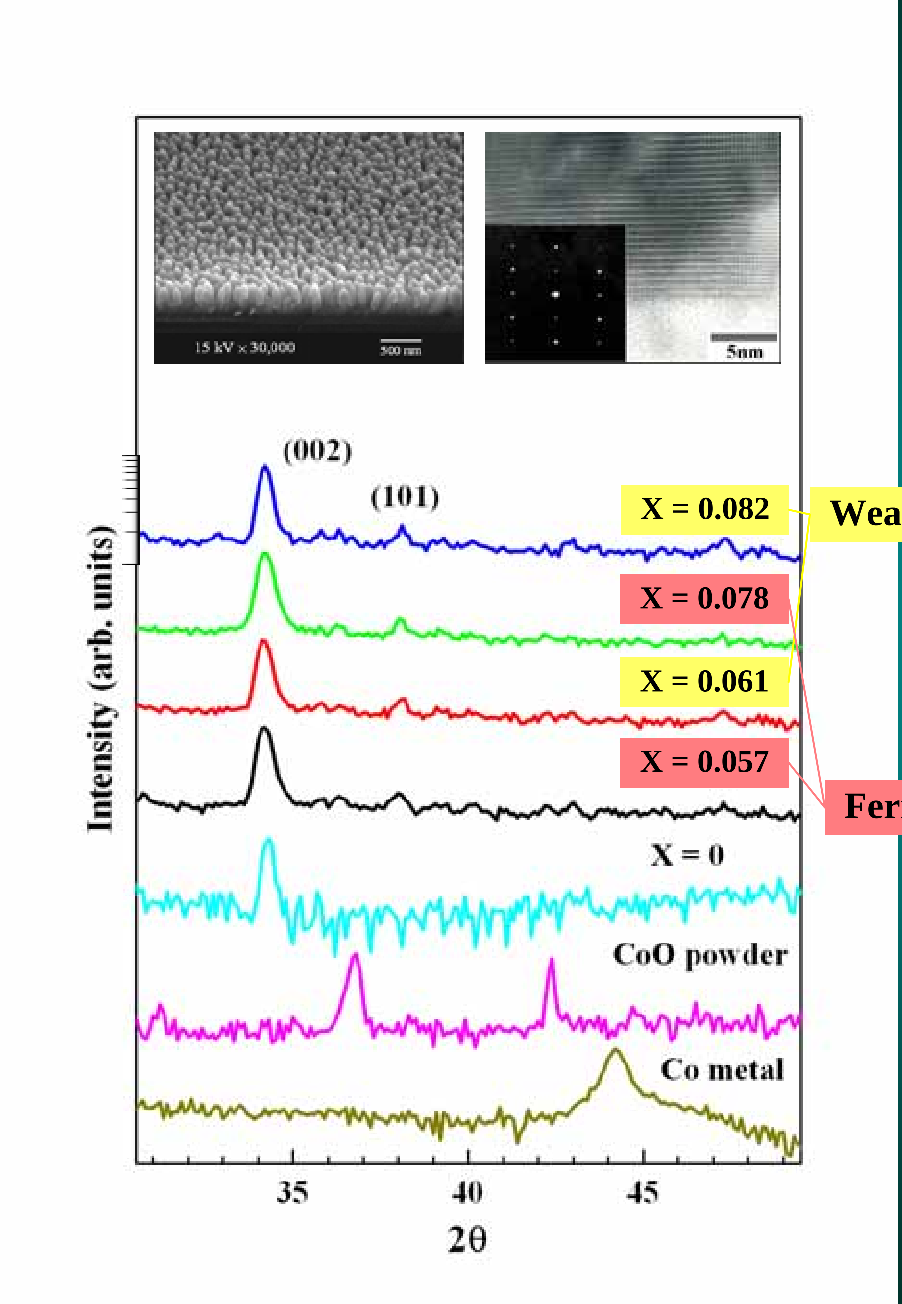


There are two sources of magnetism in dilute n-type ferromagnetic oxides :

- *One associated with 3d dopant cations*
- *The other associated with defects in the oxides*

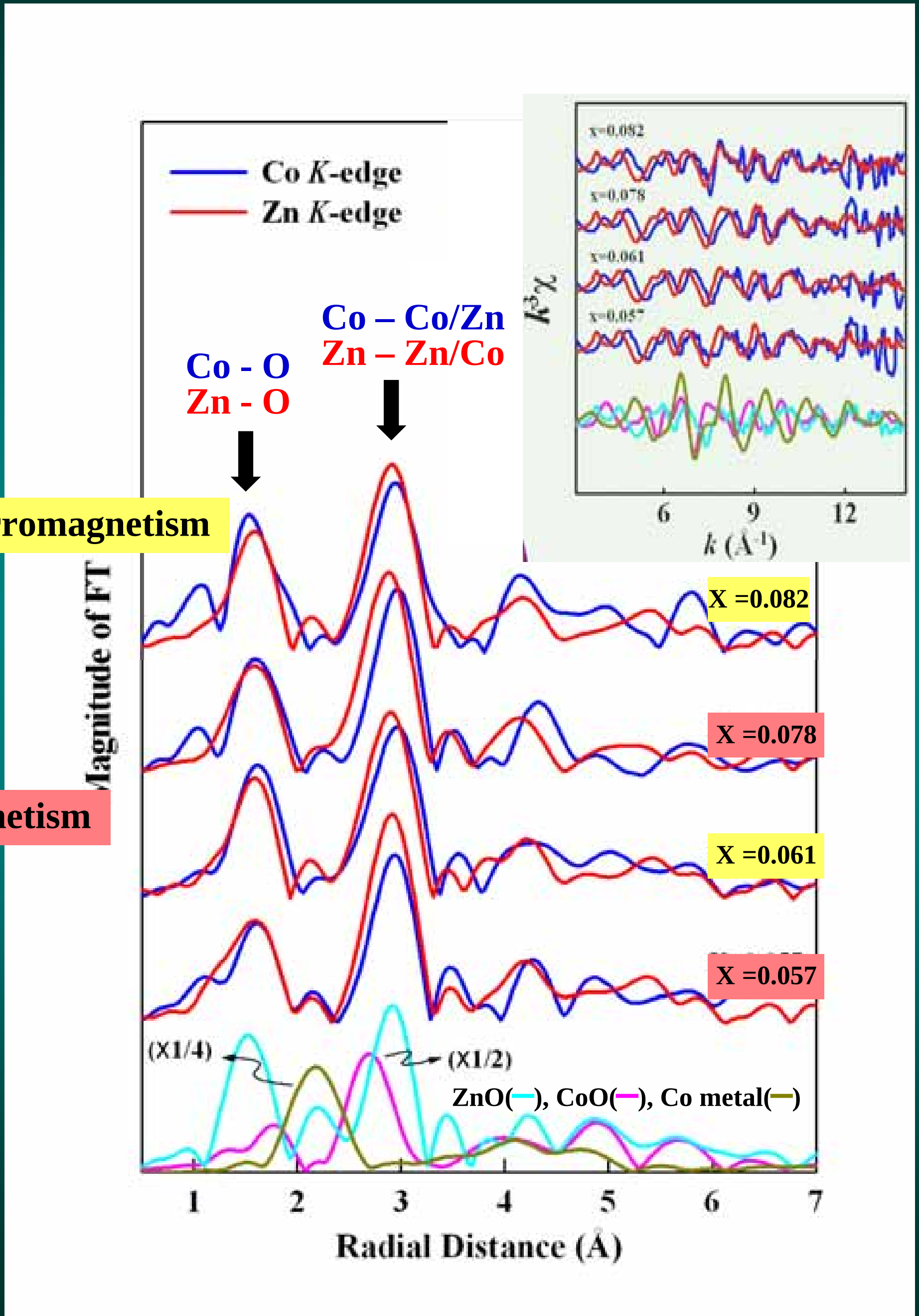
J. M. D. Coey et al., Natural Materials 4, 173 (2005)

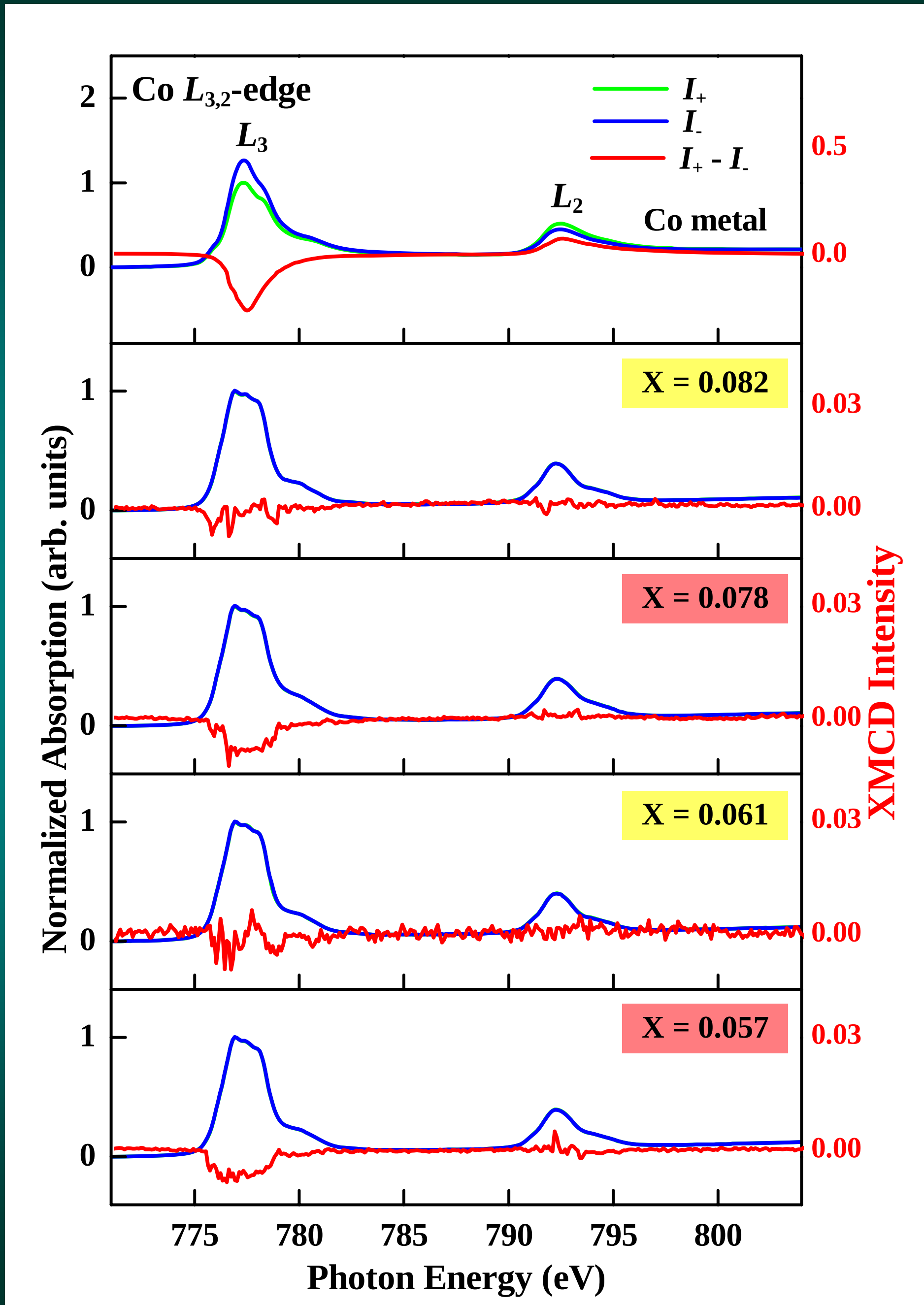
$Zn_{1-x}Co_xO$ Nanorods



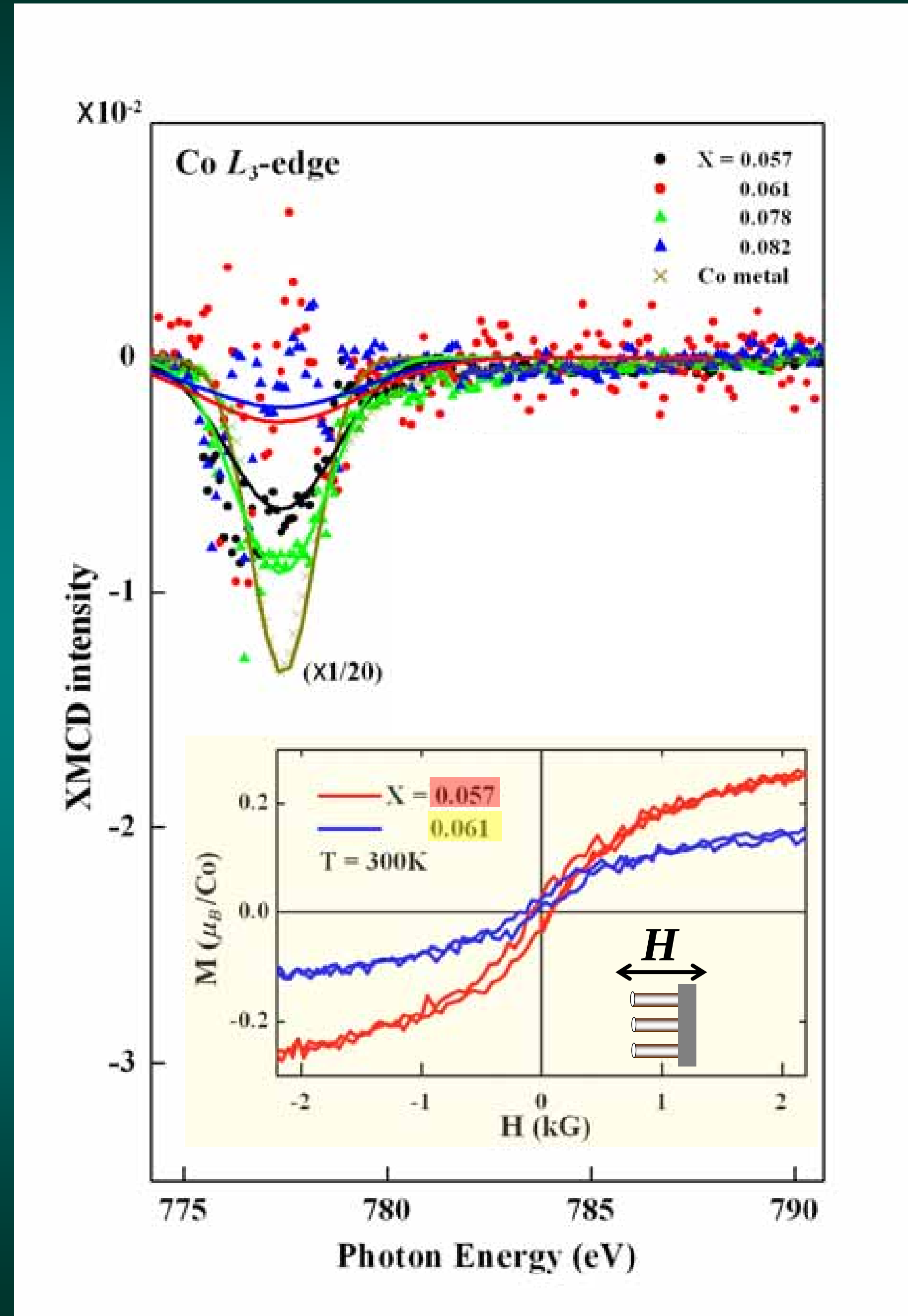
Weakly-Ferromagnetism

Ferromagnetism



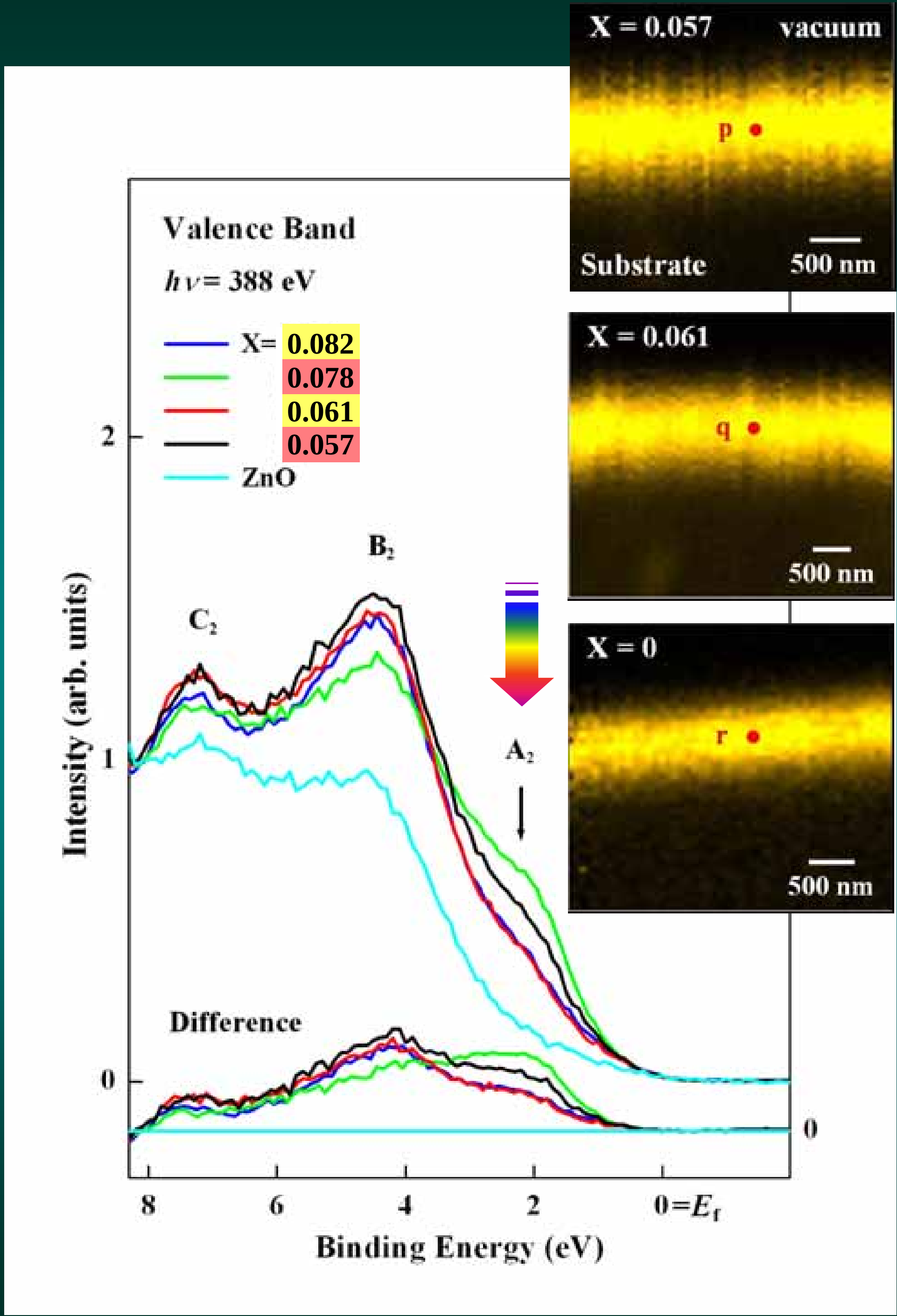


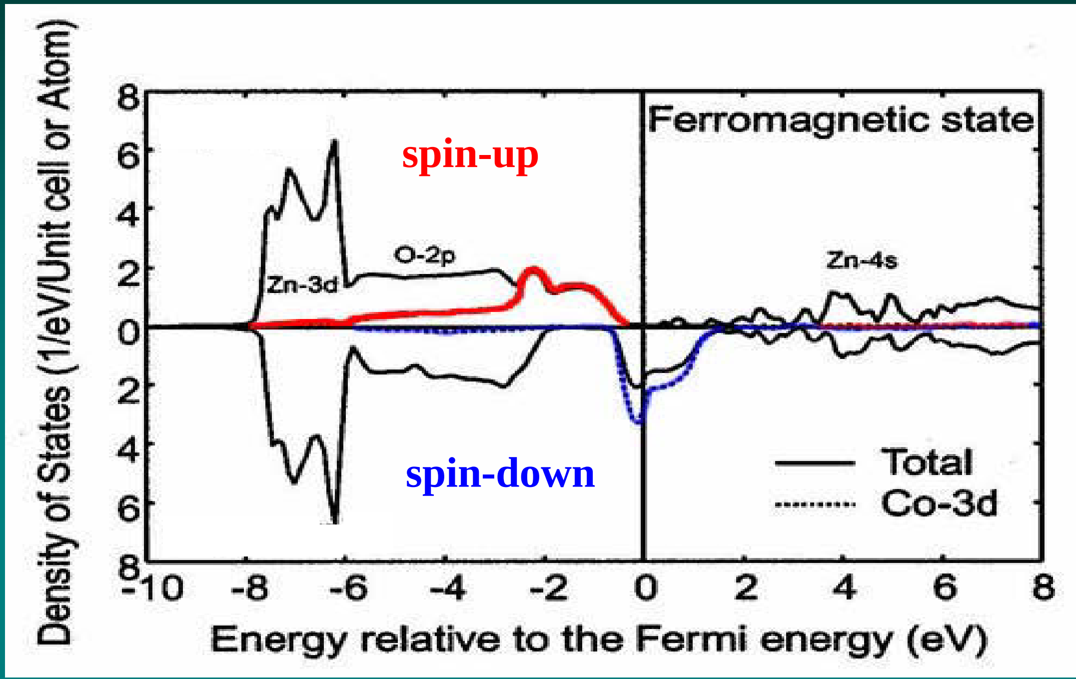
Co $L_{3,2}$-edge
L_3
L_2
I_+
I_-
$I_+ - I_-$
Co metal
X = 0.082
X = 0.078
X = 0.061
X = 0.057
Normalized Absorption (arb. units)
XMCD Intensity
Photon Energy (eV)



X10^{-2}
Co L_3-edge
X = 0.057
0.061
0.078
0.082
Co metal
(X1/20)
XMCD intensity
X = 0.057
0.061
T = 300K
M (μ_B/Co)
H (kG)
H
Photon Energy (eV)

$Zn_{1-x}Co_xO$



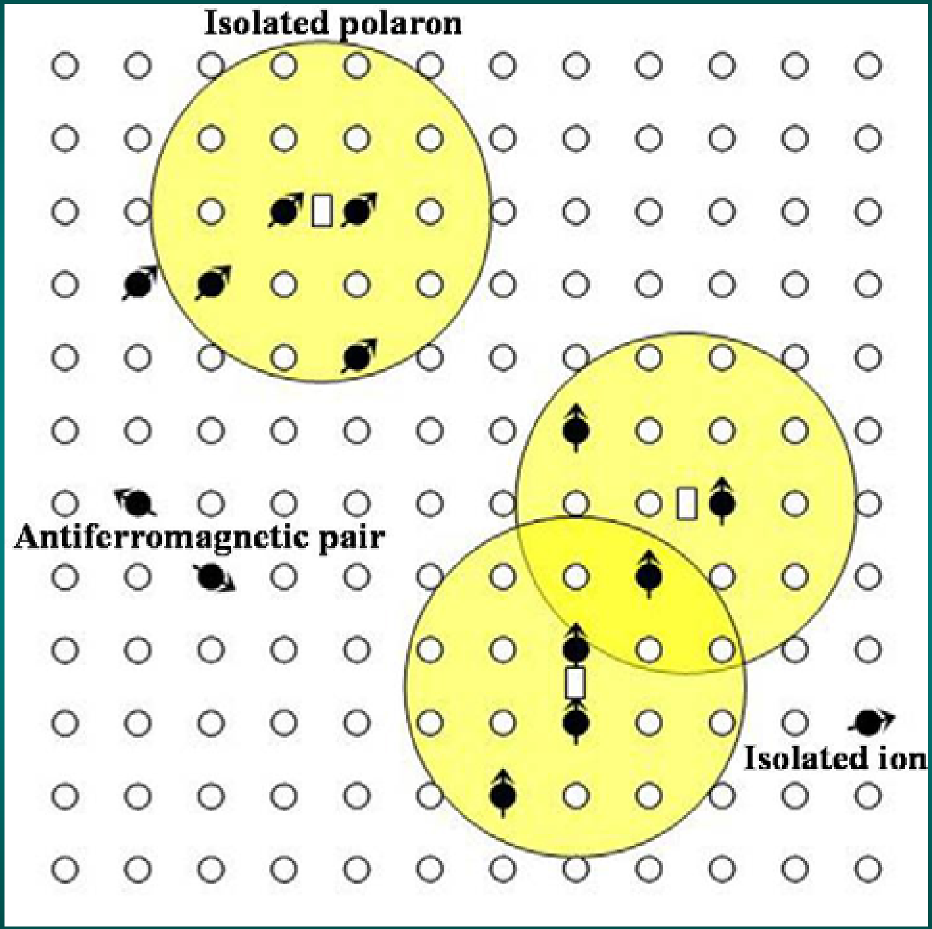


Local spin-density approximation

K. Sato and H. Katayama-Yoshida, Jpn J. Appl. Phys., L334 (2001)

- Since a larger intensity of feature A_2 corresponds to more localized Co 3*d* orbitals and consequently larger Co magnetic moment.

Exchange Interactions



$$-J_{sd}S.s|\psi(r)|^2\Omega$$

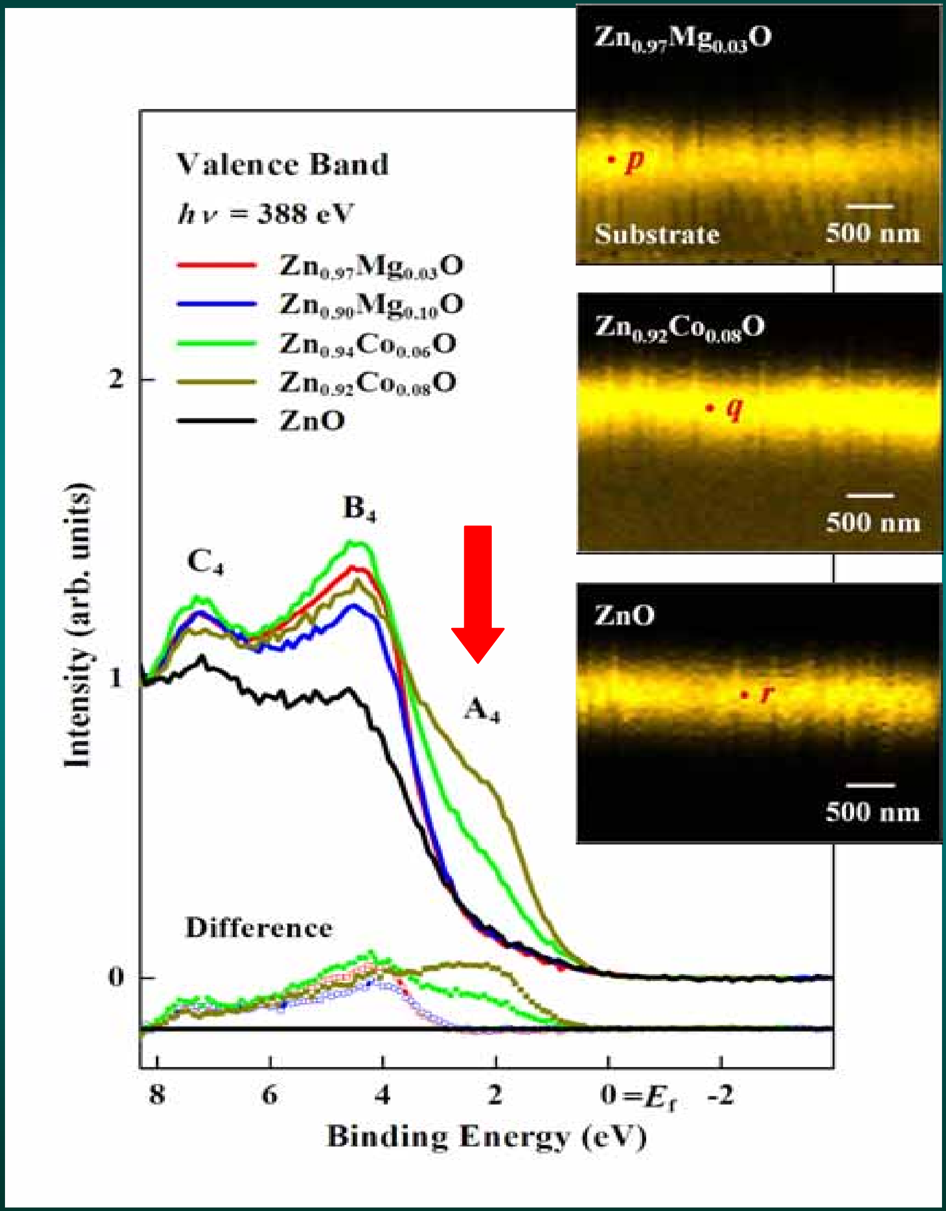
$$T_C = \left[S(S+\mathbf{1})s^2x\delta n/\mathbf{3}\right]^{1/2} J_{sd}\omega_c/k_B$$

Defects were formed bound magnetic polarons and coupled with Co 3d moments

The overlapping of two similar magnetic polarons to induce spin-spin interactions between Co ions

J. M. D. Coey *et. al.*, Nature Materials 4, 173 (2005)

$Zn_{1-x}Co_xO$ v.s. $Zn_{1-x}Mg_xO$



J. W. Chiou *et. al.*, Appl. Phys. Lett. 89, 043121 (2006)

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