物構研シンポジウム'09「放射光・中性子・ミュオンを用いた表面・界面科学の最前線」
平成21年11月17～ 18 日，つくば国際会議場エポカル

軟X線磁気円二色性によるスピントロニクス材料の研究

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分光測定

片岡隆史，Vijay Raj Singh，山崎陽，小林正起（東大理・新領域）
小出常晴，朝倉大輔，間宮一敏（物構研PF）
竹田幸治，岡根哲夫，大河内拓雄，斎藤祐児 (原子力機構)
F.-H. Chang, C.-S. Yang, L. Lee, H.-J. Lin, D.-J. Huang, C.T. Chen（NSRRC, Taiwan）

試料

田中雅明，大矢 忍，ファムナムハイ（東大工）$Ga_{1-x}Mn_xAs$
福村知昭，山田 良則，上野 和紀，川崎雅司（東北大金研・WPI材料機構）$Ti_{1-x}Co_xO_2$
黒田眞司，石川弘一郎，張 珂（筑波大物質工）$Zn_{1-x}Cr_xTe$
K.V. Rao, M. Kapilashrami, L. Belova (Royal Inst Tech, Swedem) $Zn_{1-x}Mn_xO$薄膜
D. Karmakar (BARC), S.K. Mandal, T.K. Nath (IIT Kharagpur), I. Dasgupta (IACS)
$Zn_{1-x}Fe_xO$, $Zn_{1-x}(Fe, Co)_xO$, $Zn_{1-x}(Mn, Co)_xO$ ナノ粒子

理論

田中 新（広大先端物質）多重項計算，クラスター計算

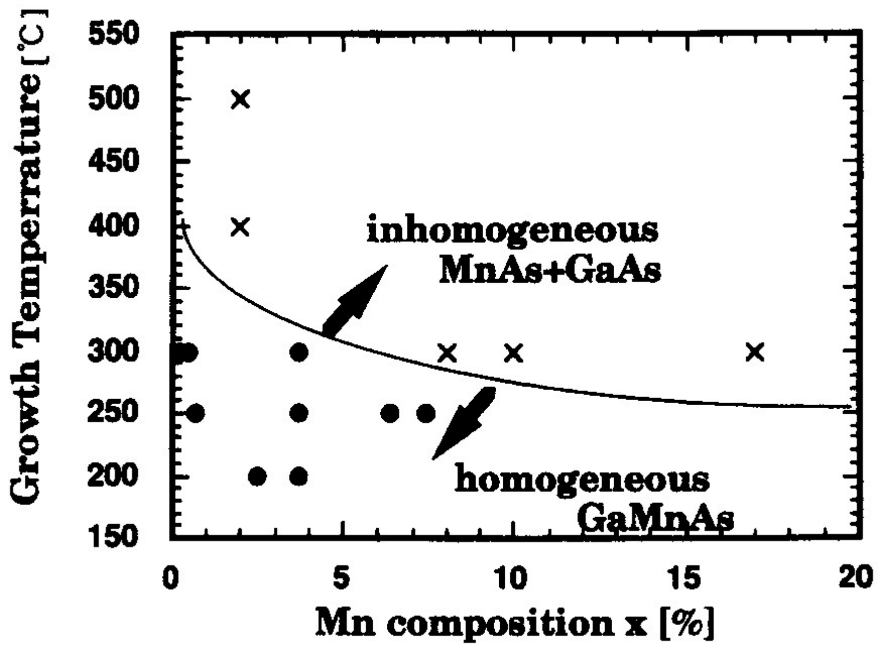
Discovery of ferromagnetism in MBE-grown Mn-doped III-V-based DMS

VOLUME 63, NUMBER 17 PHYSICAL REVIEW LETTERS 23 OCTOBER 1989

Diluted Magnetic III-V Semiconductors

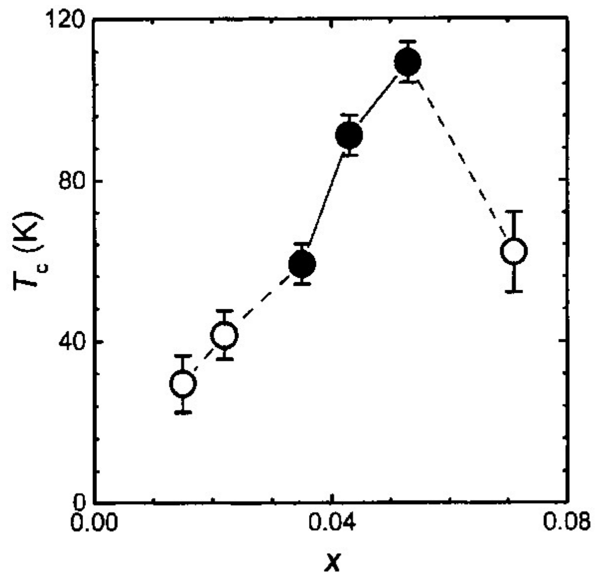
H. Munekata, H. Ohno,[a] S. von Molnar, Armin Segmüller, L. L. Chang, and L. Esaki
IBM T. J. Watson Research Center, P.O. Box 218, Yorktown Heights, New York 10598
(Received 8 August 1989)

Growth "phase diagram" of $Ga_{1-x}Mn_xAs$



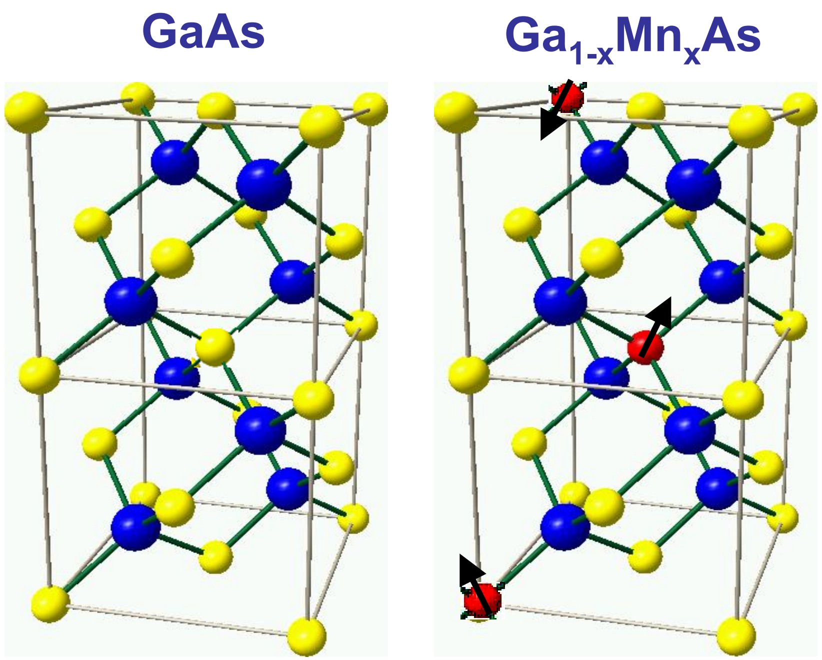
T. Hayashi, M. Tanaka, J. Cryst. Growth, '97

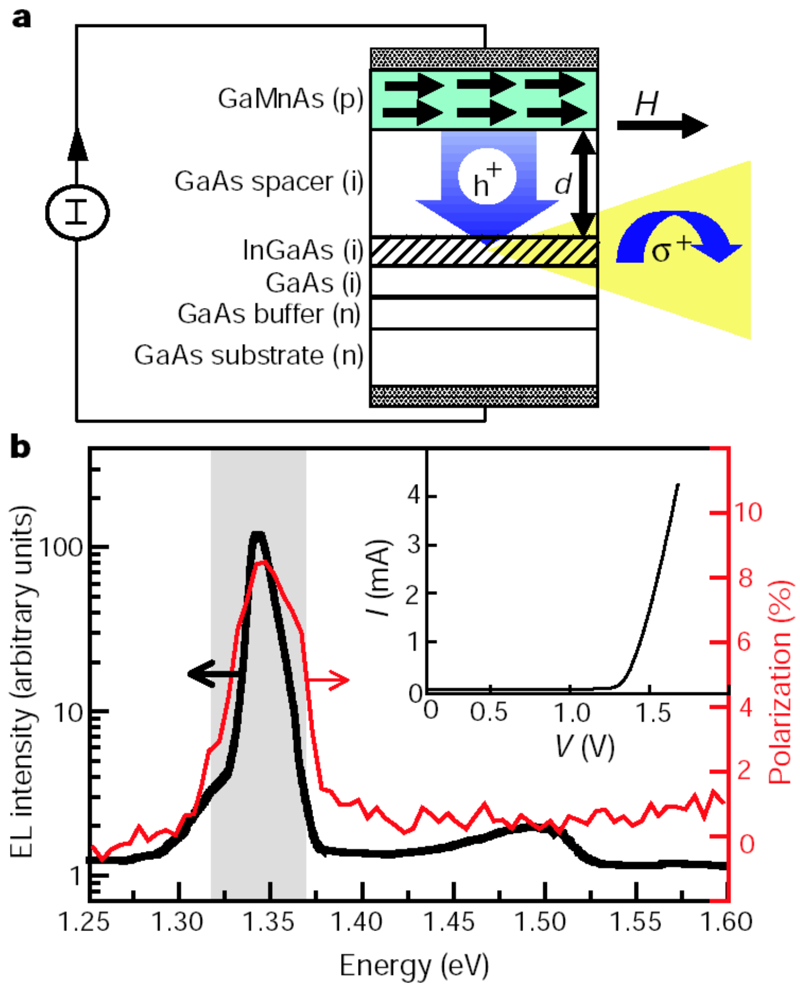
Curie temperature of $Ga_{1-x}Mn_xAs$



H. Ohno et al., JMMM, '99

Diluted magnetic semiconductors (DMS): Expected for future *spintronics* applications



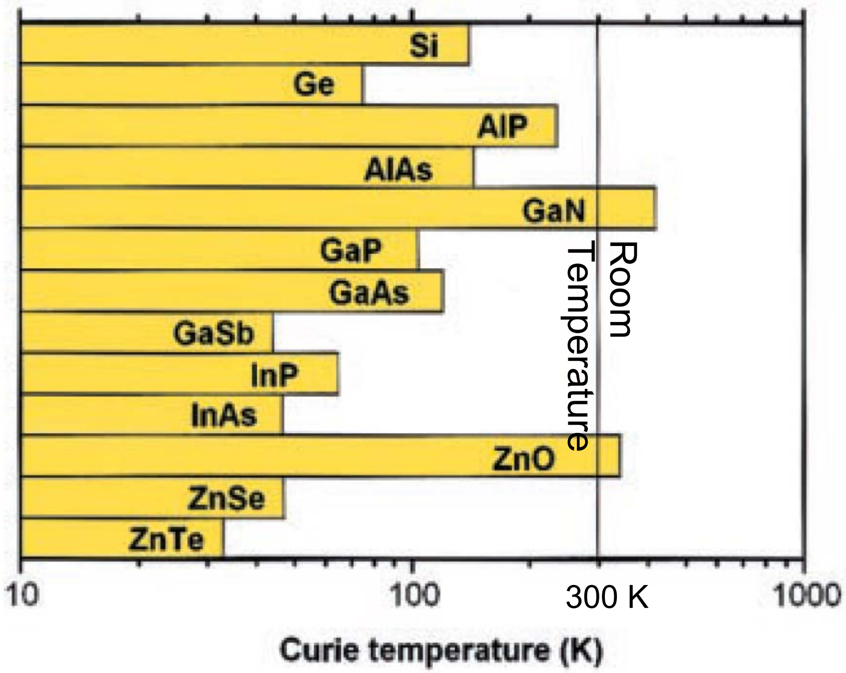


- GMR devices
- Non-volatile memories
- New logic circuits
- New devices utilizing spin injection
  - Circularly polarized LED
  - Magnetization control by spin current

Y. Ohno et al., Nature '99

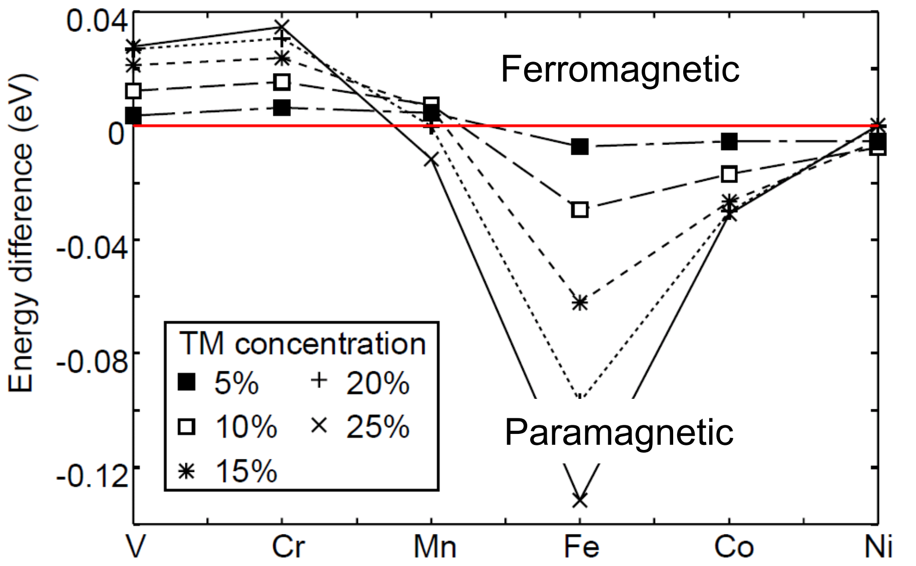
Theoretical prediction of room-temperature ferromagnetism in DMS

T_C of Mn-doped semiconductors in *p-d* exchange mechanism



T. Dietl et al. Science '00

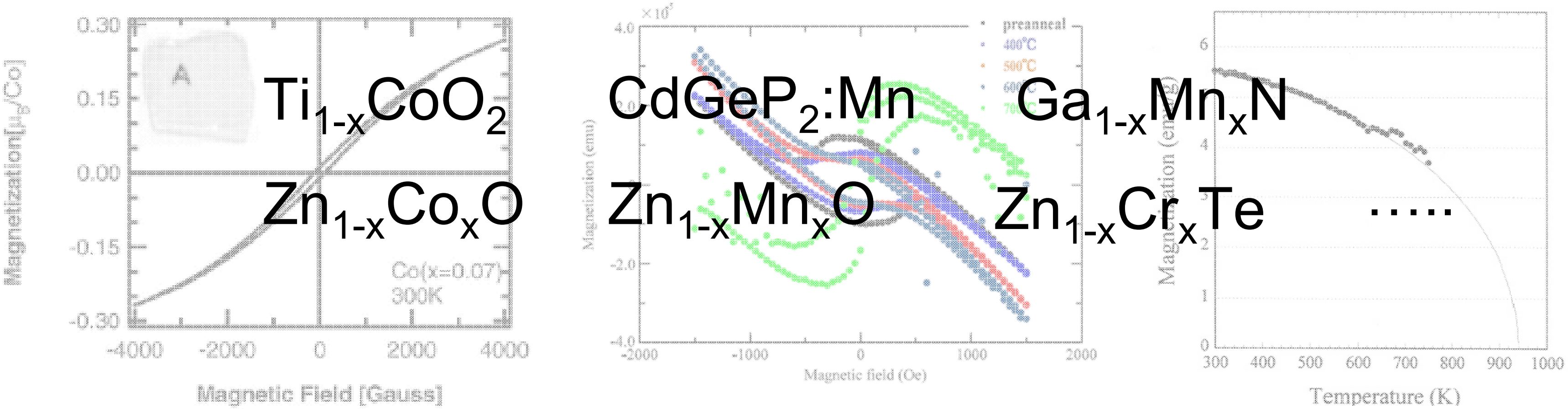
Stability of magnetic states in DMS in double-exchange mechanism



K. Sato et al. JJAP '00.

Wide-gap semiconductors such as ZnO, GaN, and TiO_2 are promising host materials for room-temperature ferromagnetic DMS.

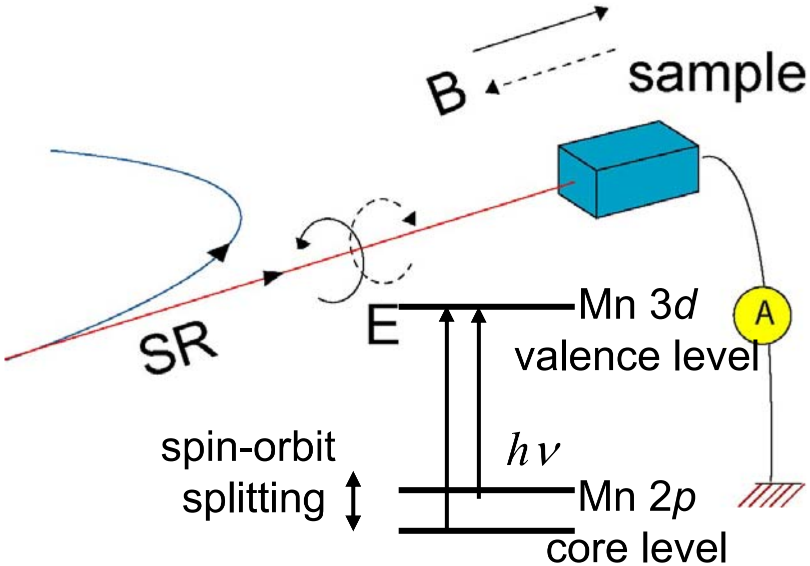
Rom-temperature ferromagnetic DMS

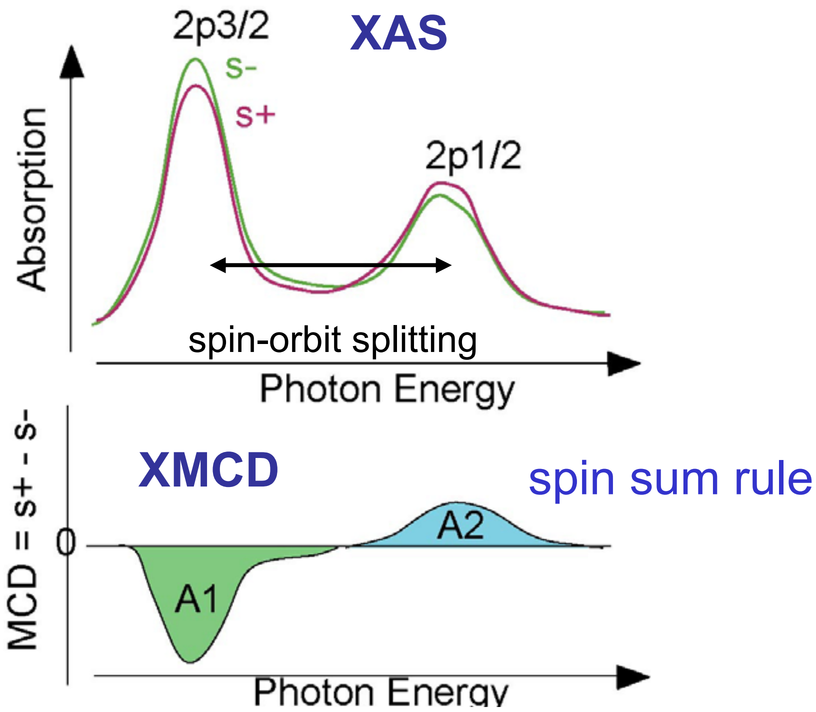


- Are they intrinsic DMS?
  - No ferromagnetic contamination such as Fe metal?
  - No precipitation of second phases, etc?

- To answer these questions:
  - SQUID measurements are not sufficient
  - Anomalous Hall effect is useful but controversial

X-ray magnetic circular dichroism (XMCD) in core-level x-ray absorption spectra (XAS)





Element-specific

Chemical environment-specific

Contamination-insensitive

Magnetism-selective

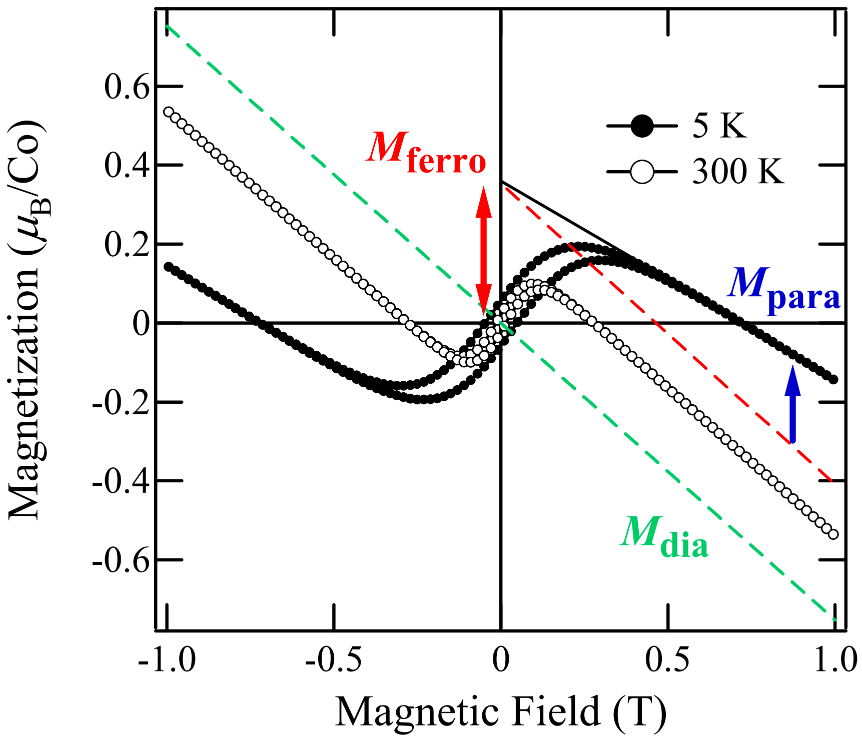
Drawback: Surface sensitivity

B. T. Thole et al., PRL '01, P. Carra et al., PRL '93

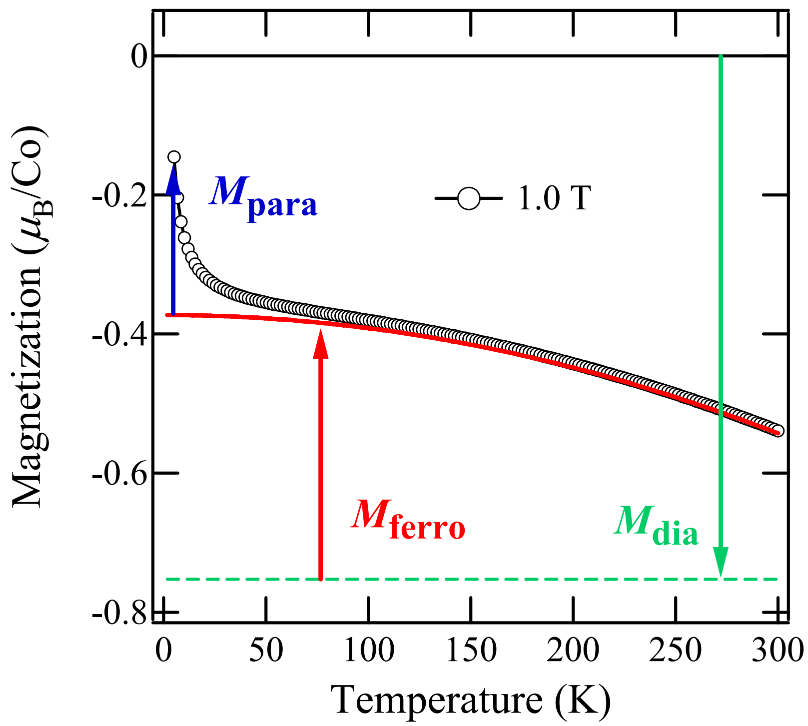
Ferromagnetic, paramagnetic and non-magnetic components in XMCD vs SQUID signals

SQUID data of a DMS thin film sample

M-H curve

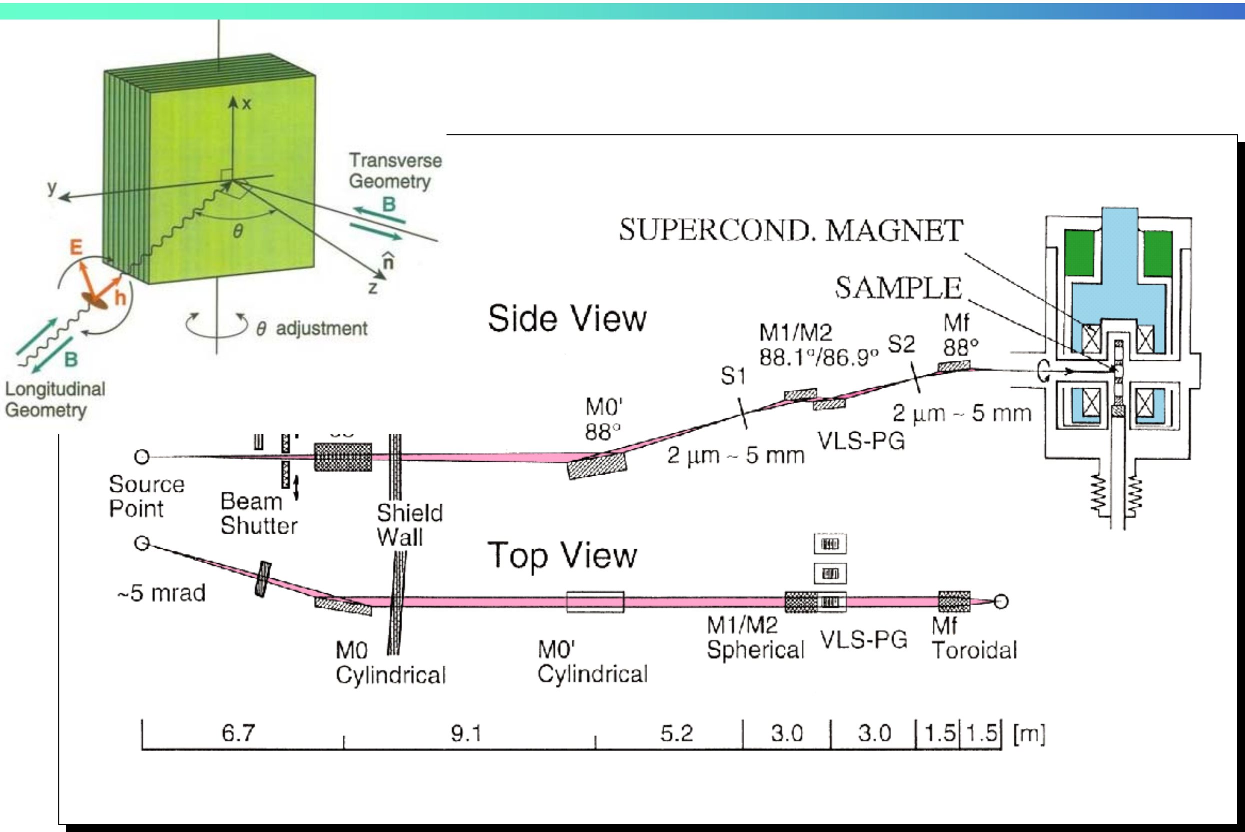


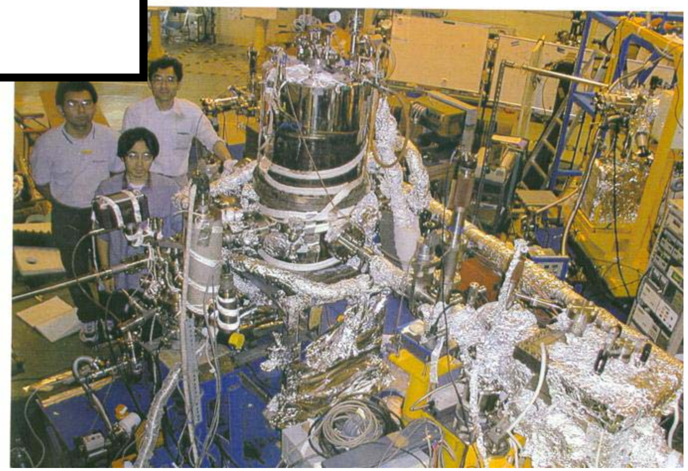
M-T curve



$M = M_{dia} + M_{ferro} + M_{para}$ → XMCD signals, chemically decomposed

XMCD experiment at BL11-A of Photon Factory (previous)

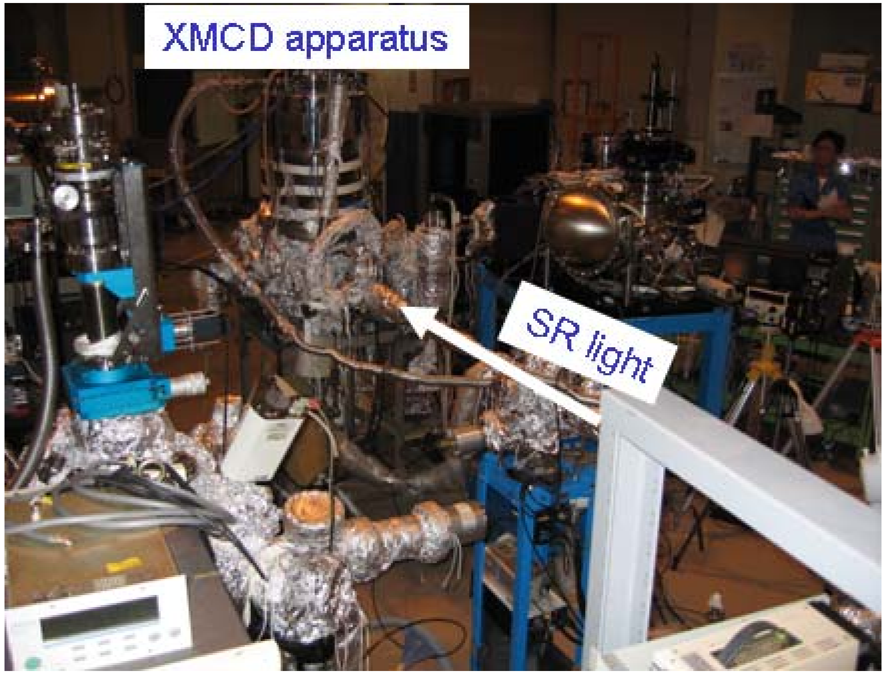




SC magnet *H* <5 T
T >10 K
Angle dependence

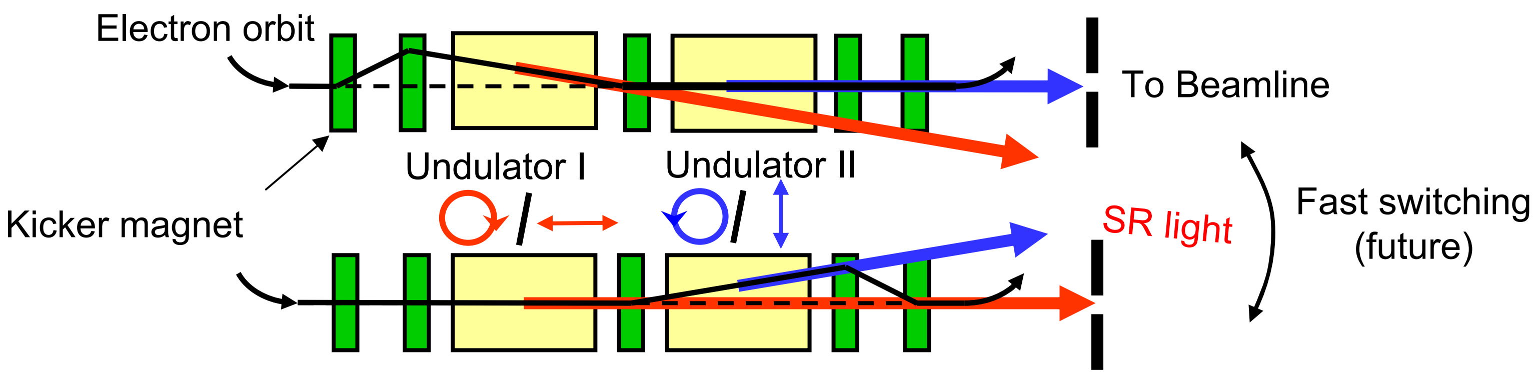
T. Koide et al. Rev. Rev. Sci. Instr. 63, 1462 (1992)

XMCD endstation at BL-16A of Photon Factory (present)

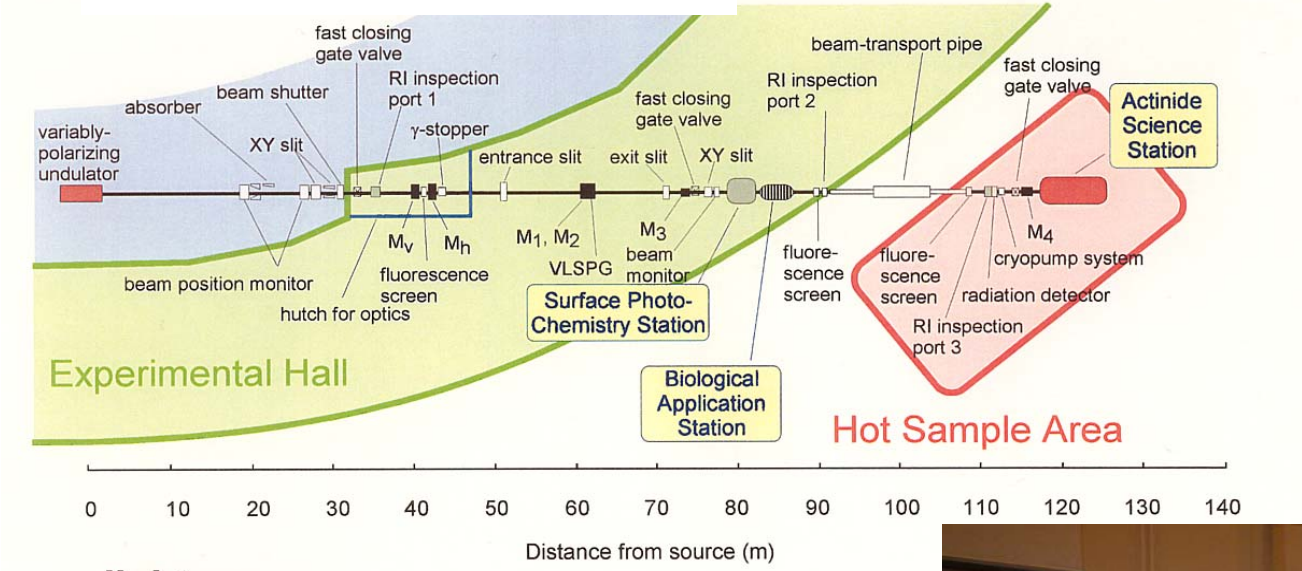


Superconducting magnet, up to 5 T
Low temperature down to ~10 K
Angular-dependent XMCD (L, T)

T. Koide et al. Rev. Rev. Sci. Instr. 63, 1462 (1992)



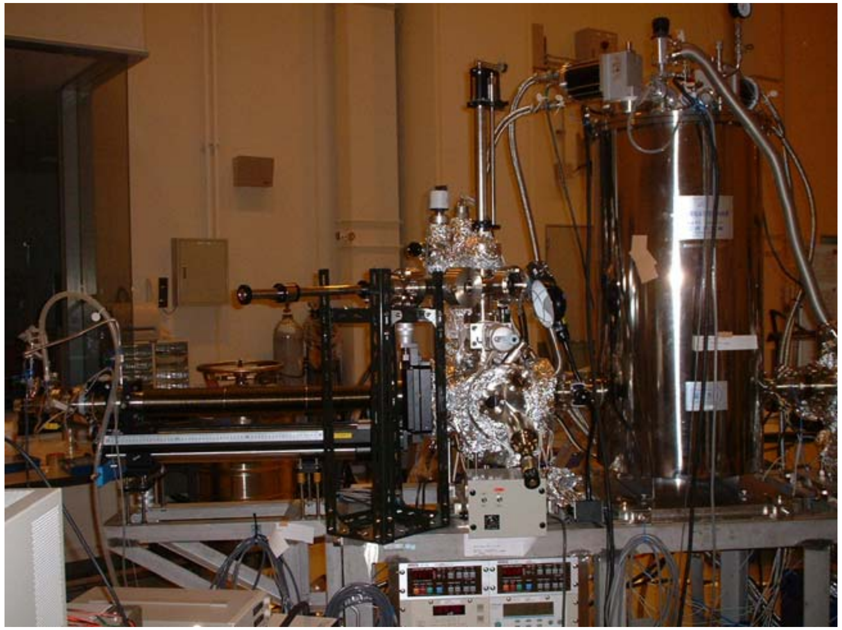
XMCD endstation at JAEA beamline BL-23SU of SPring-8



Helical undulator with phase modulation

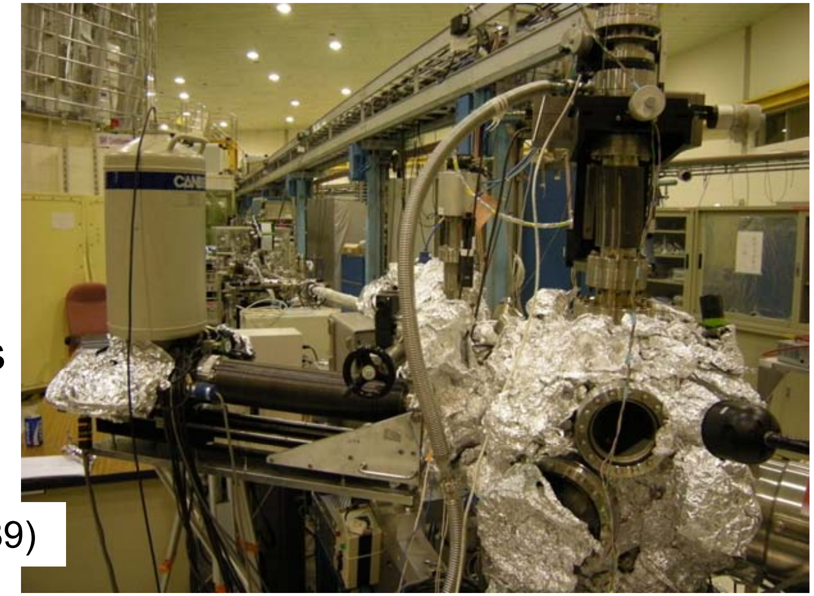
Superconducting magnet, up to 10 T
Low temperature, down to ~6 K
High energy resolution and brightness monochromator

Y. Saitoh et al., Nucl. Instrum. Meth. A ‘01



XMCD endstation at the Dragon beamline BL-11A at NSRRC

NSRRC, Taiwan



Bending magnet
Electro-magnet, up to 1 T
Low temperature down to 20 K
Total-electron-yield (TEY) and total-fluorescence-yield (TFY) mode detections

C.T. Chen and F. Sette, Rev. Sci. Instr. 60, 1616 (1989)

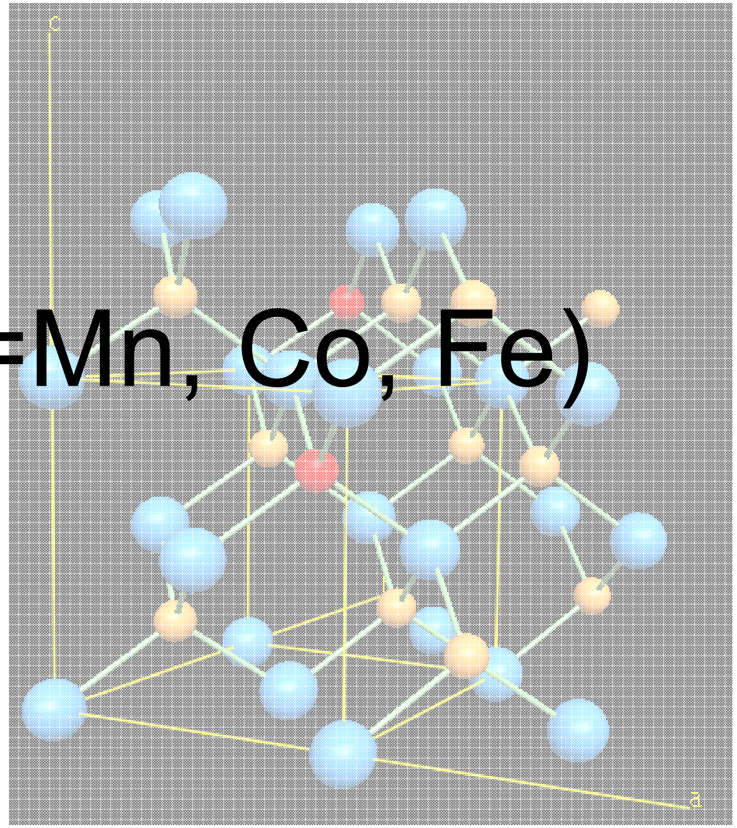
Outline

$Ga_{1-x}Mn_xAs$

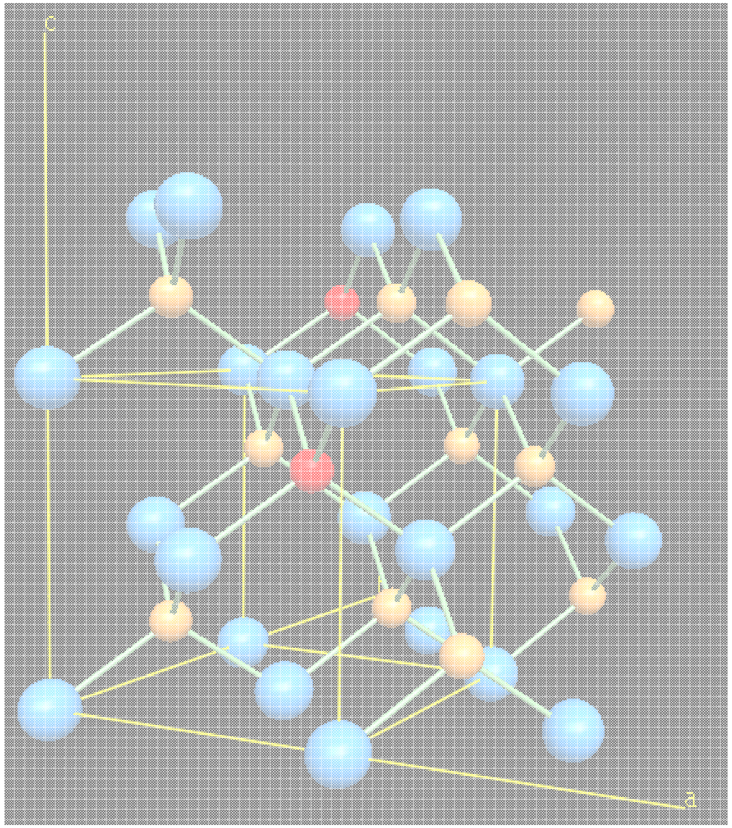
$Ti_{1-x}Co_xO_2$

$Zn_{1-x}Cr_xTe$

$Zn_{1-x}T_xO$ (T=Mn, Co, Fe)

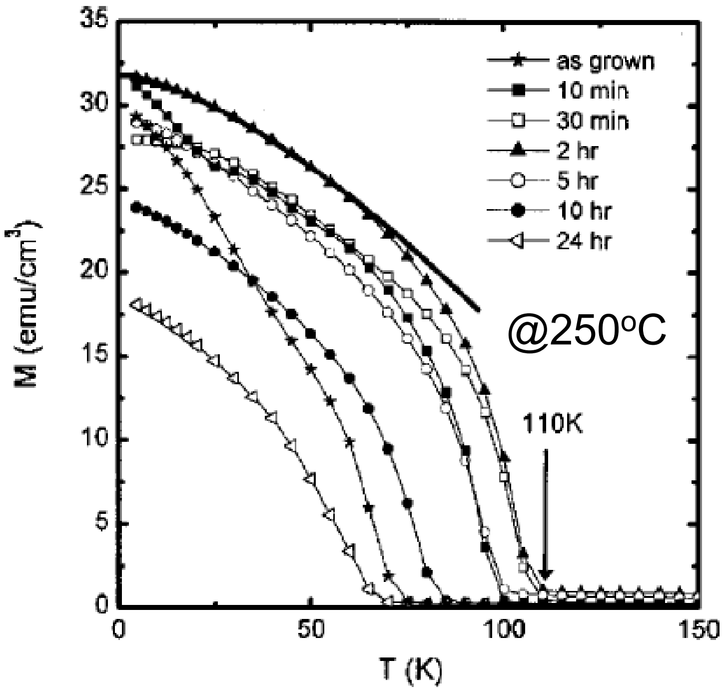


$Ga_{1-x}Mn_xAs$



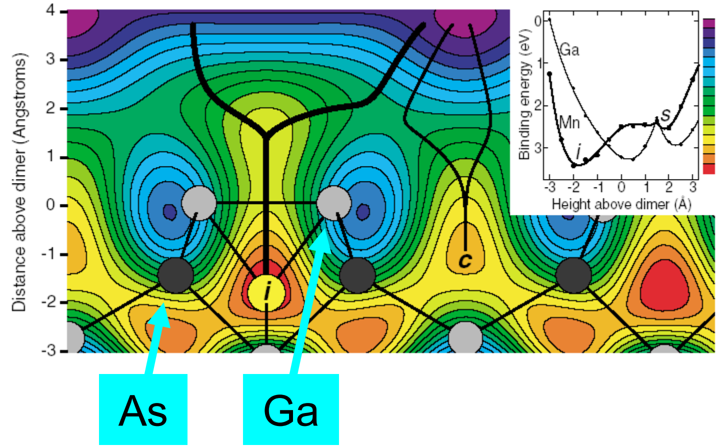
Effects of low-temperature post-annealing in $Ga_{1-x}Mn_xAs$

Change of T_C by post-annealing



S.J. Potashnik et al., APL ‘01
T. Hayashi et al., APL ‘01

Molecular dynamic calculation

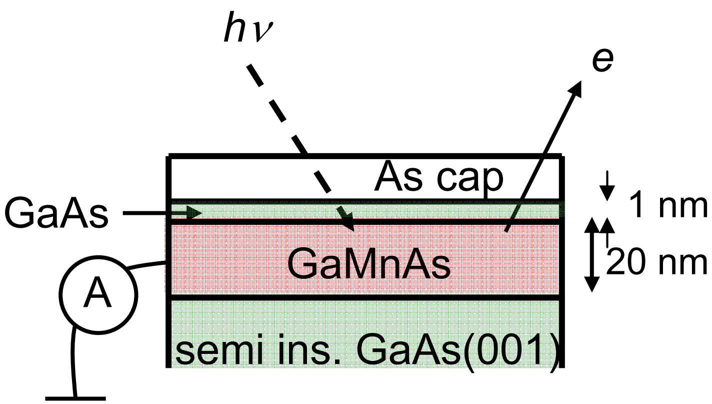


Mn first enters interstices then substitutes Ga.

S.C. Erwin and A.G. Petukhov PRL ‘02

$Ga_{1-x}Mn_xAs$ samples

Sample: as grown $Ga_{1-x}Mn_xAs$



As-grown: x =0.042, 0.078

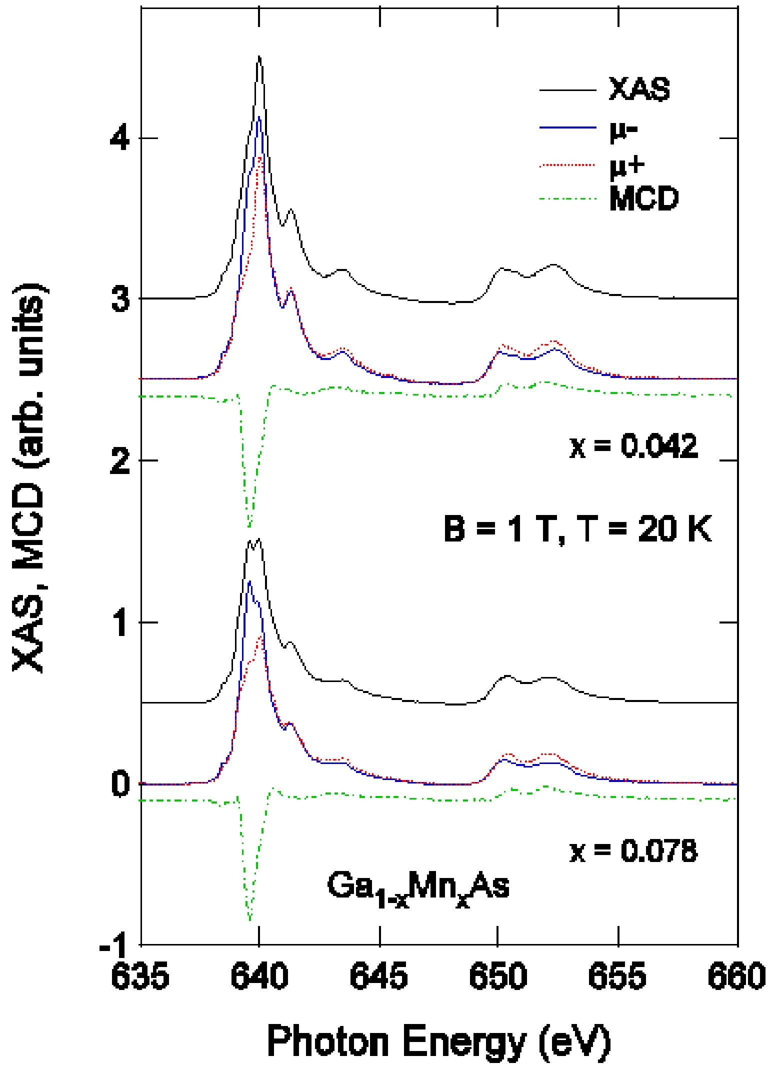
T_C ~ 60 K

Post-annealed: x =0.04, @270°C, 2 *h*

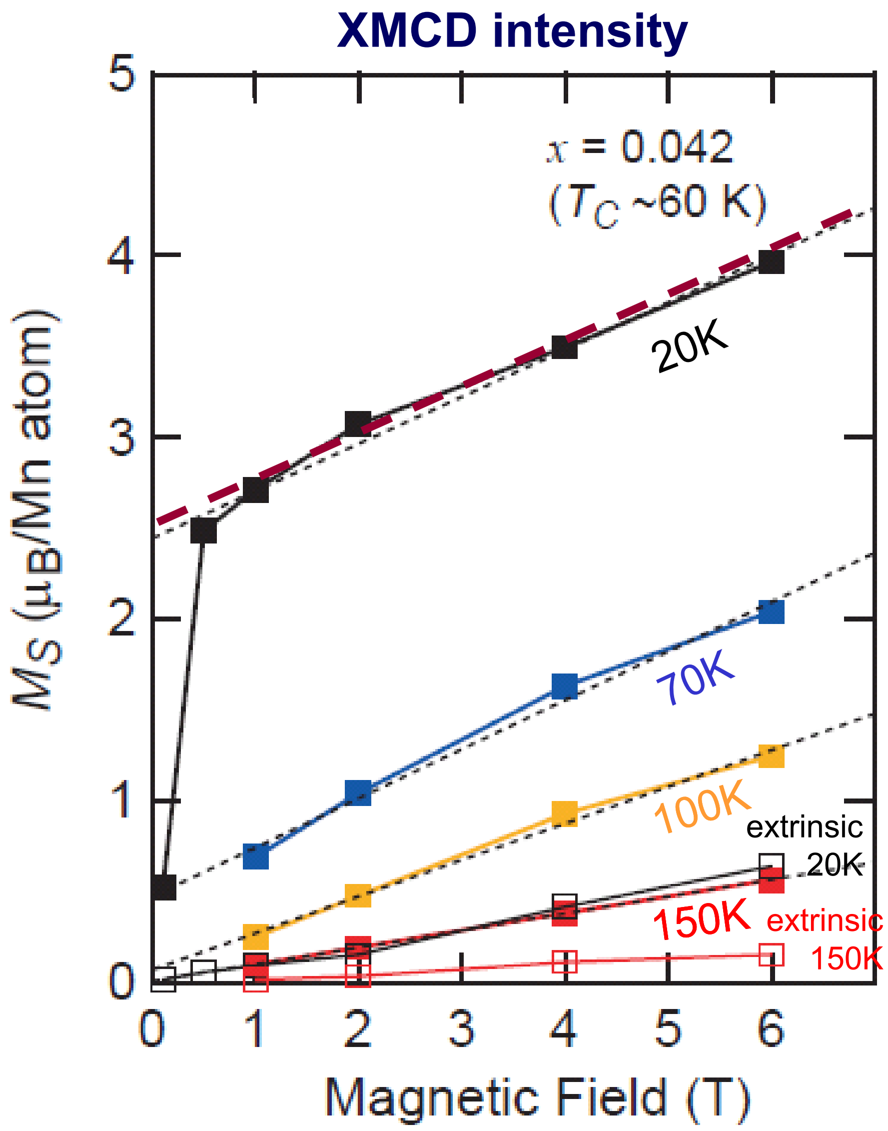
T_C ~ 120 K

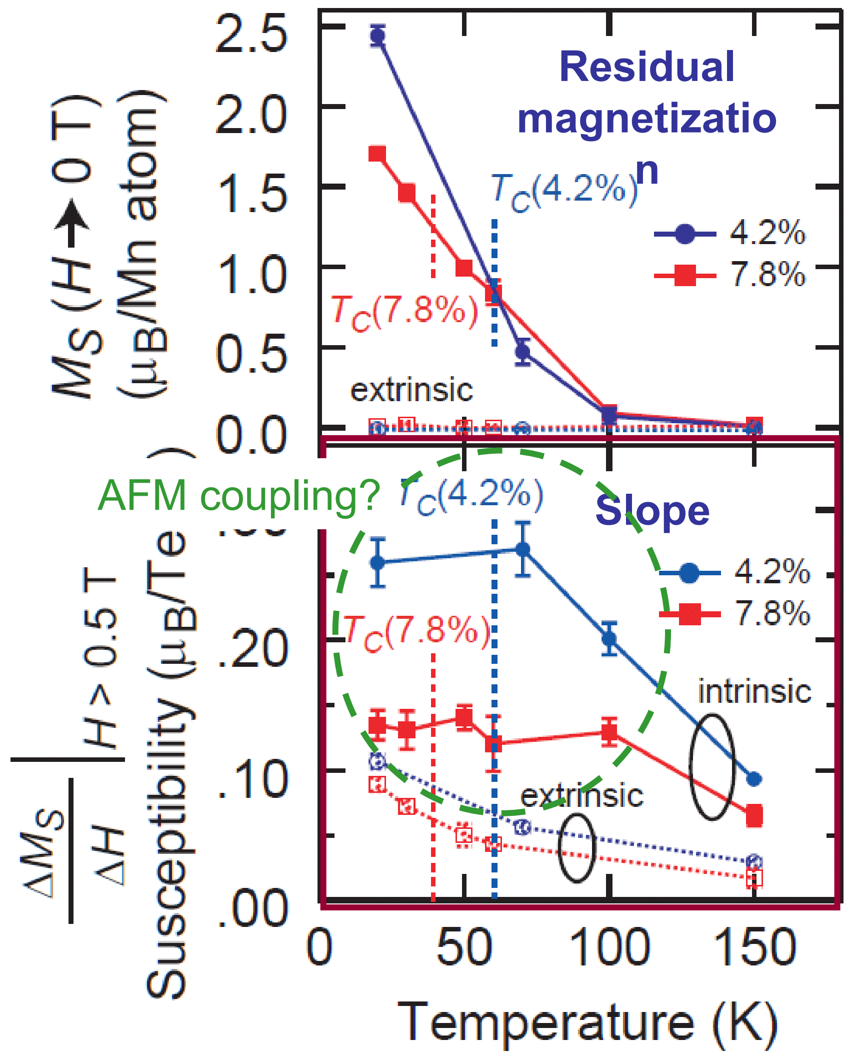
SPring-8 BL23SU

XAS and XMCD spectra



Paramagnetic component of XMCD *vs* *T* in as-grown $Ga_{1-x}Mn_xAs$

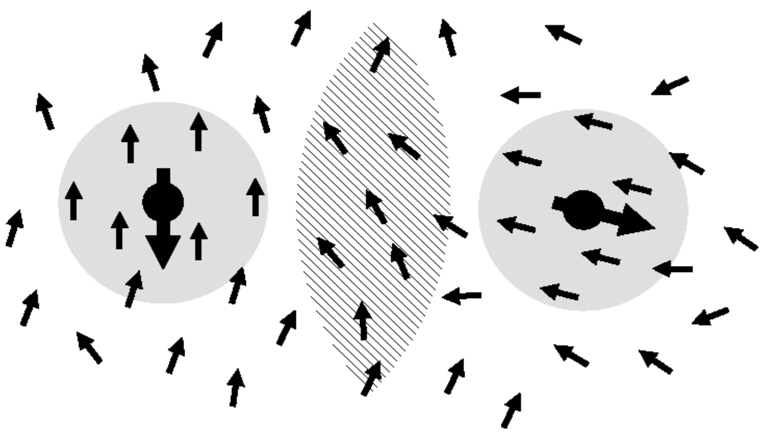




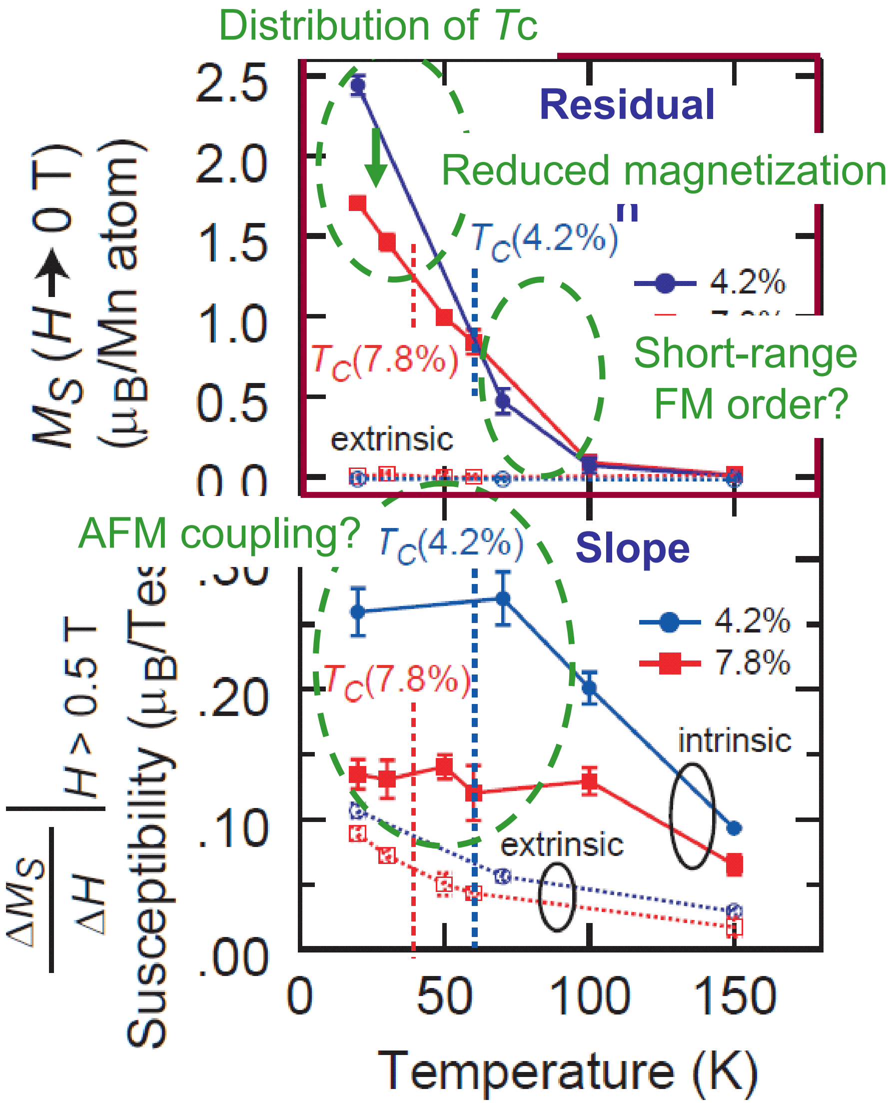
Y. Takeda et al., PRL '08

Ferromagnetic component of XMCD *vs T* in as-grown $Ga_{1-x}Mn_xAs$

Magnetic polarons?

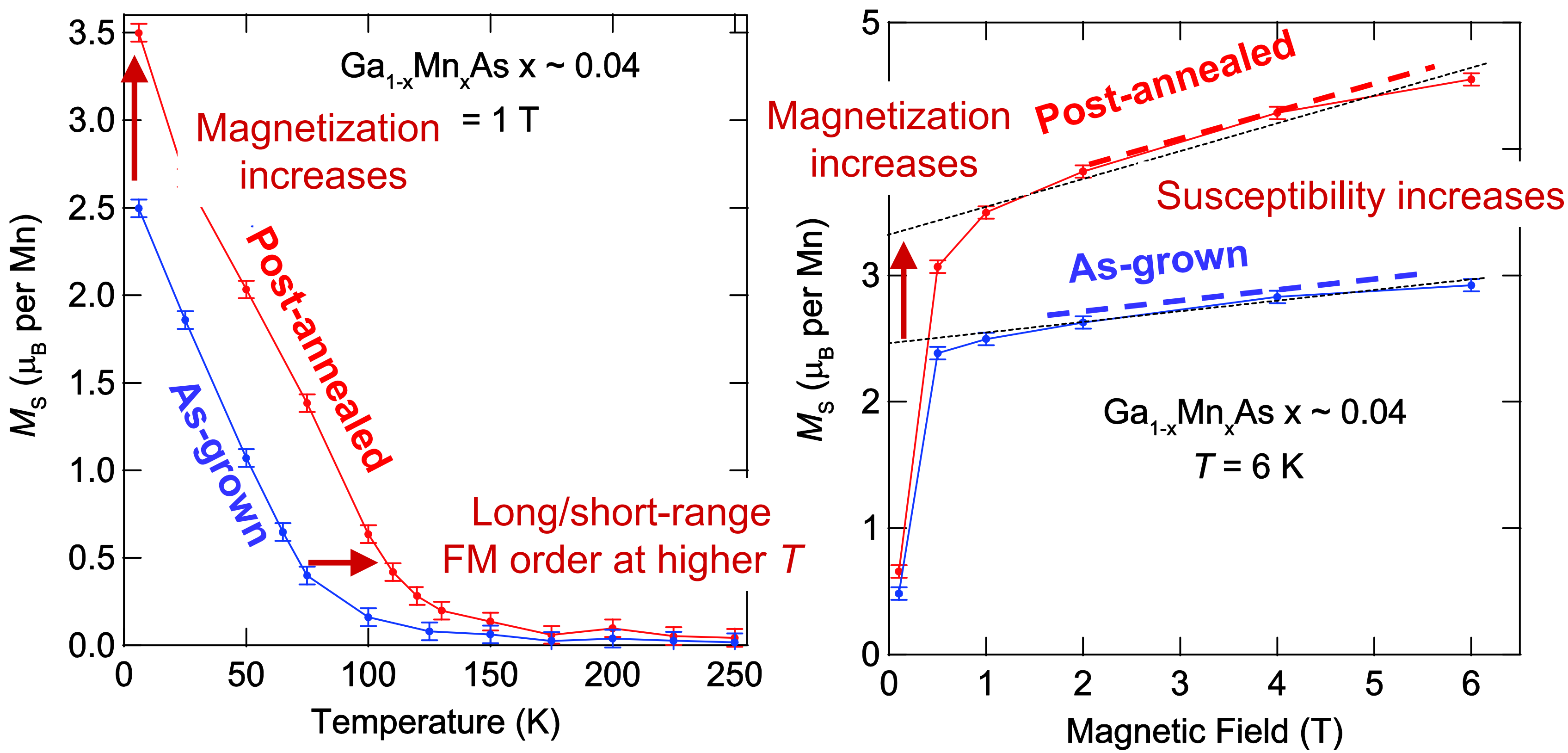


A. Kaminski and S. Das Sarma, PRL '02



Y. Takeda et al., PRL '08

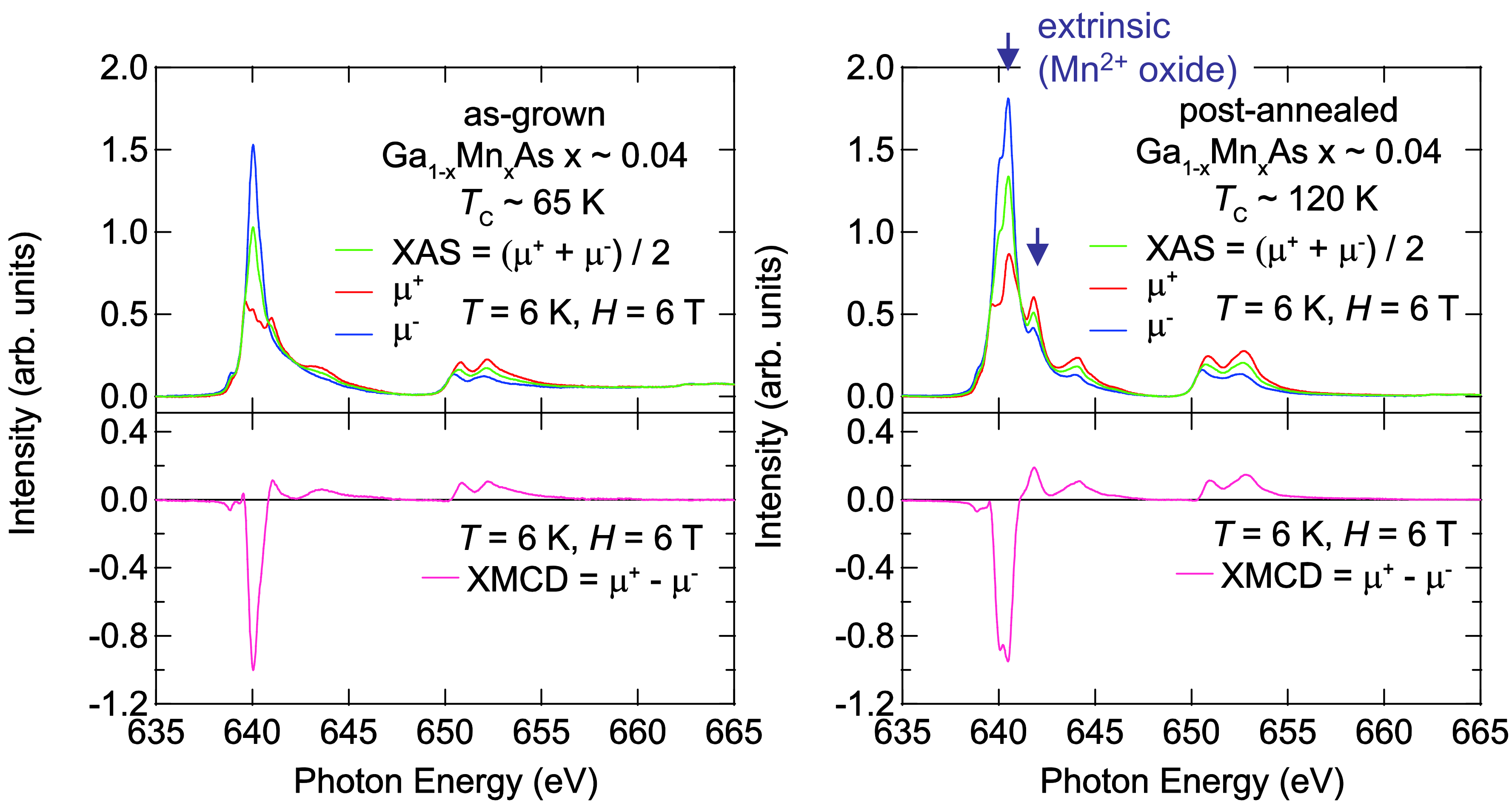
Effects of post annealing on XMCD intensities *vs T* & *H* in $Ga_{1-x}Mn_xAs$



Post annealing diminishes AF interaction by reducing the number of *interstitial* Mn ions.

Y. Takeda et al.,

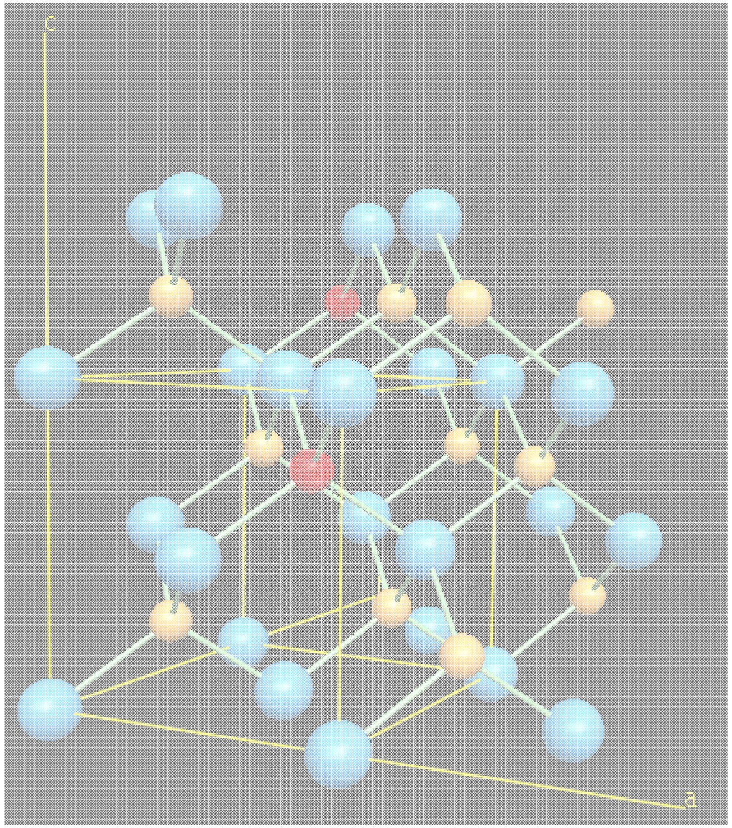
Effects of low-temperature post-annealing on XAS and XMCD of $Ga_{1-x}Mn_xAs$



Post annealing expels *interstitial* Mn ions to surface

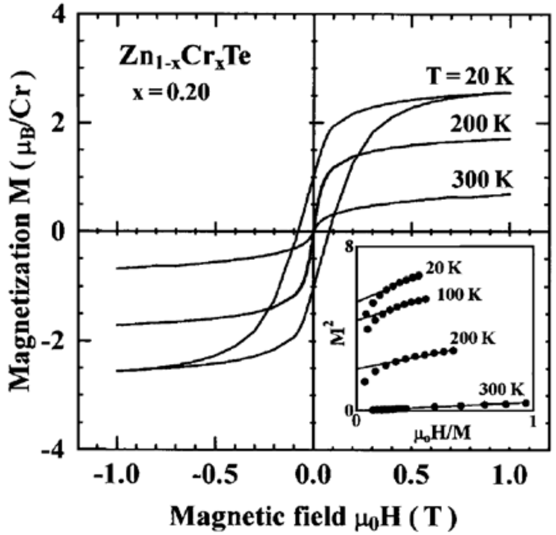
Y. Takeda et al.,

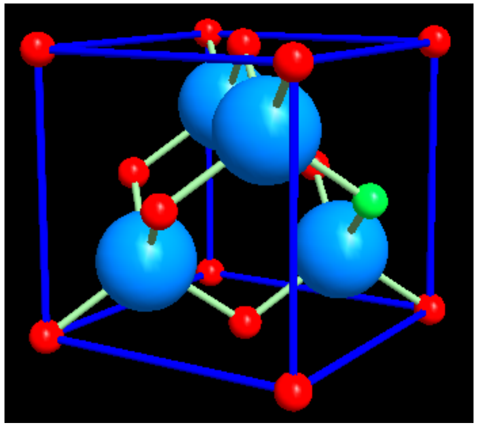
$Zn_{1-x}Cr_xTe$



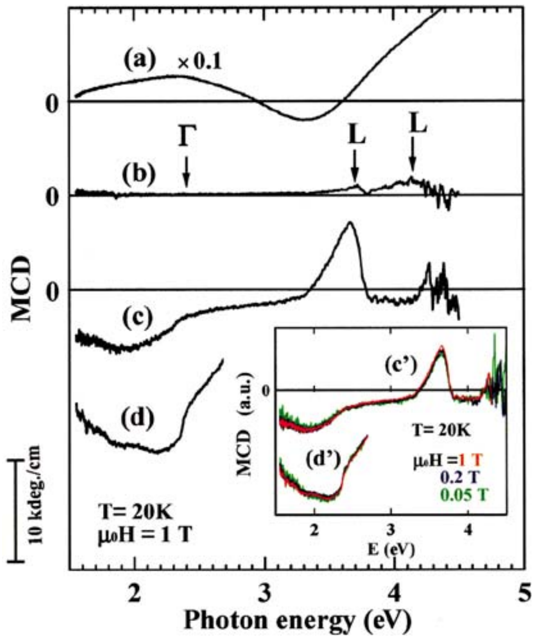
Diluted ferromagnetic semiconductor $Zn_{1-x}Cr_xTe$

M-H curves

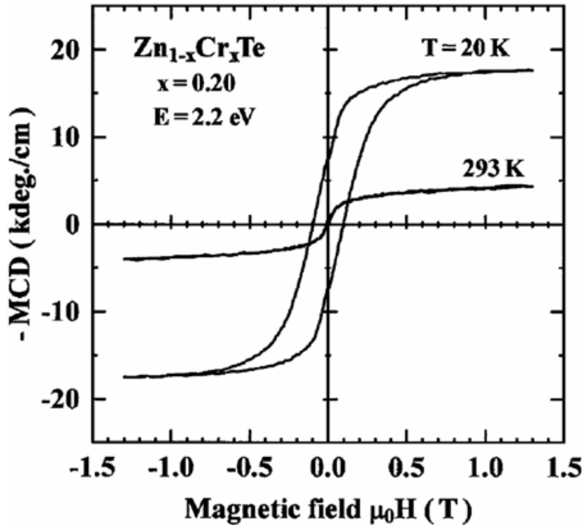




VIS-UV MCD

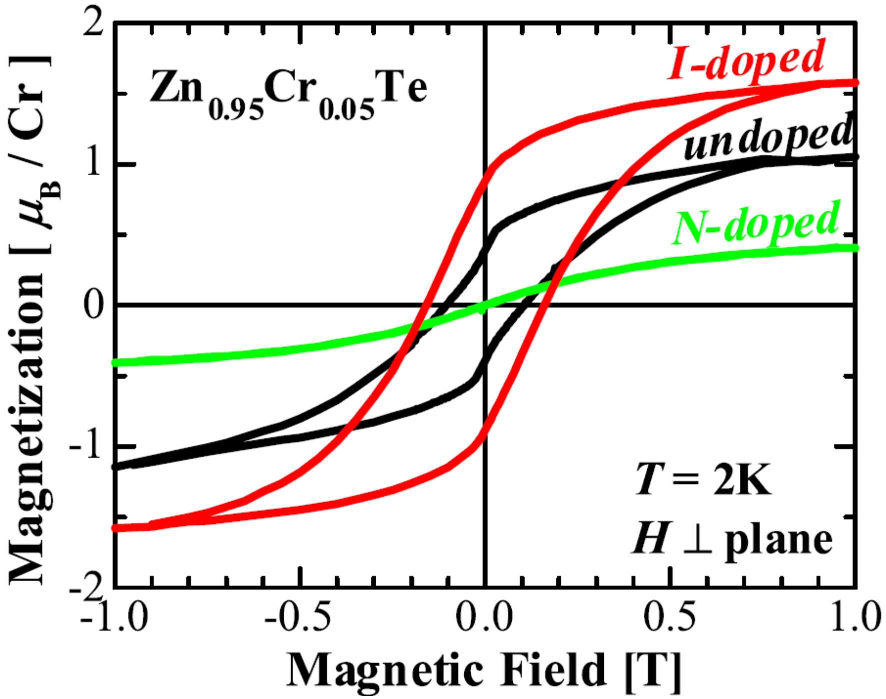


MCD vs *H*



H. Saito et al., PRL '03

Doping effects in $Zn_{1-x}Cr_xTe$

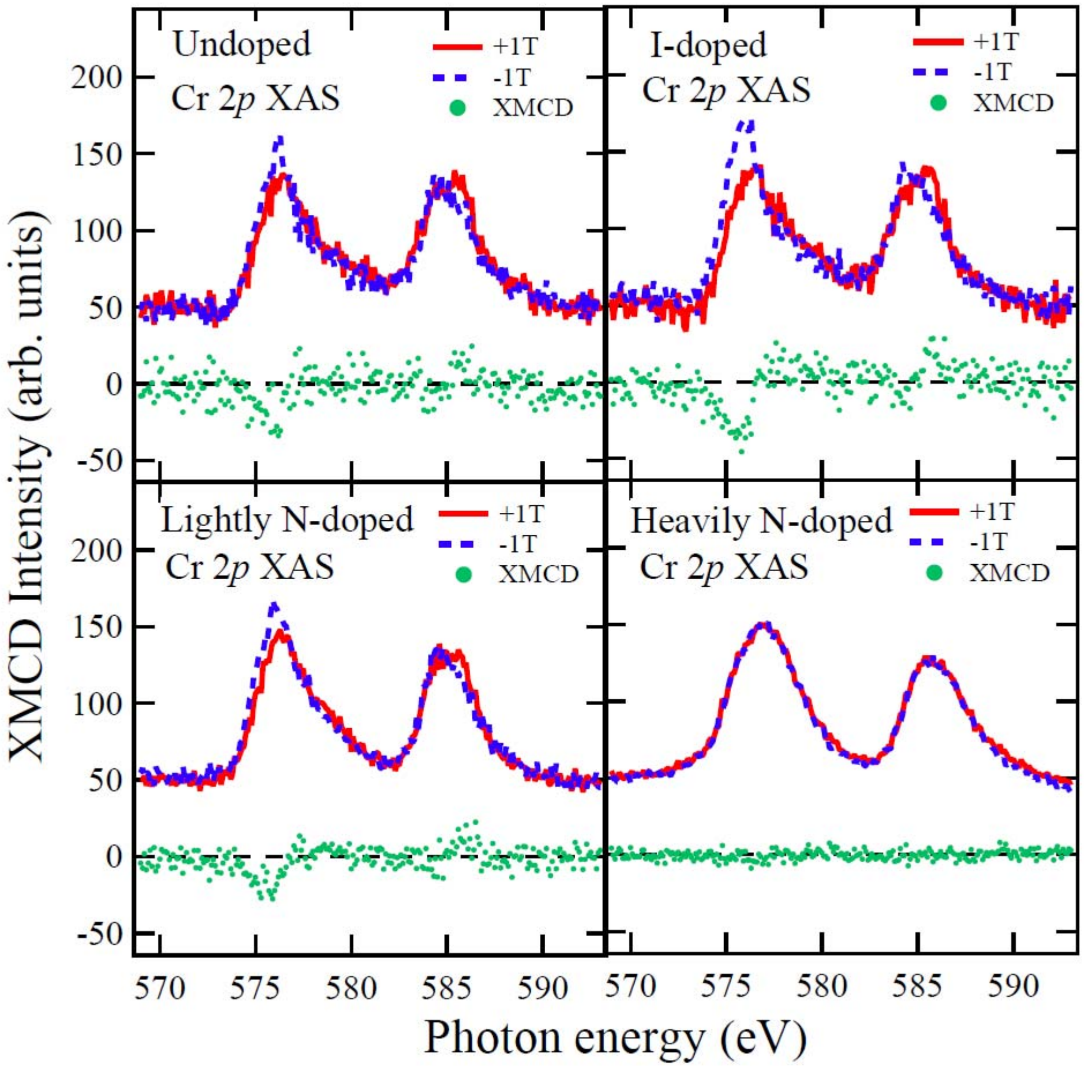


I-doping: Electron-doped

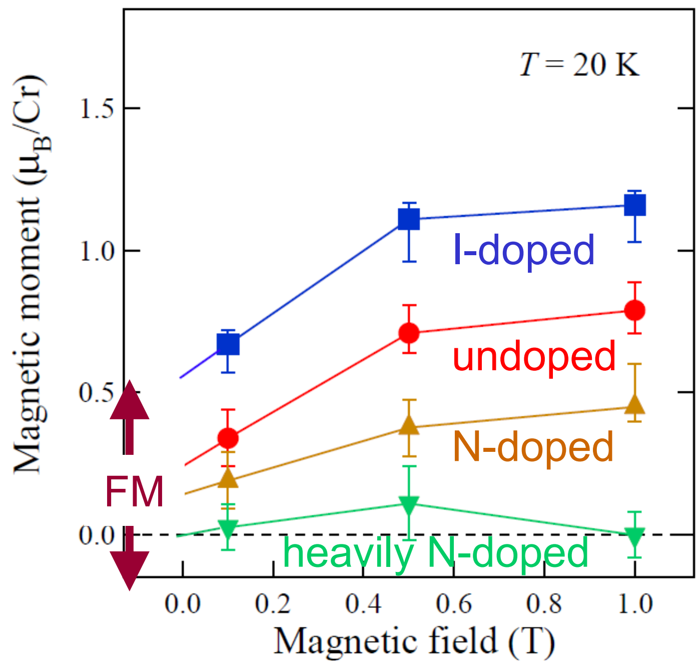
N-doping: Hole-doped

N. Ozaki et al., PRL '06

Doping effects in $Zn_{1-x}Cr_xTe$: XMCD



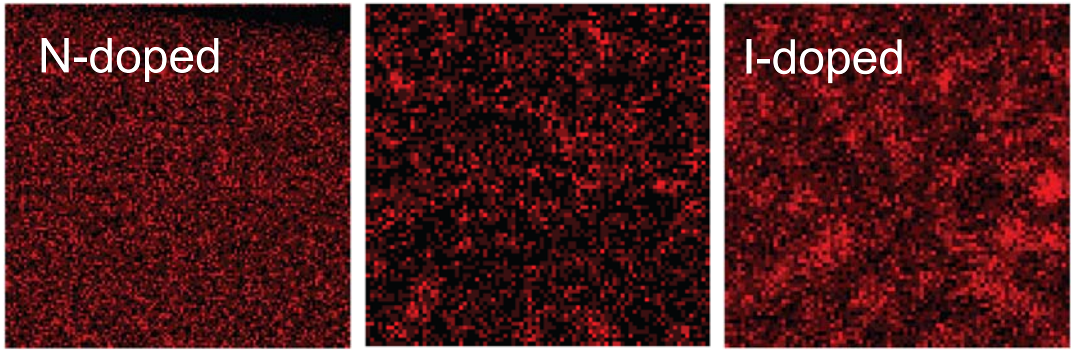
XMCD intensity *vs H*



Y. Yamazaki et al.

Inhomogeneous distribution of Cr in $Zn_{1-x}Cr_xTe$

Energy-dispersive X-ray spectroscopy image

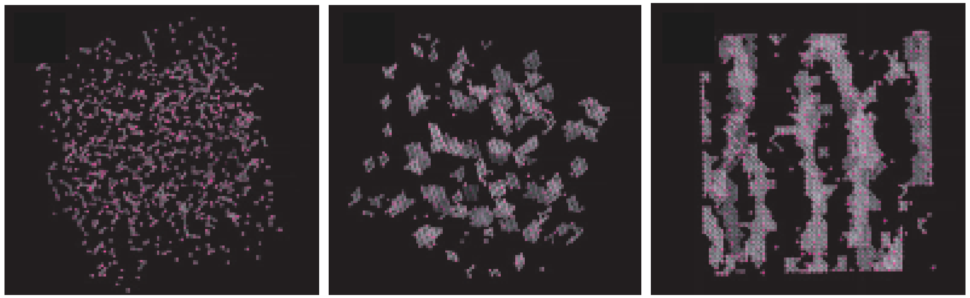


uniform ⟷ non-uniform

T_C low ⟷ T_C high

S. Kuroda et al., Nat. Mater. '07

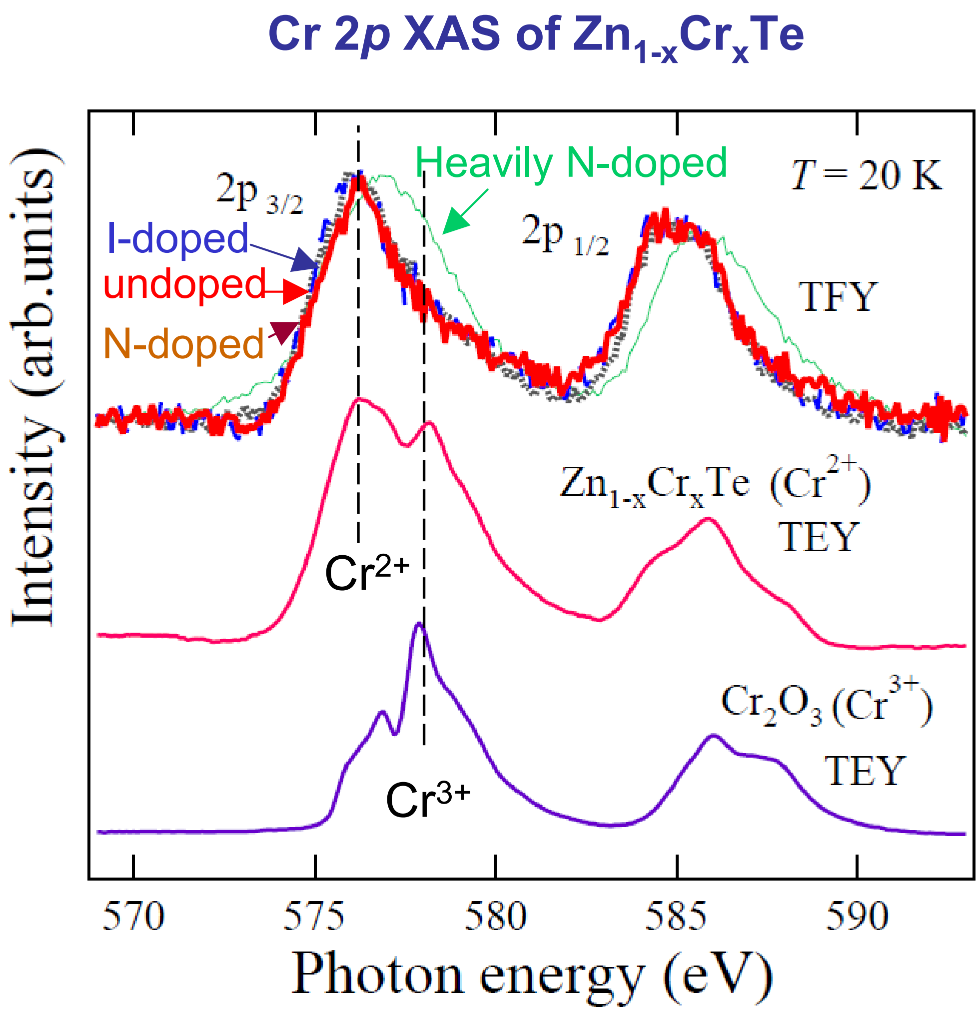
Spinodal decomposition in high-T_C DMS's

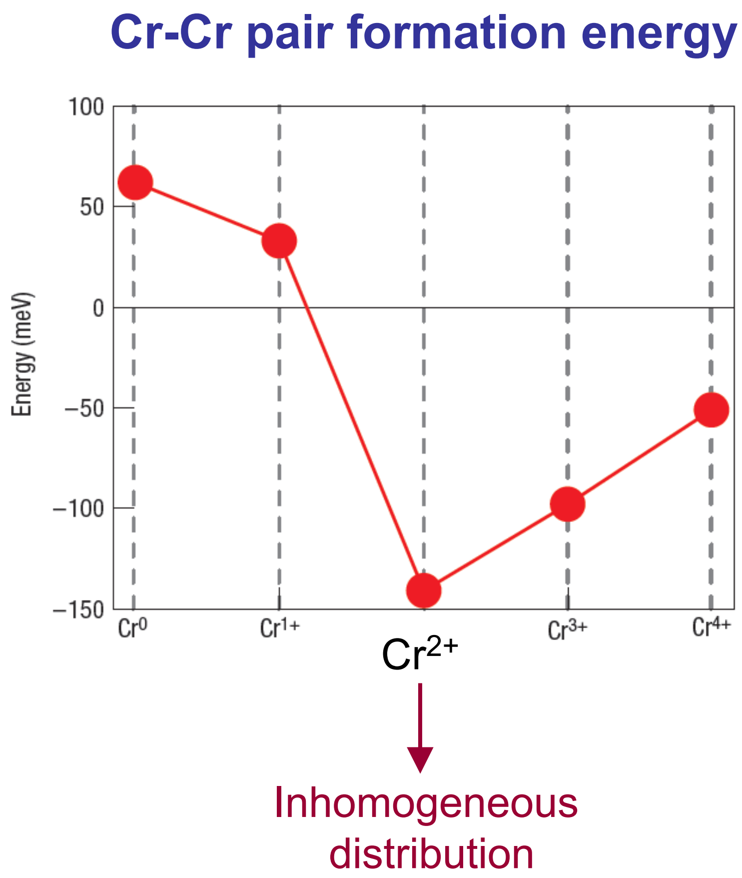


K. Sato et al., JJAP '05

T. Fukushima et al., JJAP '06

Cr valence *vs* inhomogeneous distribution of Cr in $Zn_{1-x}Cr_xTe$

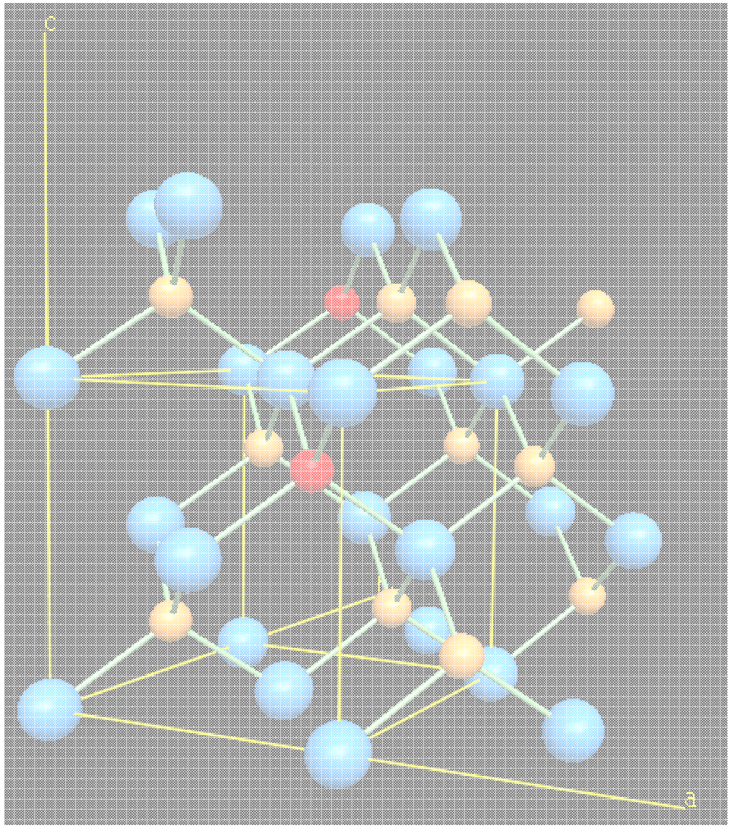




Y. Yamazaki et al.

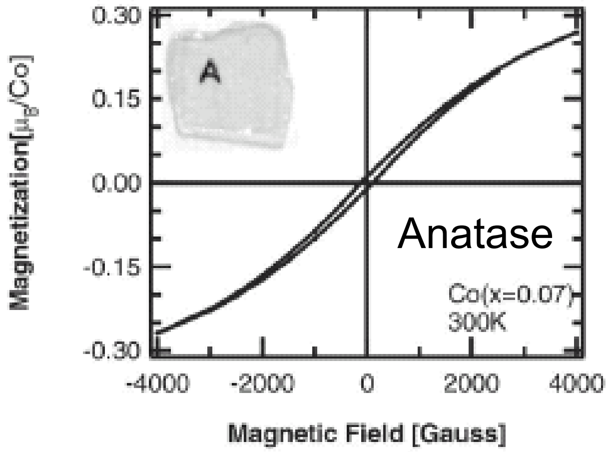
S. Kuroda, T. Dietl et al., Nat. Mater. '07

$Ti_{1-x}Co_xO_2$

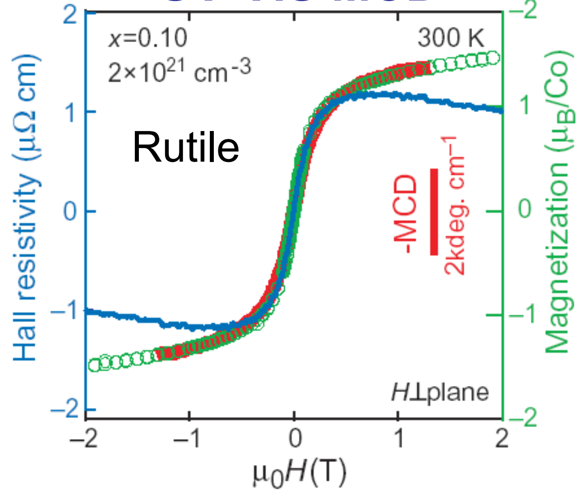


Room-temperature ferromagnetism in $Ti_{1-x}Co_xO_2$

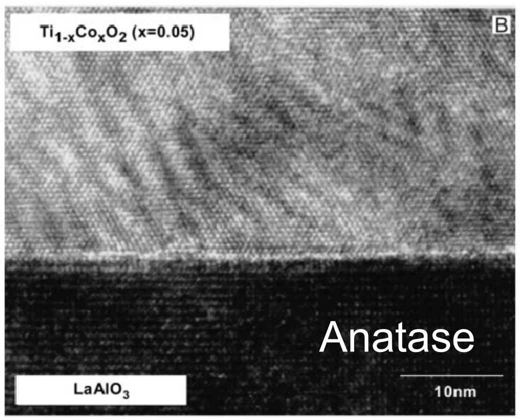
SQUID



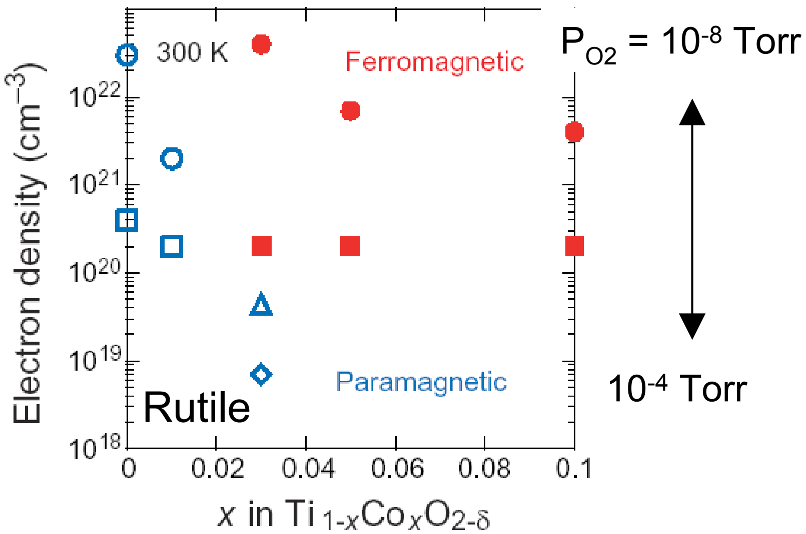
UV-VIS MCD



TEM



"Phase" diagram



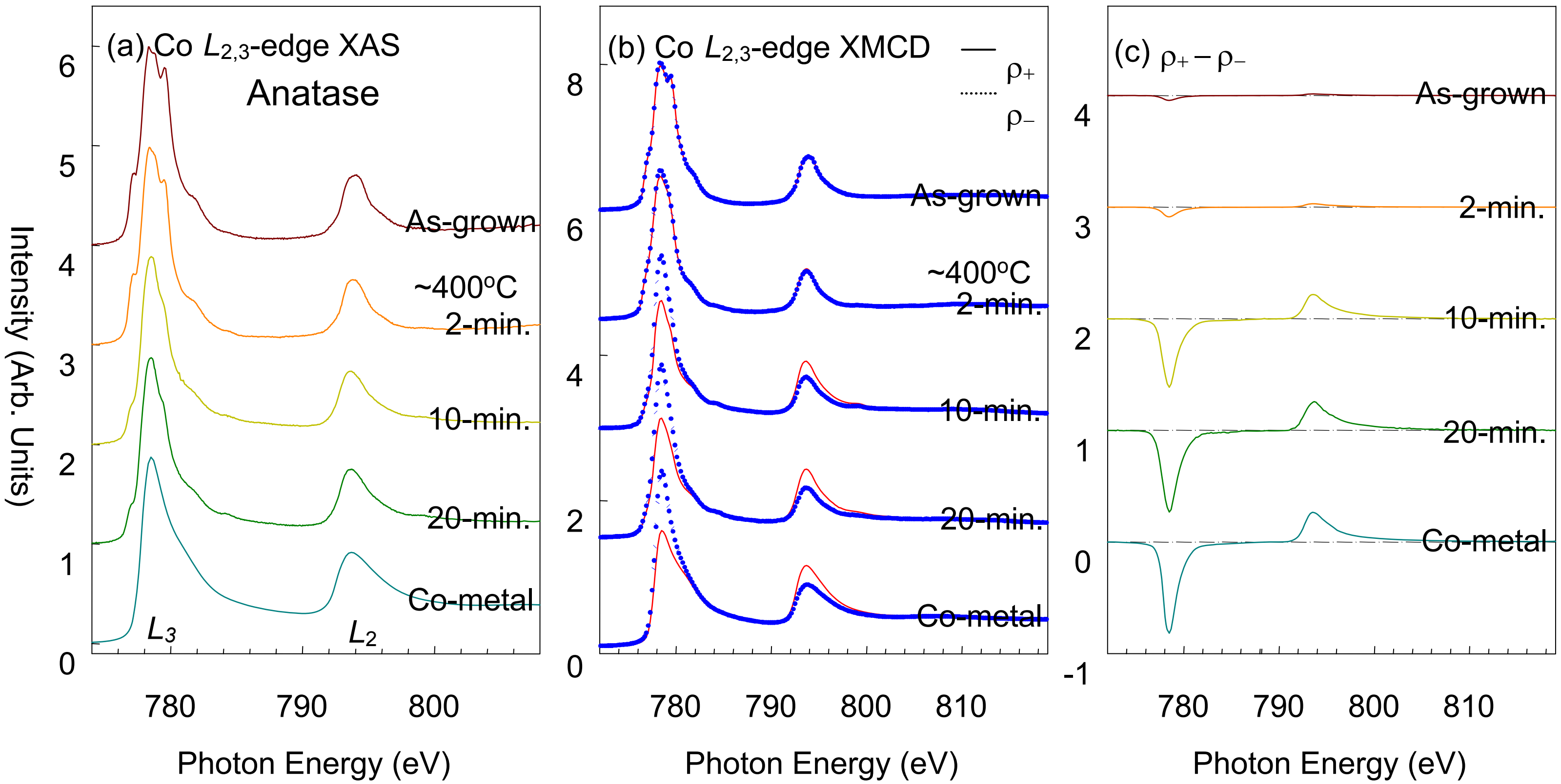
No precipitation

Y. Matsumoto et al., Science '01

T. Fukumura, New J. Phys. '08

Co 2*p* core-level XAS and XMCD of $Ti_{1-x}Co_xO_2$: Effect of high-*T* annealing in vacuum

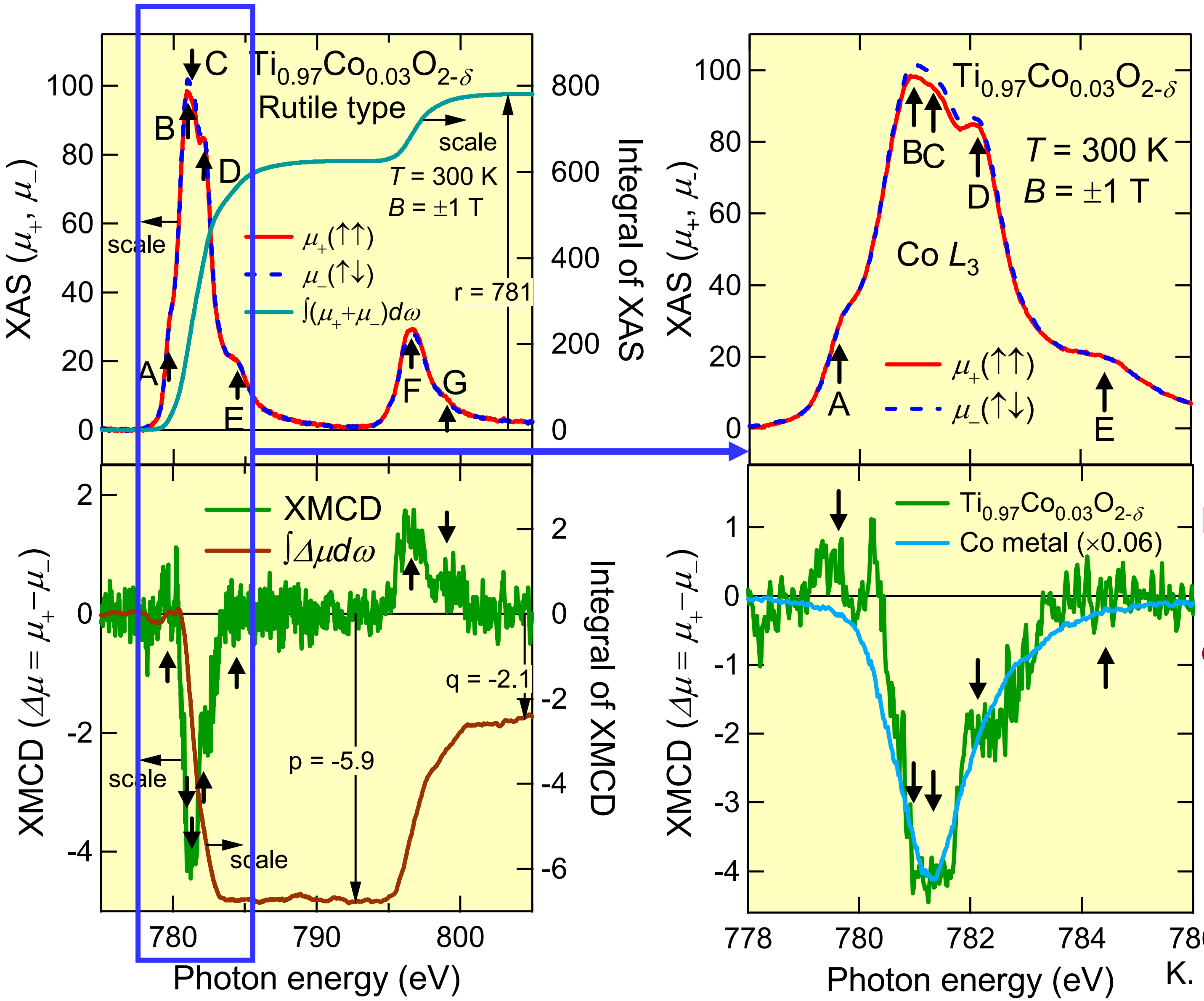
XAS | **XAS (σ_+ - σ_-)** | **XMCD**



“Ferromagnetism is due to segregated Co metal.”

Y.J. Kim et al. PRL ‘03

Co 2*p* core-level XMCD of $Ti_{1-x}Co_xO_2$ without high-*T* annealing



Ferromagnetism is due to Co^{2+} ion

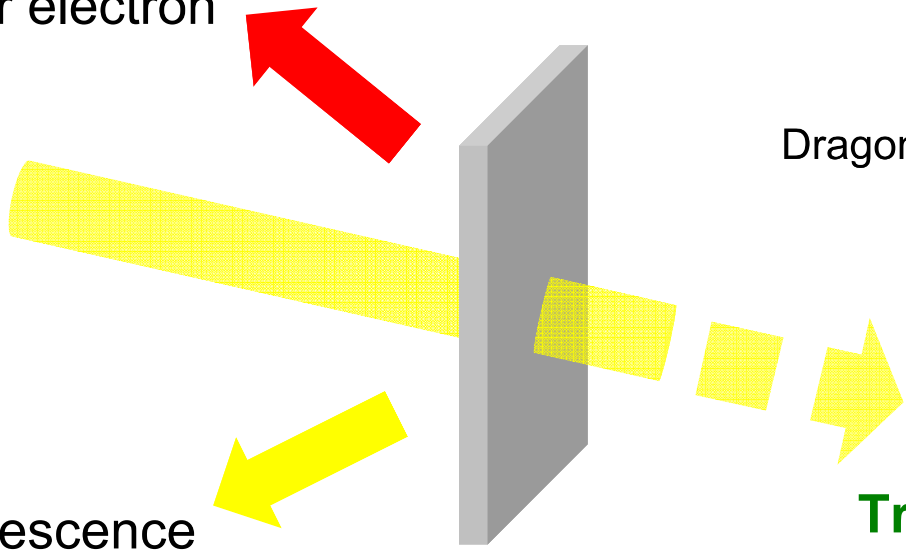
However, moment is very small: ~ 0.13 μ_B/Co
cf. SQUID ~ 1 μ_B/Co

K. Mamiya et al. APL '06

Surface- and bulk-sensitive modes of XAS and XMCD measurements

Total electron yield (TEY) mode

probing depth ~ 3-5nm



Dragon beamline @NSSRC

Transmission mode

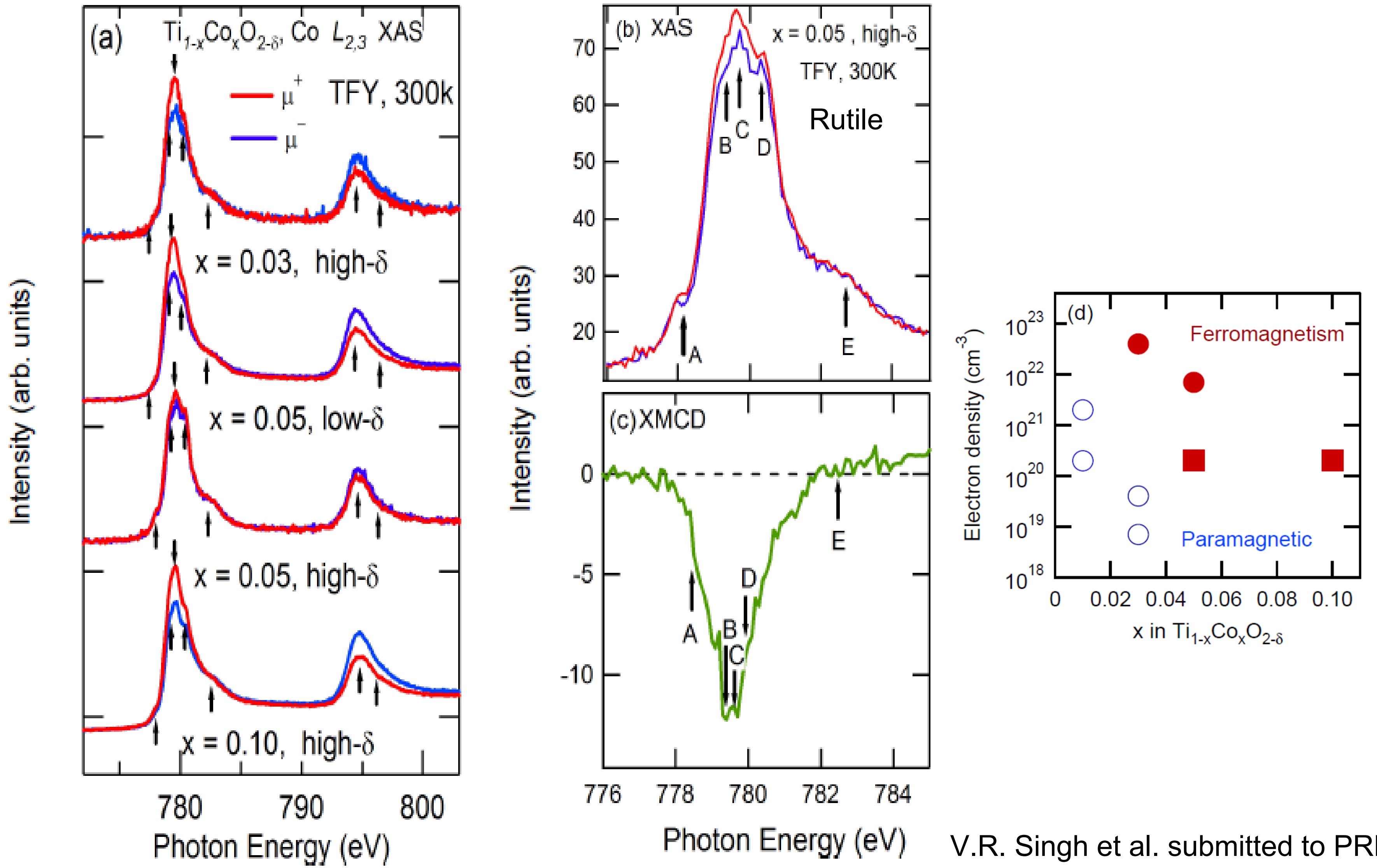
Bulk

Prohibited by ~mm thik substrate

Total fluorescence yield (TFY) mode

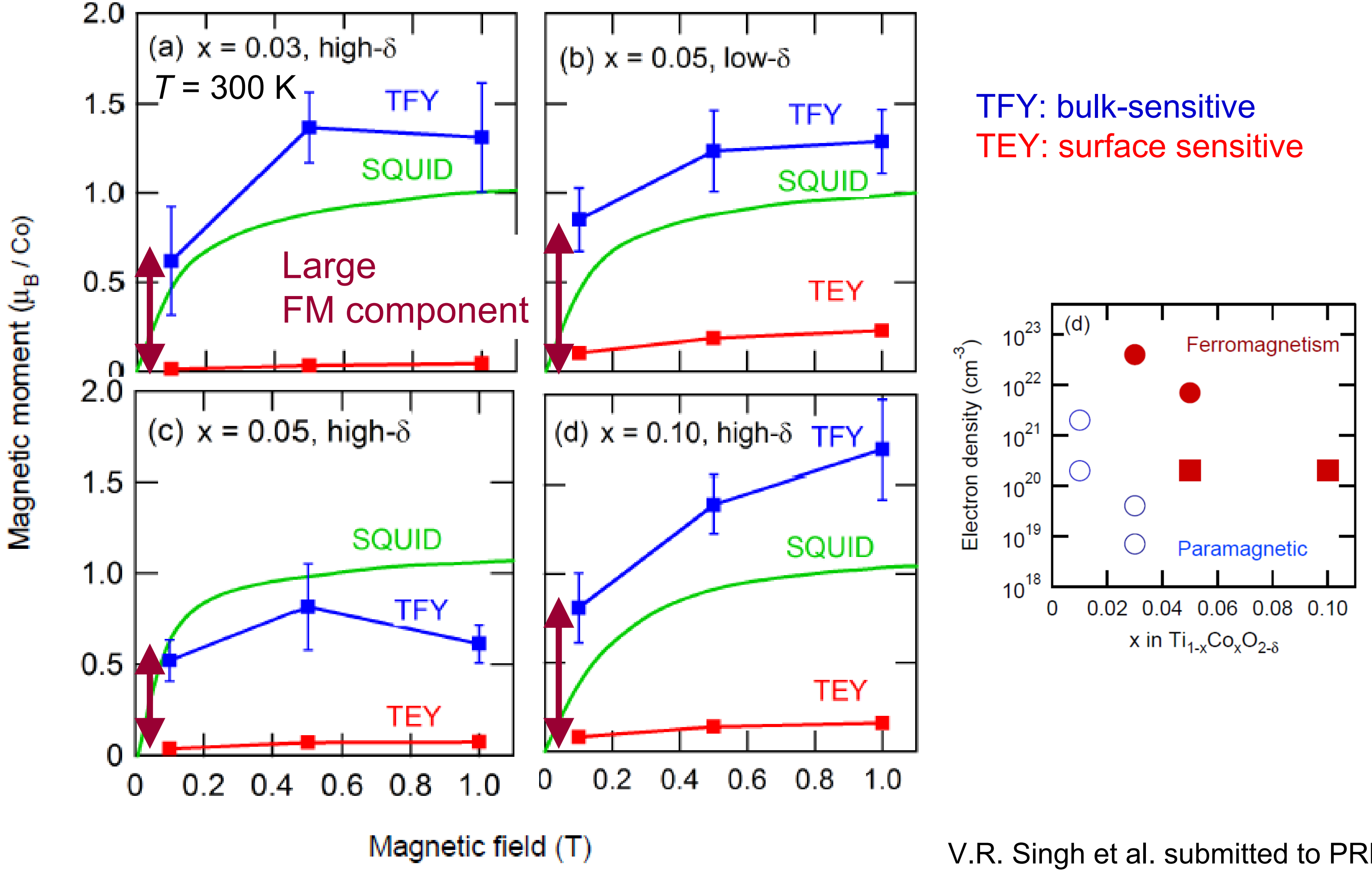
probing depth ~ 100nm ~ sample thickness

Co 2p XAS and XMCD of $Ti_{1-x}Co_xO_2$ measured by bulk-sensitive TFY mode



V.R. Singh et al. submitted to PRL

XMCD intensity and magnetization *vs* *H* for $Ti_{1-x}Co_xO_2$



TFY: bulk-sensitive

TEY: surface sensitive

V.R. Singh et al. submitted to PRL

Surface dead layer on $Ti_{1-x}Co_xO_2$ film

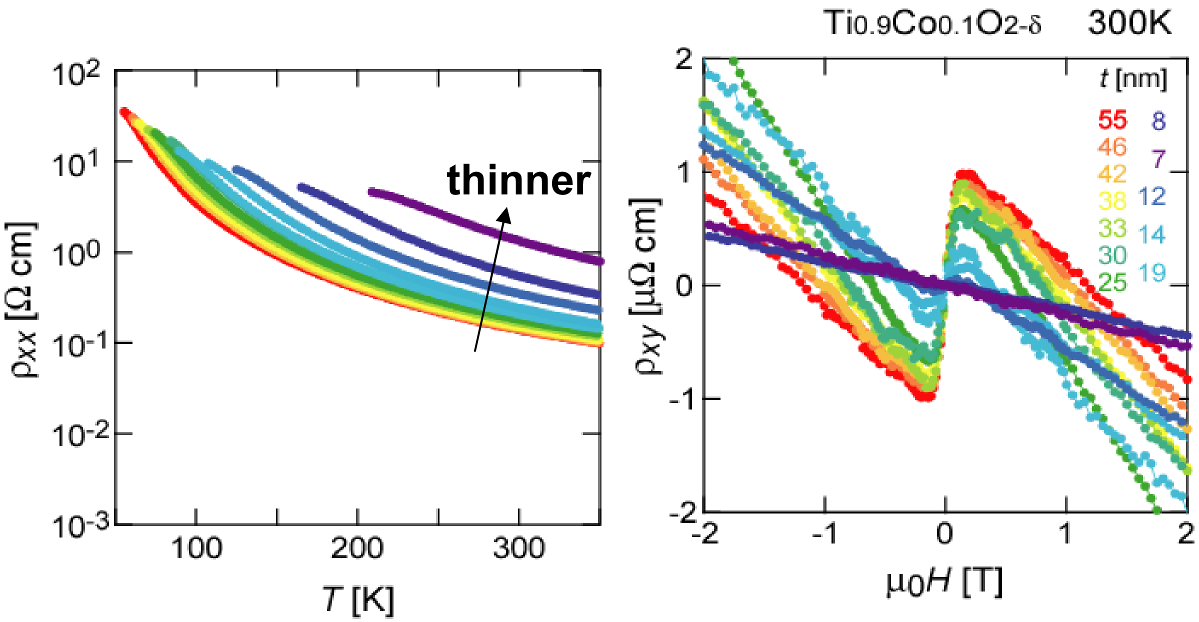
Total fluorescence yield (TFY) mode (probing depth ~ 100nm)

→ Strong XMCD intensity

Total electron yield (TEY) mode (probing depth ~ 3-5nm)

→ Weak XMCD intensity

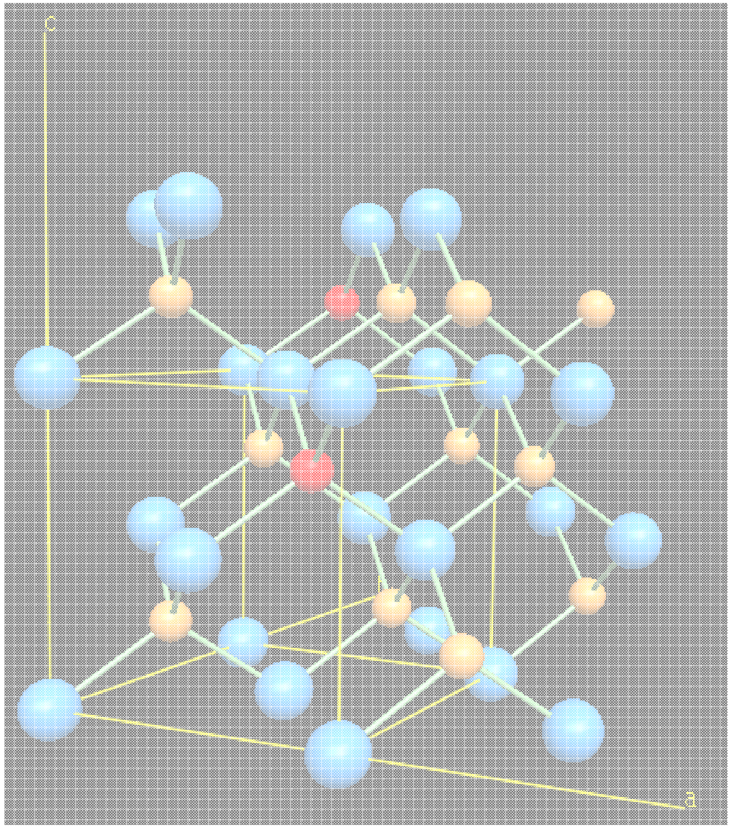
Suppression of AHE for $Ti_{1-x}Co_xO_{2-\delta}$ films



T. Fukumura et al., submitted to APL

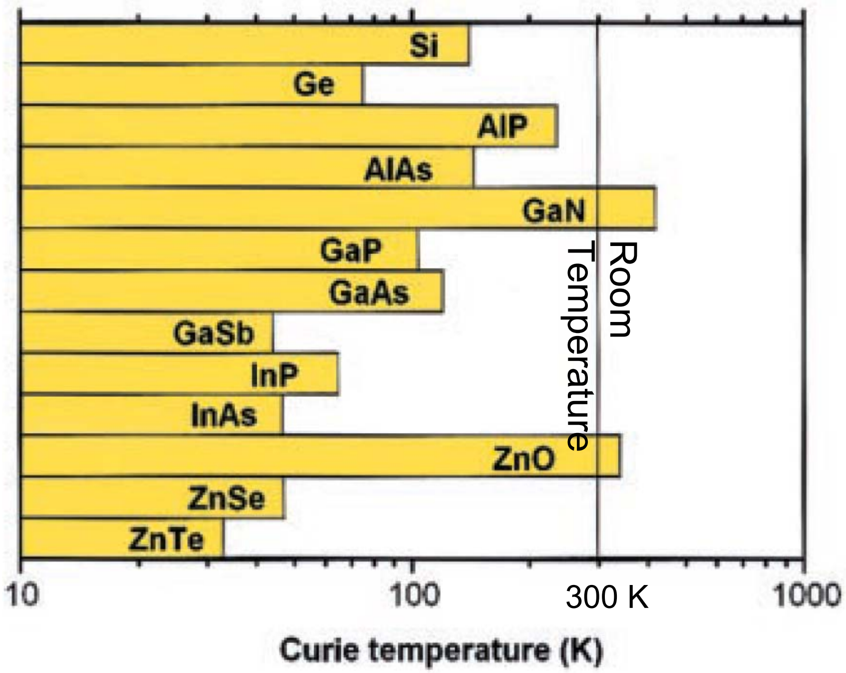
Surface layer of ~5 nm is magnetically dead due to carrier depletion.

ZnO-based DMS



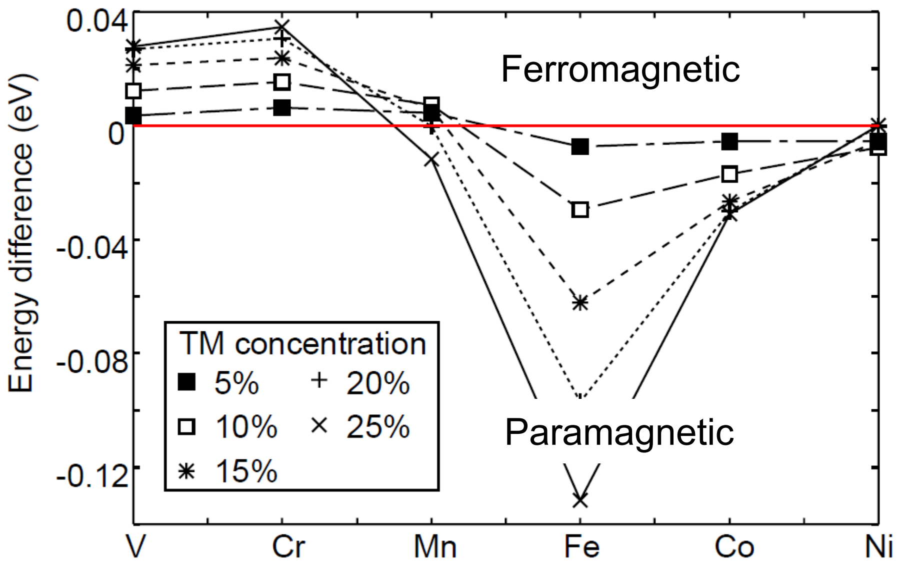
Theoretical prediction of room-temperature ferromagnetism in DMS

T_C of Mn-doped semiconductors in *p-d* exchange mechanism



T. Dietl et al. Science '00

Stability of magnetic states in DMS in double-exchange mechanism

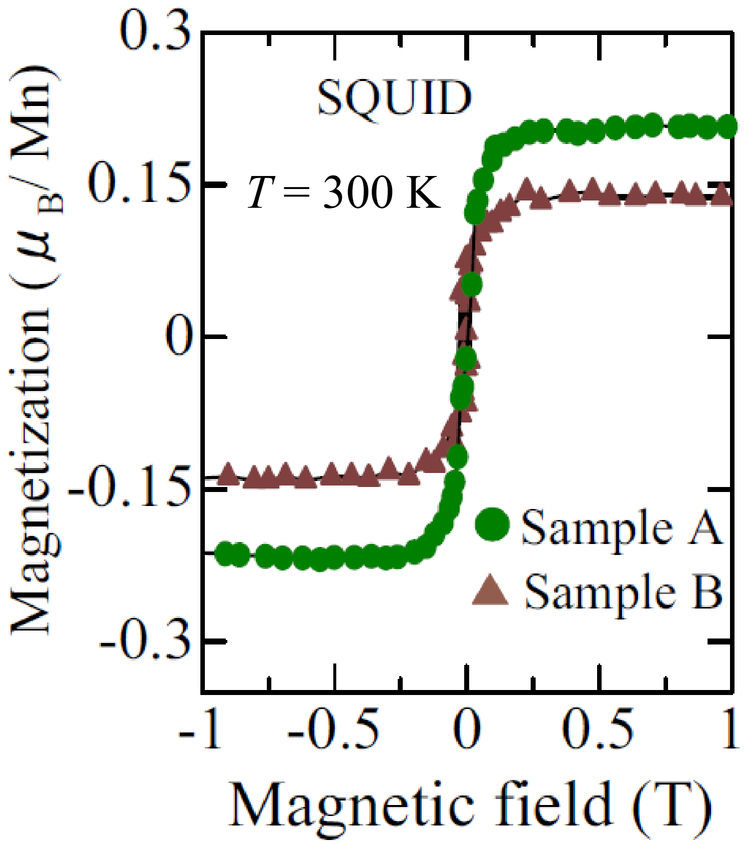


K. Sato et al. JJAP '00.

Wide-gap semiconductors such as ZnO, GaN, and TiO_2 are promising host materials for room-temperature ferromagnetic DMS.

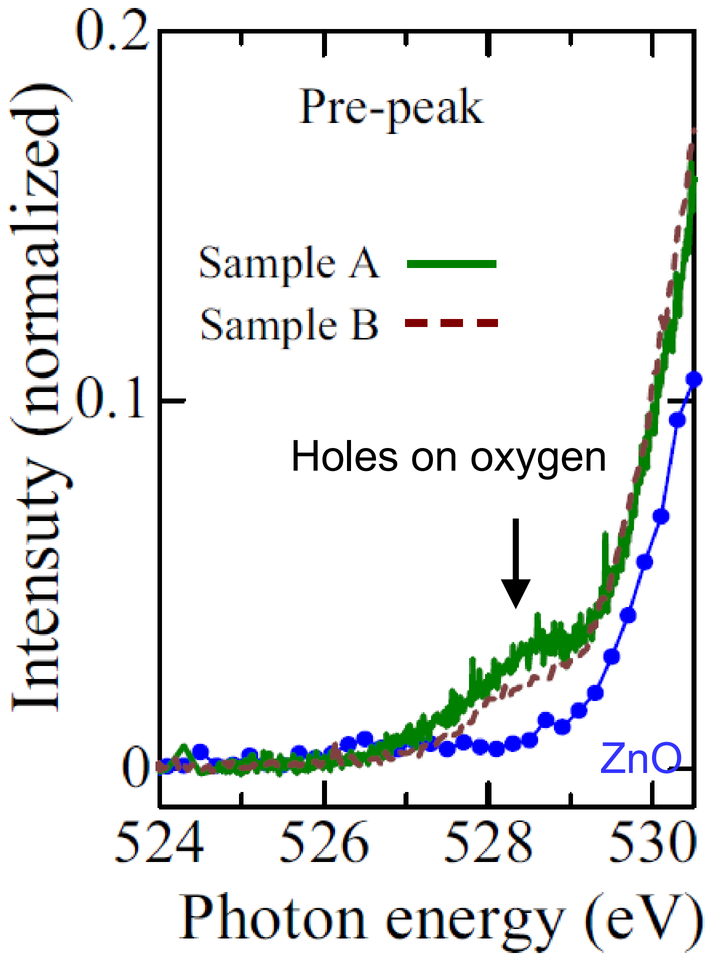
$Zn_{0.98}Mn_{0.02}O$ films prepared under N_2 atmosphere

Magnetization



Sample A: P_{N2} = 1.5 x 10^{-4} mbar
Sample B: P_{N2} = 4.0 x 10^{-4} mbar

O 1s XAS spectra

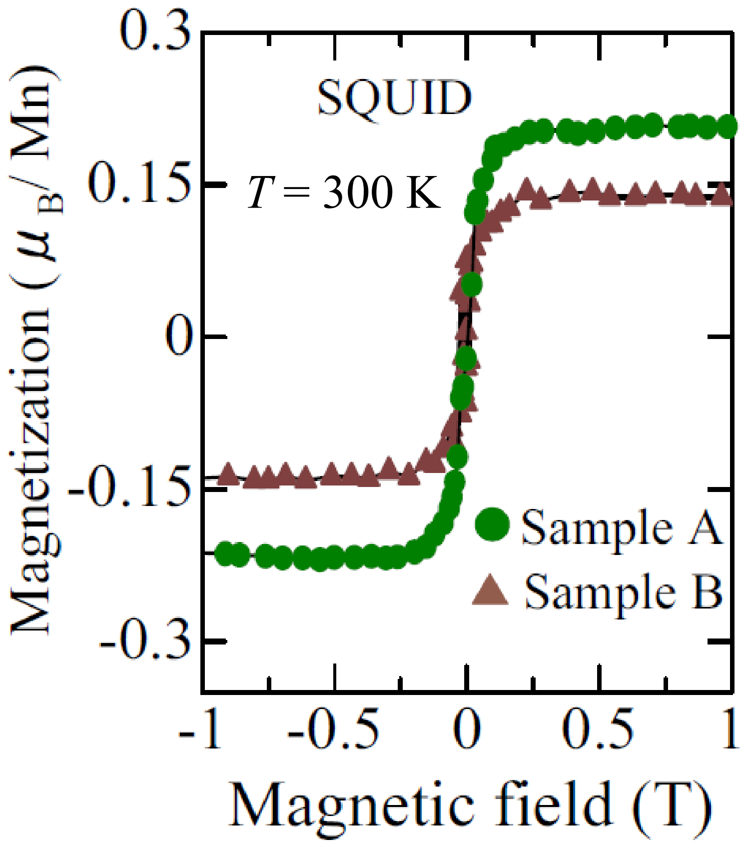


T. Kataoka et al.

cf) P. Sharma et al., Nature Mater '03.

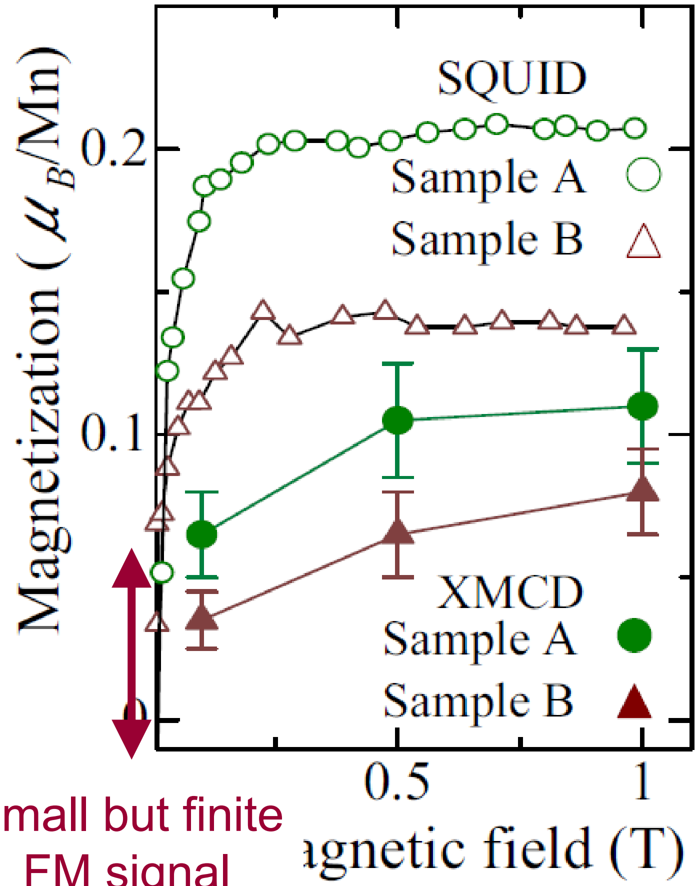
XMCD intensity and magnetization *vs H* in N-doped $Zn_{0.98}Mn_{0.02}O$ films

Magnetization



Sample A: P_{N2} = 1.5 x 10^{-4} mbar
Sample B: P_{N2} = 4.0 x 10^{-4} mbar

Comparison of magnetization and XMCD intensity



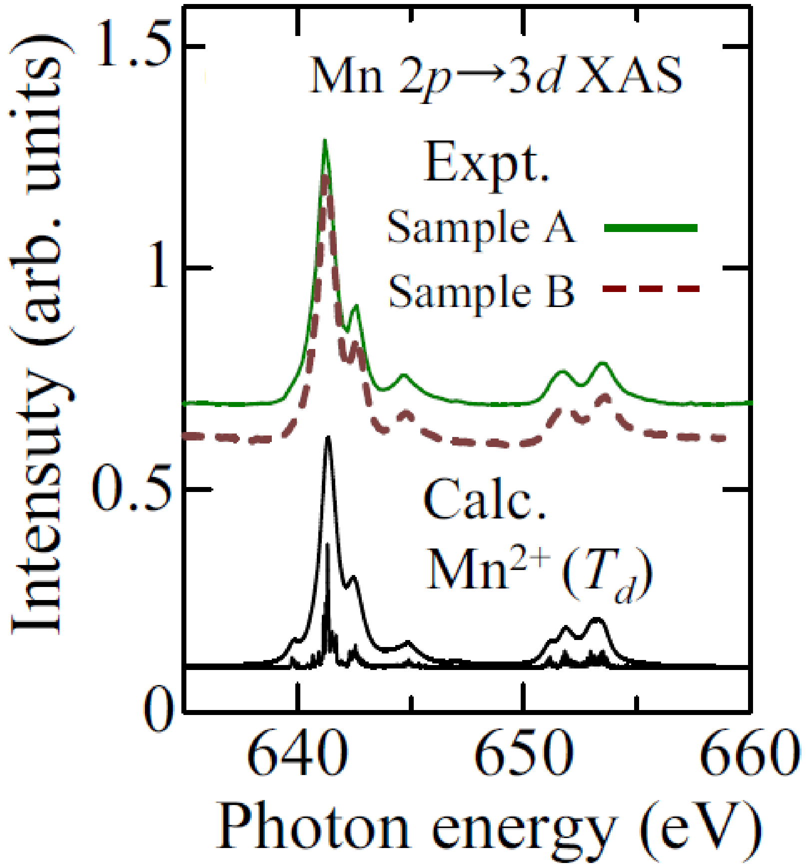
Small but finite FM signal

cf) P. Sharma et al., Nature Mater '03.

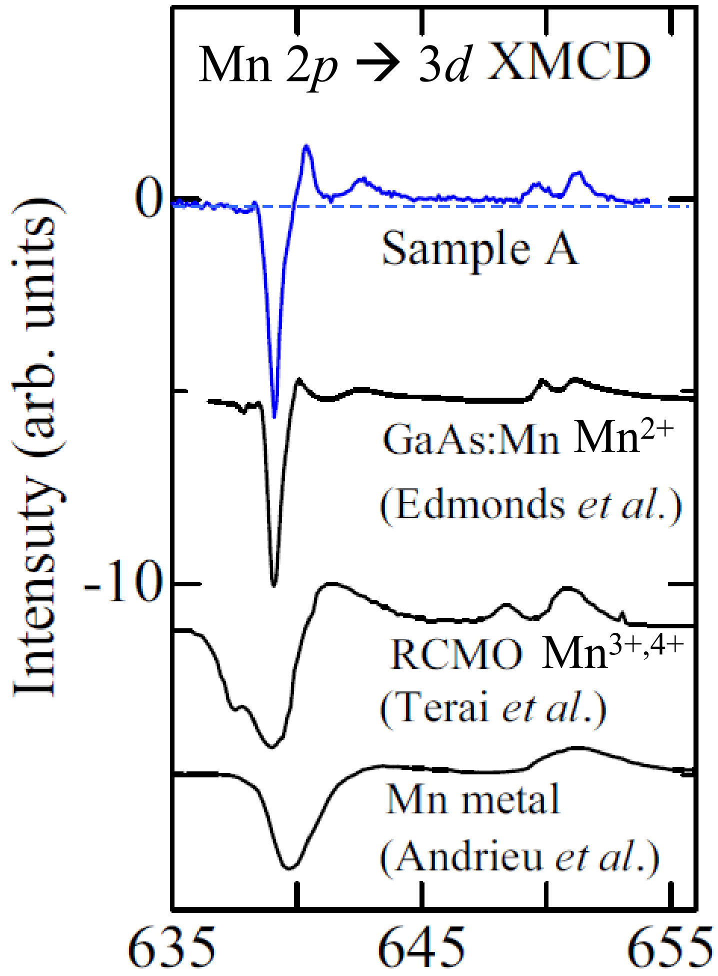
T. Kataoka et al.

Mn 2*p* XAS and XMCD of N-doped $Zn_{0.98}Mn_{0.02}O$ films

Mn 2*p* XAS spectra

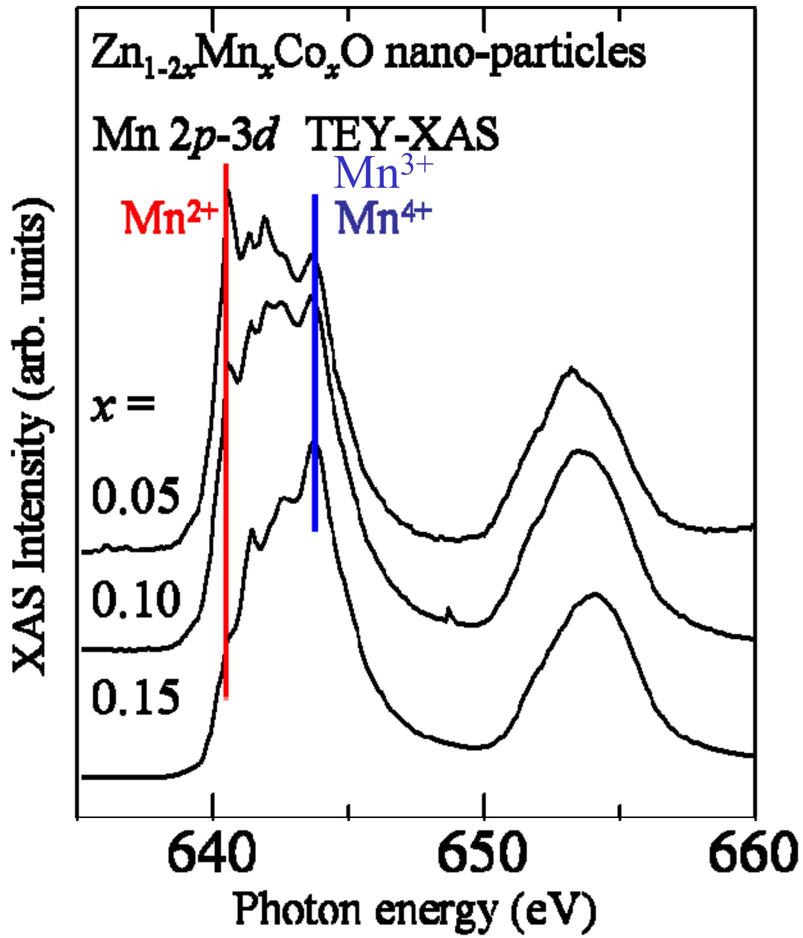


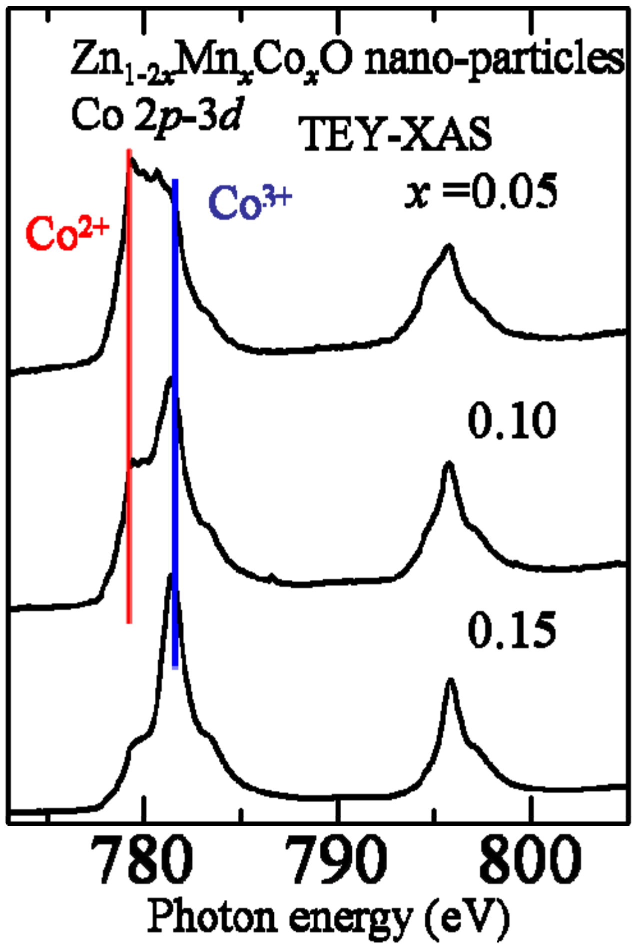
Mn 2*p* XMCD spectra



T. Kataoka et al.

Mn and Co 2*p* core-level XAS and XMCD of $Zn_{1-2x}Mn_xCo_xO$ nano-particles

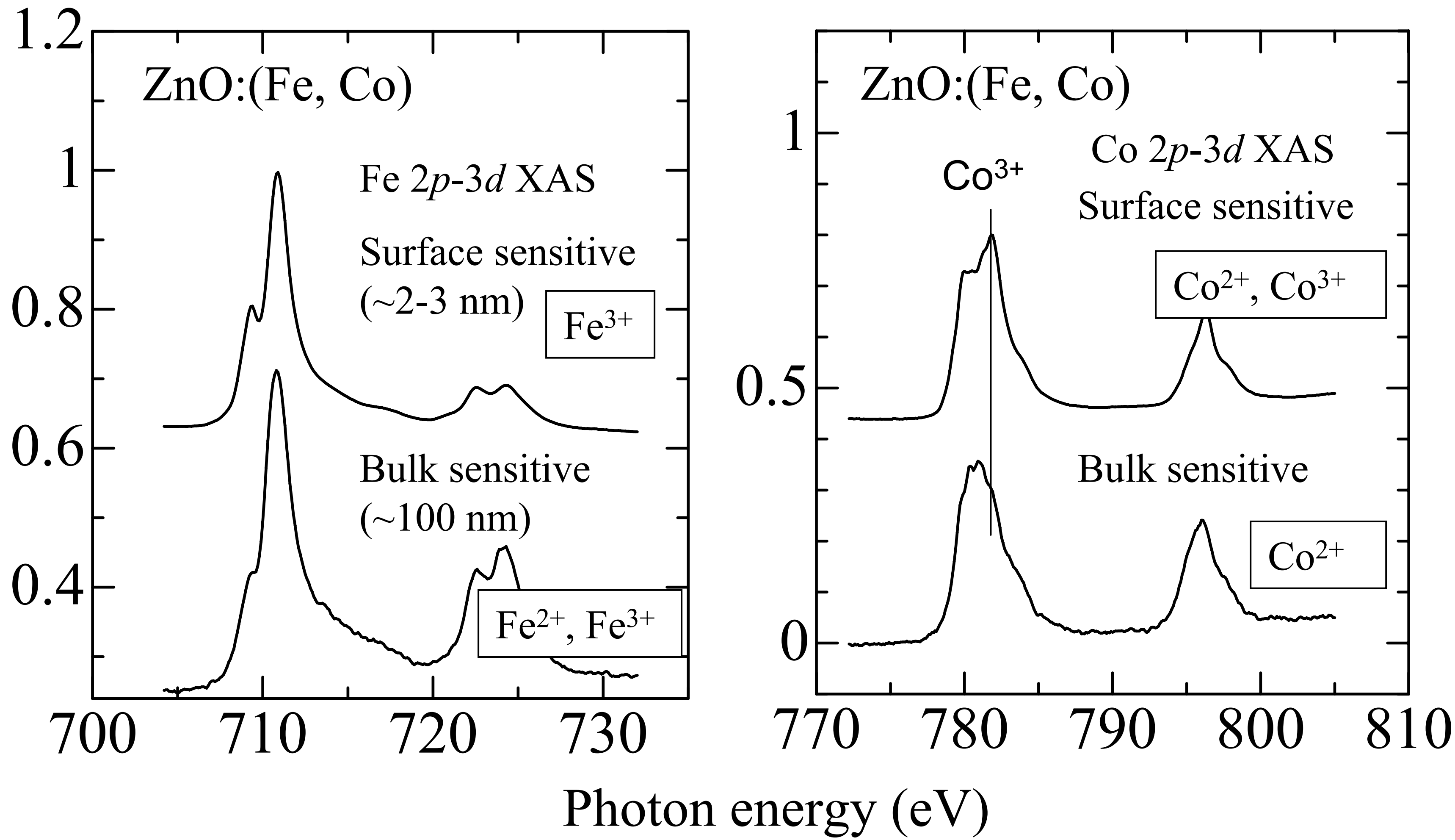




Paramagnetic, unfortunately.

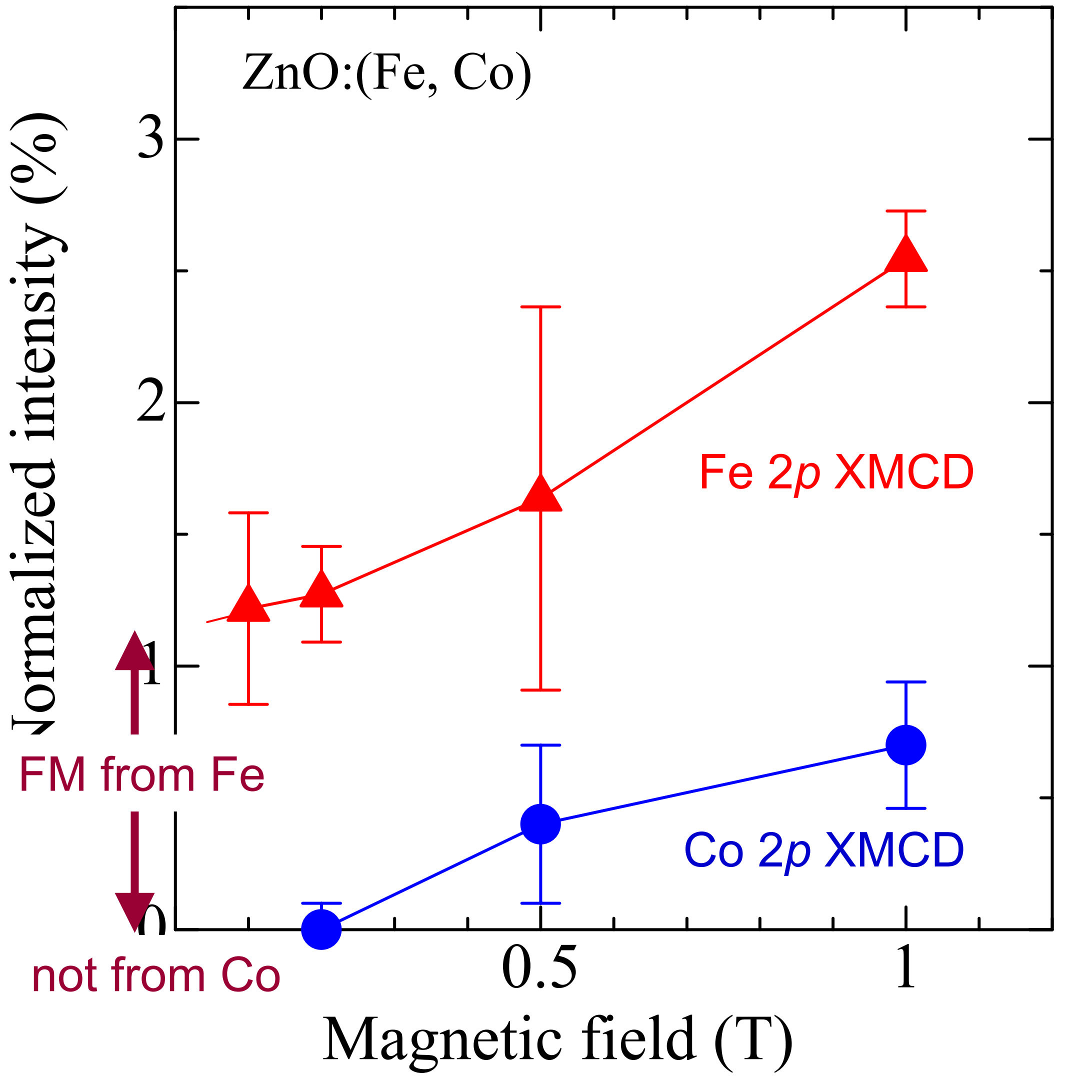
T. Kataoka et al.

Mn and Co 2*p* core-level XAS and XMCD of $Zn_{1-2x}Fe_xCo_xO$ nano-particles



T. Kataoka et al.

XMCD intensity *vs* *H* of $Zn_{1-2x}Fe_xCo_xO$ nano-particles

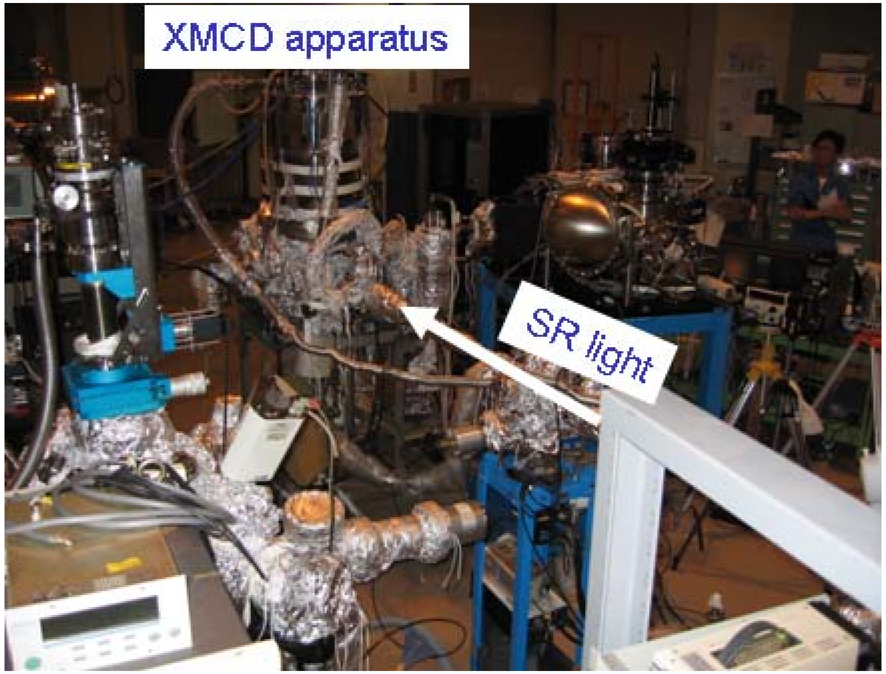


T. Kataoka et al.

Conclusion

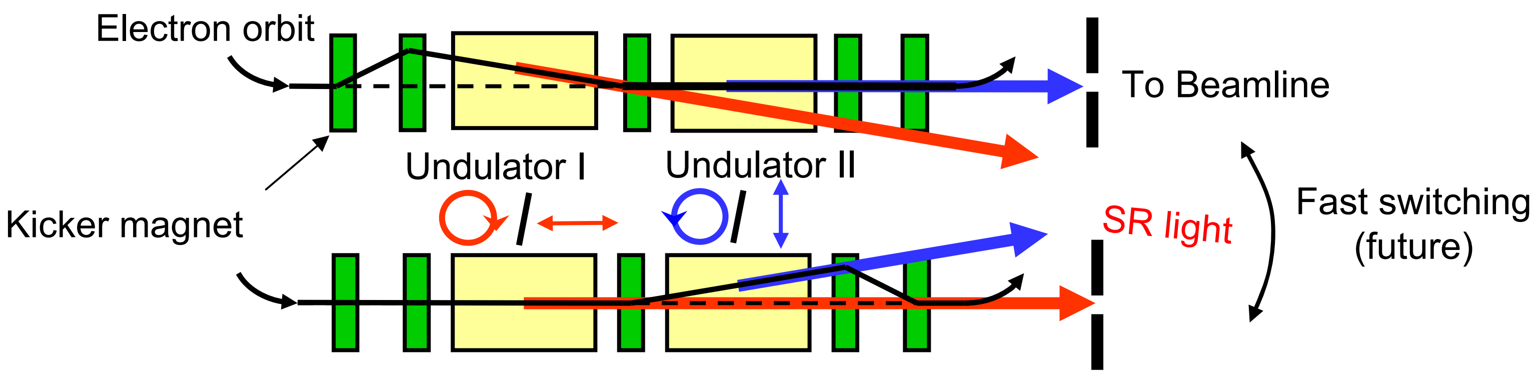
- XMCD of measurements as a function of *T* and *H* provide unique and important information about dilute magnetism in semiconductors.
- $Ga_{1-x}Mn_xAs$:
  - Interstitial Mn are AFM-coupled to substitutional Mn.
  - Low-temperature annealing expels interstitial Mn toward surface and increase the FM moment in bulk.
- $Ti_{1-x}Co_xO_2$:
  - Co^{2+} ions are responsible for the large FM moment.
  - There exists a magnetically dead layer of ~5 nm thickness.
- $Zn_{1-x}Cr_xTe$
  - Cr^{2+} drives inhomogeneous distribution of Cr ions and thereby increases T_C.
- ZnO-based DMS:
  - <u>Films</u>: Hole doping creates FM component.
  - <u>Nano-particles</u>: Valence of TM ions increases in the surface region.

XMCD endstation at BL-16A of Photon Factory (present)



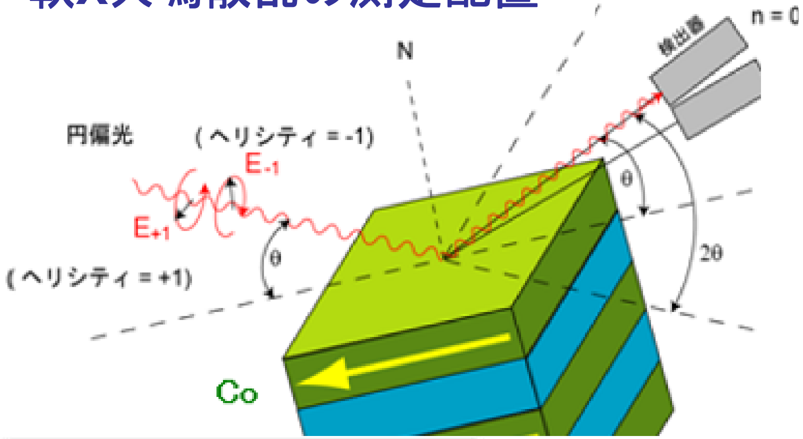
Superconducting magnet, up to 5 T
Low temperature down to ~10 K
Angular-dependent XMCD (L, T)

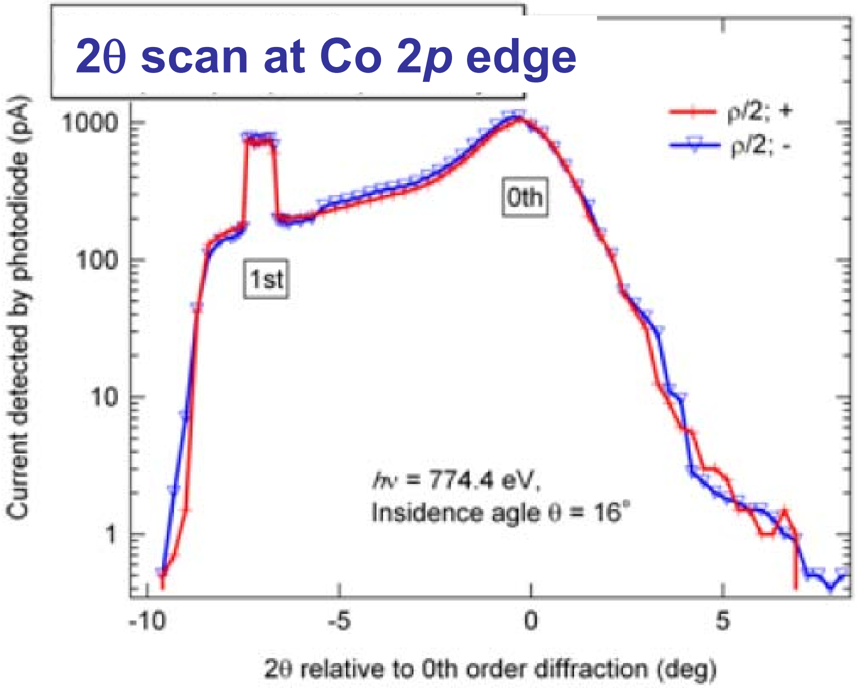
T. Koide et al. Rev. Rev. Sci. Instr. 63, 1462 (1992)

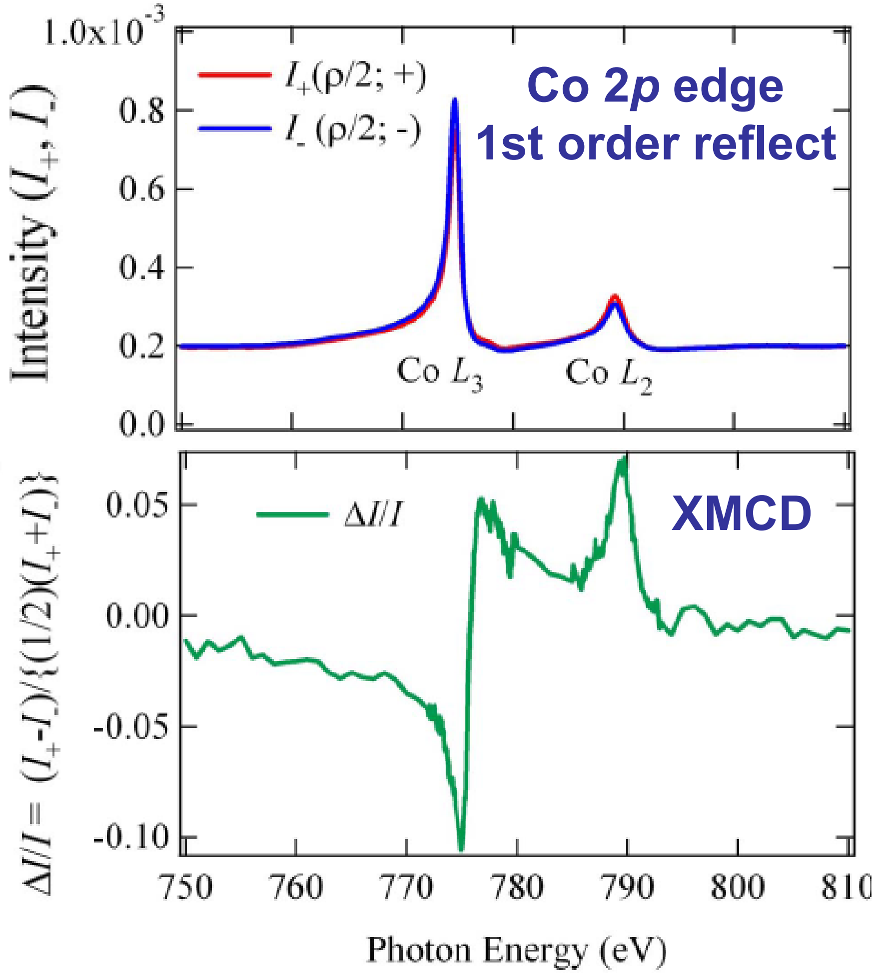


Co(4ML)/Pt(10ML)多層膜に対する予備実験結果

軟X共鳴散乱の測定配置



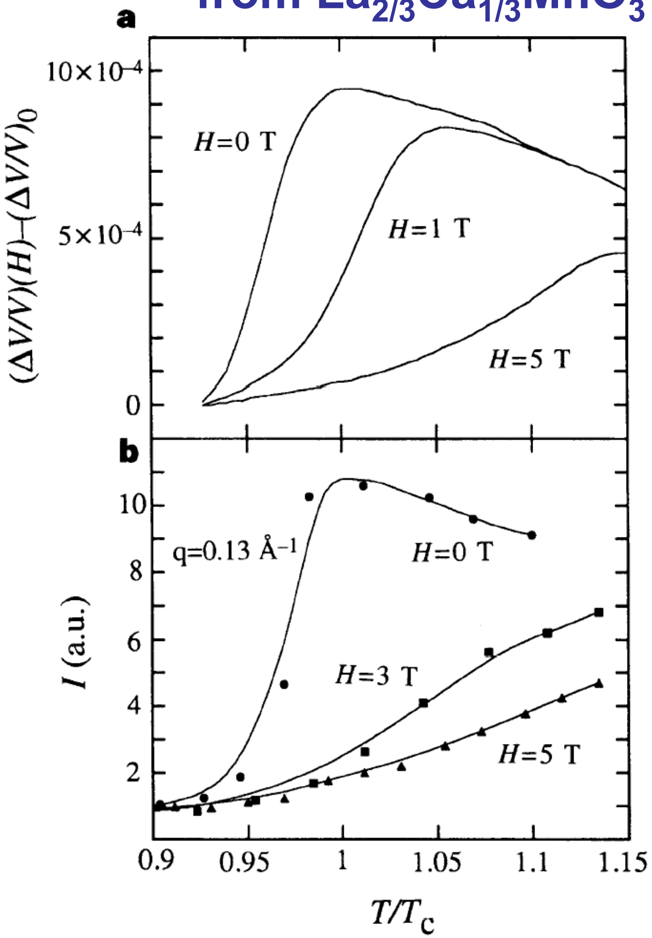




小出，朝倉

Inhomogeneous chemical and electronic states in high-T_C DMS

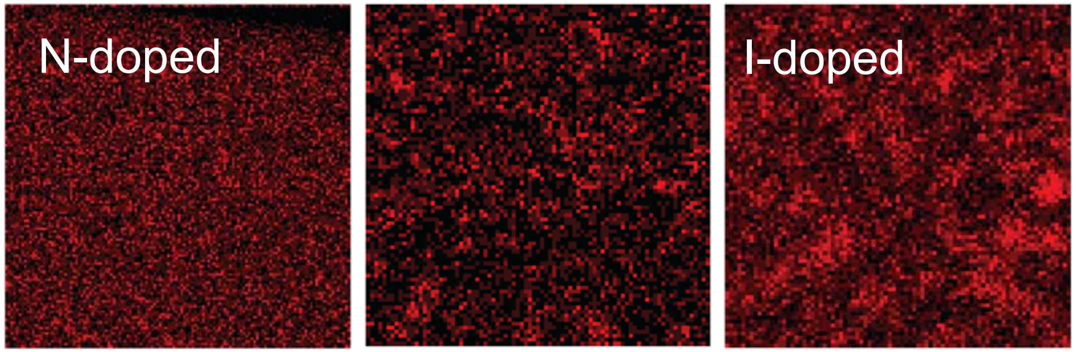
Small angle neutron scattering from $La_{2/3}Ca_{1/3}MnO_3$



Ferromagnetic nano-particles

J.M. De Teresa et al., Nature '97

Energy-dispersive X-ray spectroscopy image

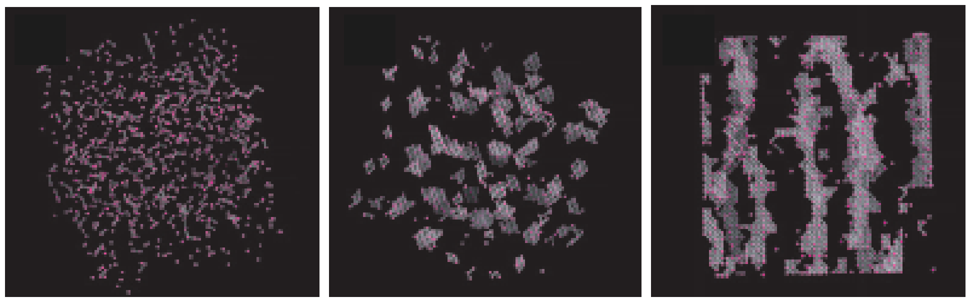


uniform ⟷ non-uniform

T_C low ⟷ T_C high

S. Kuroda et al., Nat. Mater. '07

Spinodal decomposition in high-T_C DMS's



K. Sato et al., JJAP '05, T. Fukushima et al., JJAP '06

→Cr^{2+}とCr^{3+}を分離した空間分布, ナノ粒子の電子構造分布