Growth, crystalline structure and magnetism of low-dimensional systems

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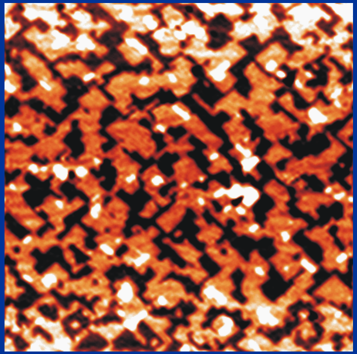
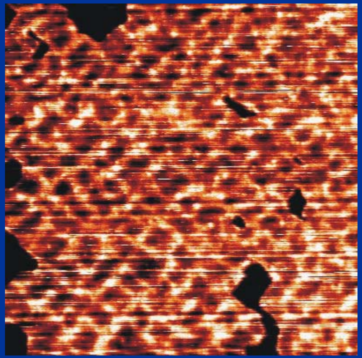
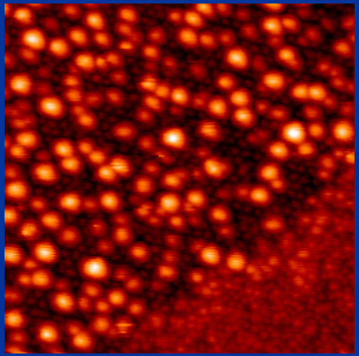
Ni/Cu_3Au(100)



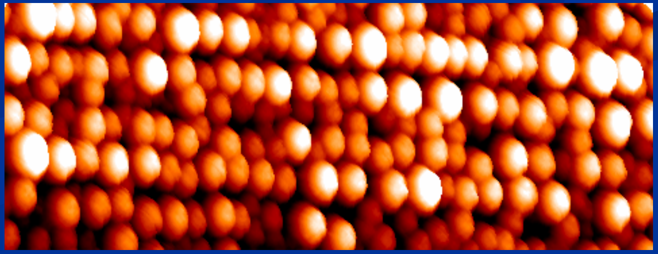
Mn/Cu_3Au(100)



Co/Si_3N_4/Si(111)



Co/Al_2O_3/NiAl(100)

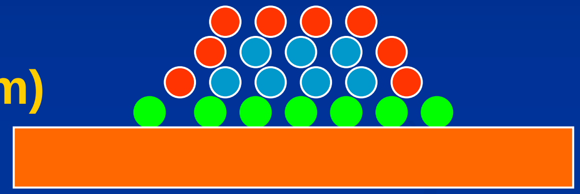


Why are low-dimentional systems interesting?

Magnetic, catalytic, structural …..properties?

1. Surface & interface effect:

ex: catalytic Au nano-particles (diameter 2~3 nm)

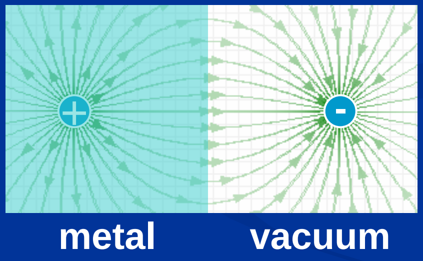


M. Valden et al, Science 281, 1647 (1998)

SRT in ultra-thin film:

M-T. Lin et al, PRB **62**, 14268 (2000)

Image potential states:

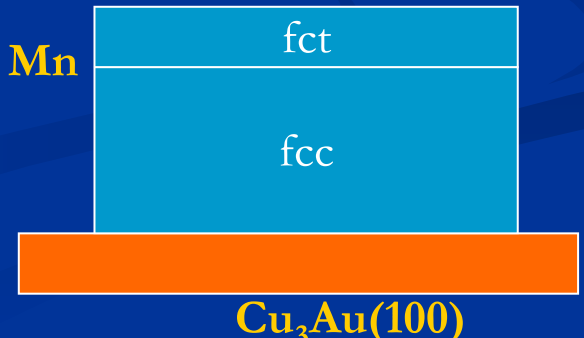


2. Artificial structure:

ex: bulk Mn → complex structure,
bulk Cu_3Au → fcc

fcc Mn/Cu_3Au(100)

W. C. Lin et al, Phys. Rev. B **74**, 765 (2007).

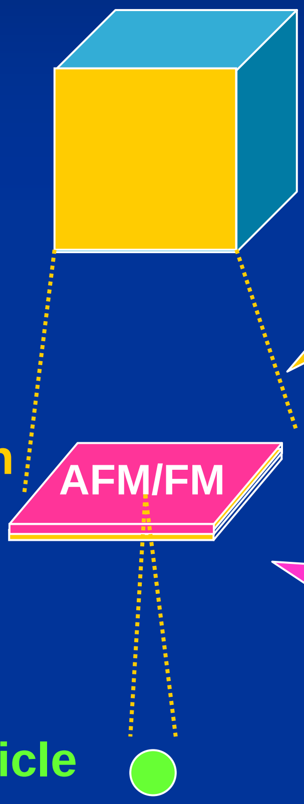


in Magnetism

Magnetic anisotropy ($E_{ani.}$): dipole-dipole, spin-orbital

Shape $E_{ani.}$ & Crystalline $E_{ani.}$

Bulk



Ultrathin film

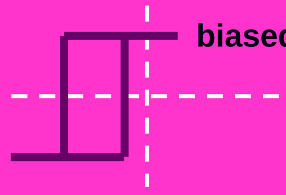
Nanoparticle

{ surface $E_{ani.}$, volume $E_{ani.}$ }
by thickness

{ shape $E_{ani.}$, crystalline $E_{ani.}$, strain-induced $E_{ani.}$ }
by strain, alloy

Manipulation of spin orientation

$E_{ani.}$ from AFM/FM exchange bias coupling



biased loop, enhanced H_c

⇒Enhanced H_{ex},
⇒Detection of AFM films

$E_{ani.}$ (~ μ eV/atom) ⟷ k_BT (~ meV): superpara.
10^3 ~10^4 atoms to overcome k_BT

Tc ↑ ($E_{ani.}$ ↑): exchange bias coupling, shape $E_{ani.}$,
other **inter-particle coupling**??

Outline

Instrumentation:

How to fabricate & characterize?

Low dimensional systems:

☐ *2-dimensional:*

- $Co_xNi_{1-x}/Cu_3Au(100)$: Manipulation of spin orientation
- $Mn/Cu_3Au(100)$: Artificial AFM structure
- Fe/Fe_xMn_{1-x} on $Cu_3Au(100)$ & Cu(100): Enhanced H_{ex}
- Cu(100): Spin-polarized multi-photon photoemission

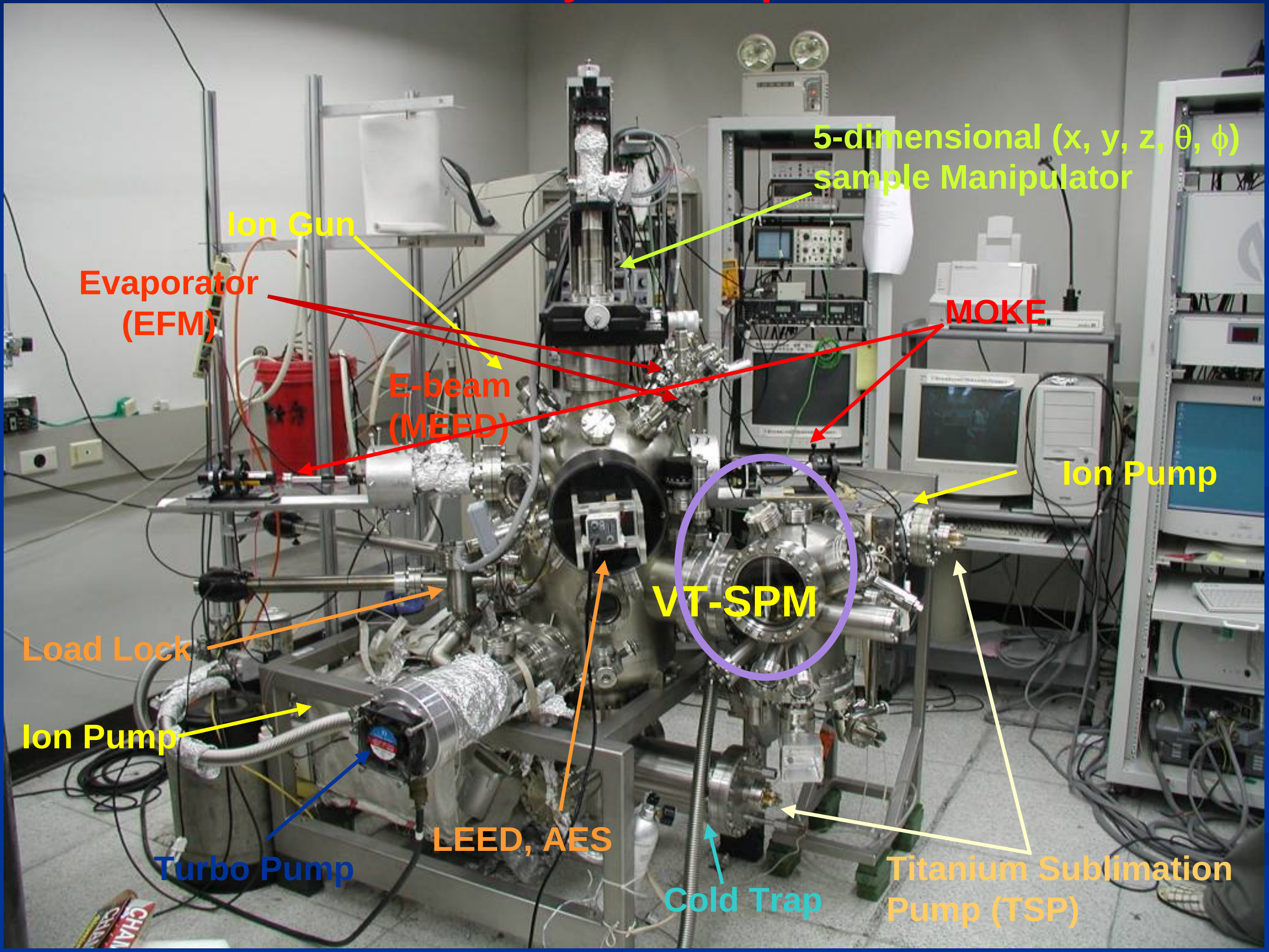
☐ *0~1-dimensional: Aligned nanoparticles*

- nano-dots/Al_2O_3/NiAl(100) : Magnetic nanostructures

Ultra-high vacuum system I

(Department of Physics, NTU)

Multi-Functional Analysis & Deposition Chamber



Ultra-high vacuum system II

(IAMS, Academia Sinica)

UHV chamber (Base pressure ~$1x10^{-10}$ torr):

Clear environment

EFM3 (e-beam evaporator):

Co-deposition of alloy films

Auger electron spectrum (AES):

Chemical element analysis

Medium electron energy diffraction (MEED) :

Thickness calibration, growth condition monitor

Low electron energy diffraction (LEED/IV-LEED) :

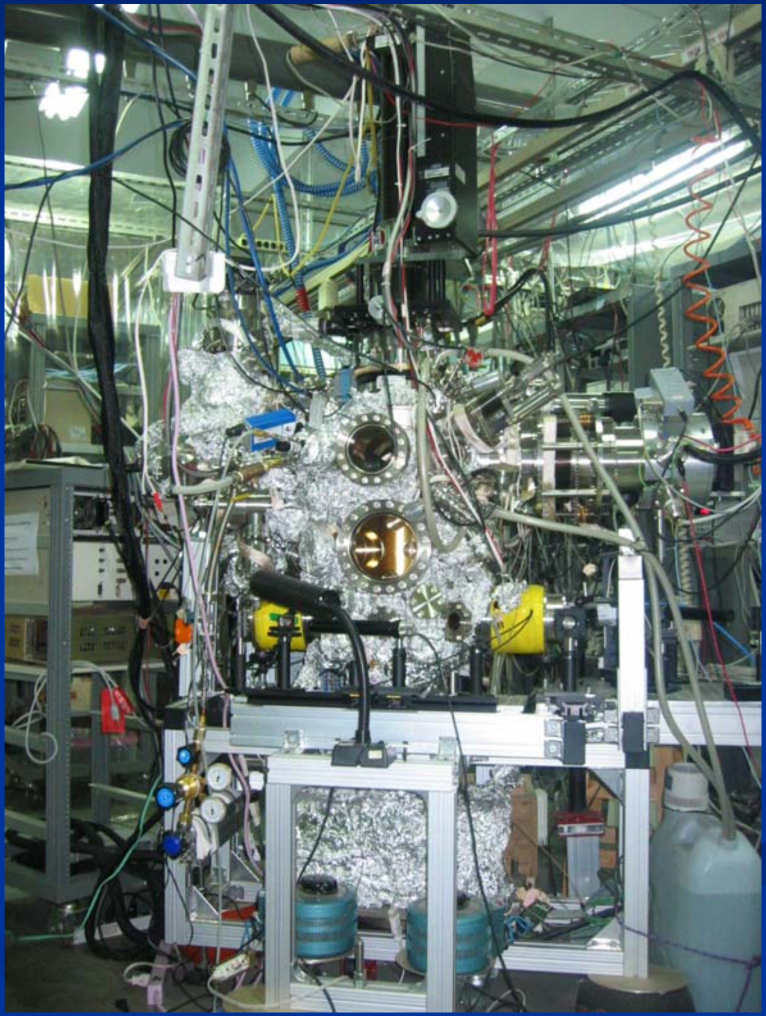
Morphology and Structure analysis

Magnetic-optical Kerr effect (MOKE):

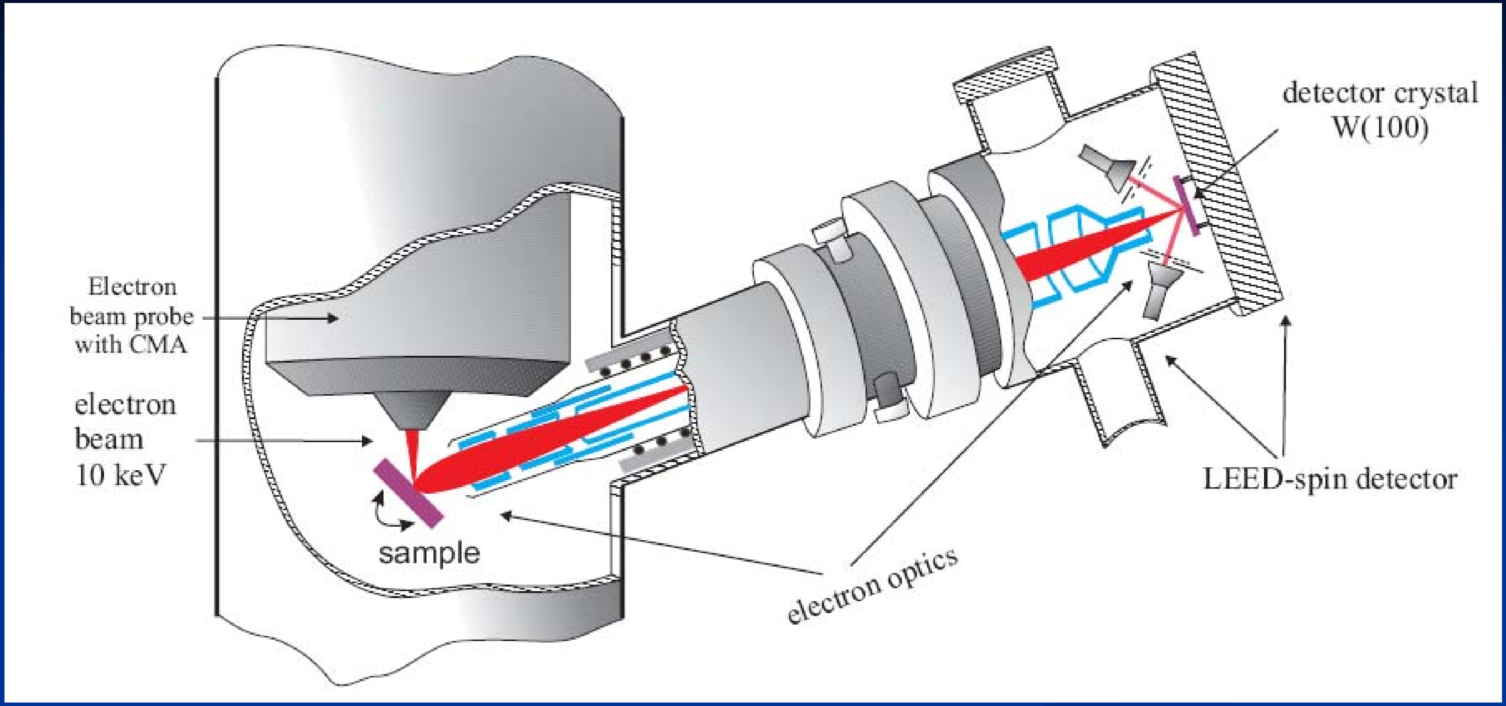
Magnetic property analysis(in-plane & perpendicular)

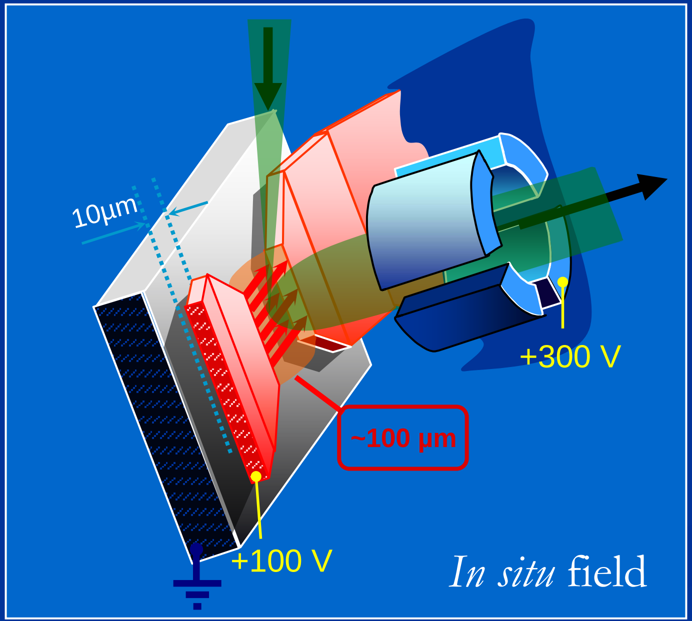
Ion sputtering (Ne^{+} 3 keV):

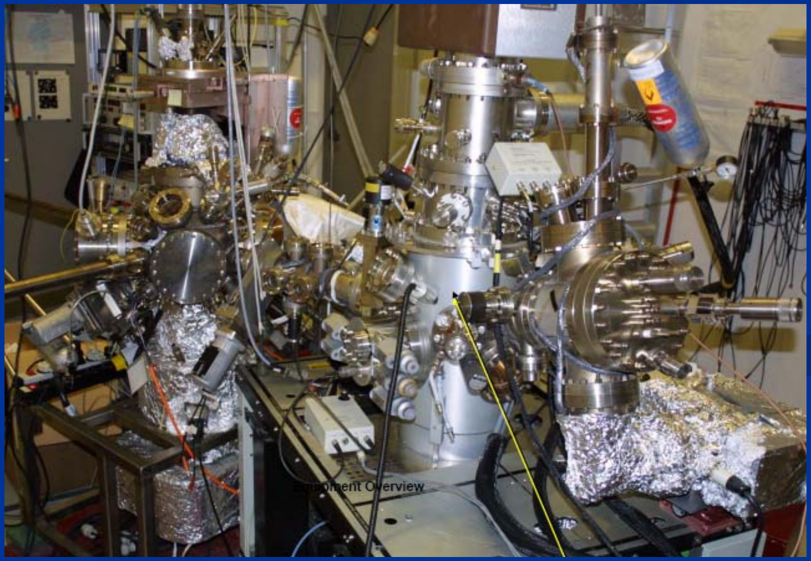
Sample cleaning



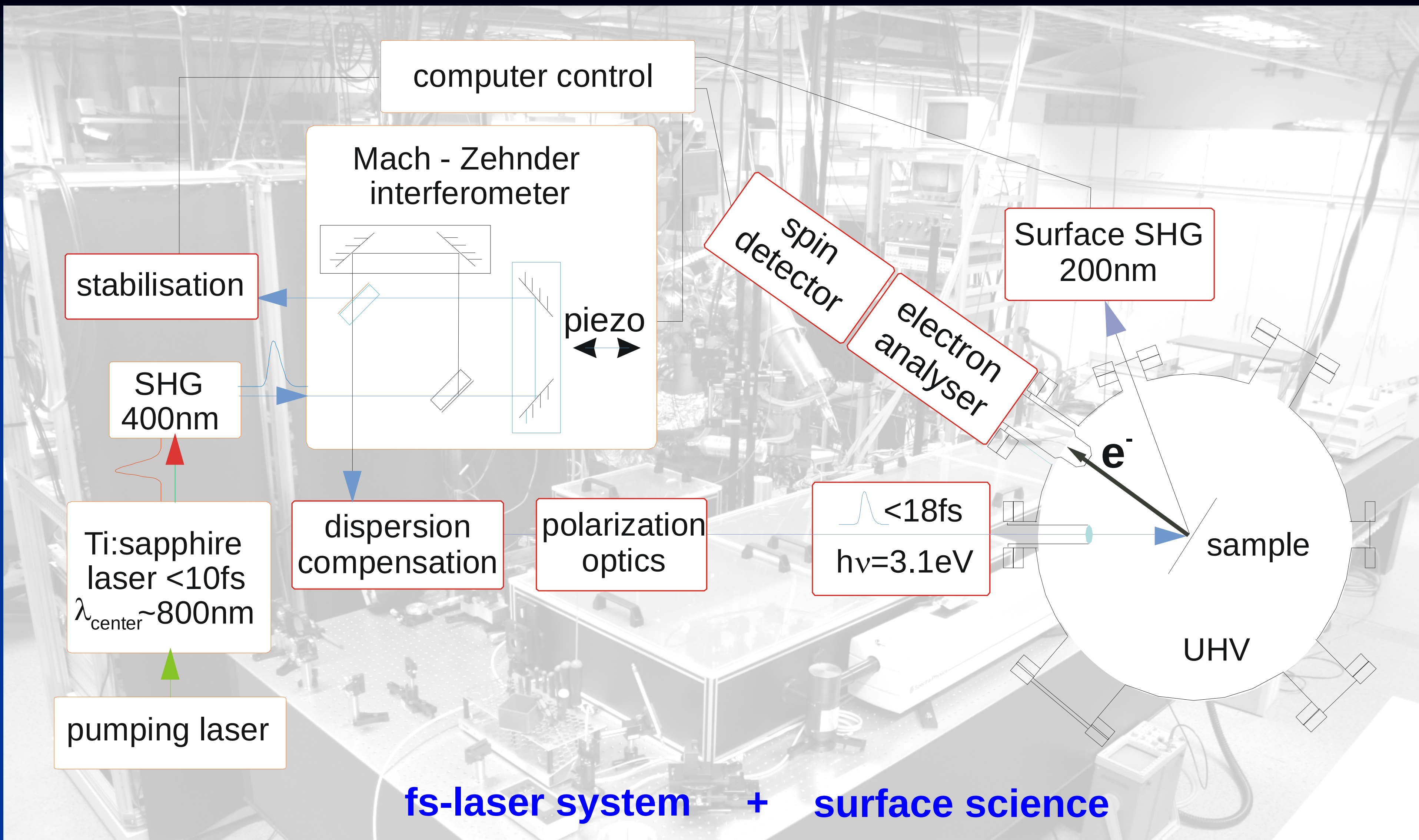
SEM with spin analysis (SEMPA)







Center for Nanophase Material Sciences, Oak Ride National Lab



Multi-photon Photoemission with Spin Analysis

Low dimensional systems:

□ *2-dimensional: Ultra-thin films*

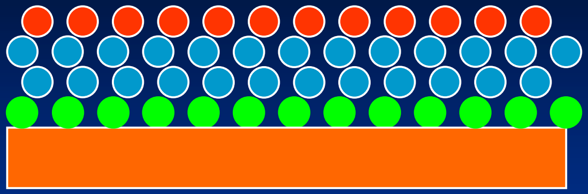
- $Co_xNi_{1-x}/Cu_3Au(100)$: Manipulation of spin orientation
- $Mn/Cu_3Au(100)$: Artificial AFM structure
- Fe/Fe_xMn_{1-x} on $Cu_3Au(100)$ & Cu(100): Enhanced H_{ex}

□ *0~1-dimensional: Aligned nanoparticles*

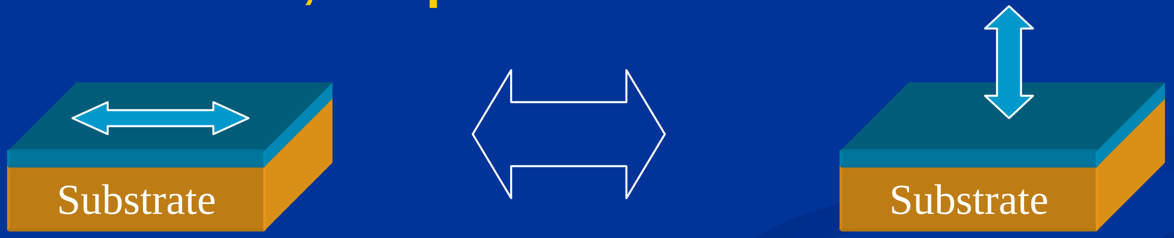
- nano-dots/Al_2O_3/NiAl(100) : Magnetic nanostructures

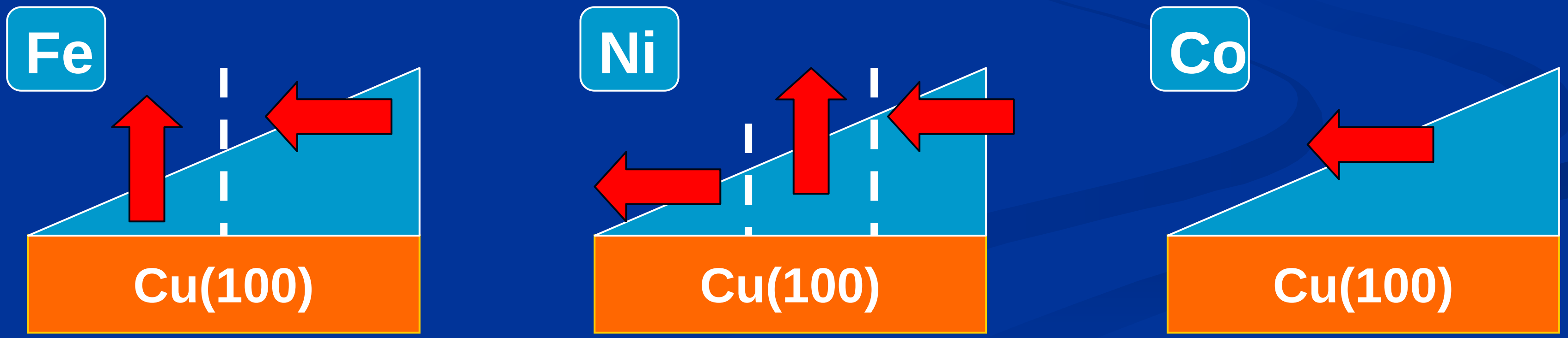
Ultrathin film:

Surface atoms v.s. **Volume atoms**



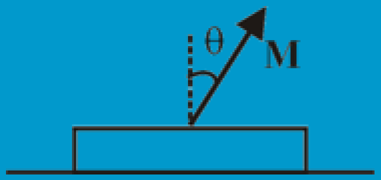
Spin-reorientation transition (SRT) by thickness, temperature or structure





In physics: alloy effect on $E_{anisotropy}$ (electronic structure)

$$E = K_{eff} \sin^2\theta = (K_V + 2K_S/t)\sin^2\theta$$



$K_{eff} > 0 \Rightarrow$ perpendicular

$K_{eff} < 0 \Rightarrow$ in-plane

$K_{eff} = 0 \Rightarrow t_c = -2K_S/K_V$ ***t : thickness***

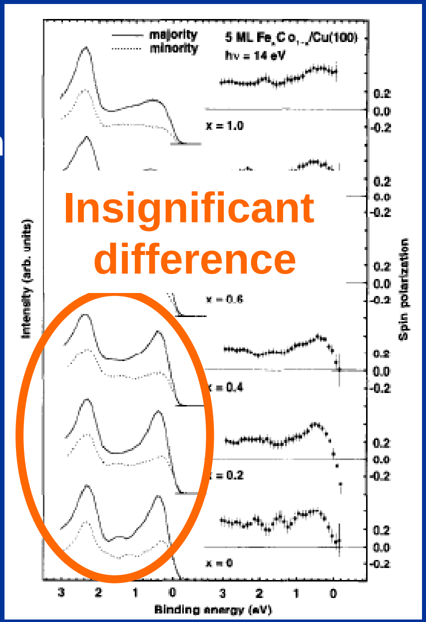
K_{eff}: $(K_{shape})_{dipole} + (K_{crystalline} + K_{magneto\text{-}elastic})_{spin\text{-}orbital\ coupling}$

	$K_{me}(\mu eV/atom)$	$K_s(\mu eV/atom)$	$M(\mu_B)$	$-2\pi M^2(\mu eV/atom)$
Co/Cu(100)[26,27]	−73.8	−55.8	1.8	−90
Ni/Cu(100)[9,27]	29	−77	0.57	−9.1

Order of *μeV/atom*

B. Schulz et al, PRB **50**, 13 467 (1994). M. Kowalewski et al, PRB **47**, 8748 (1993). R. F. Willis et al, JAP **63**, 4051 (1988).

Spin-polarized Photoemission of Co-Fe alloy films:



Insignificant difference

M. Zharnikov et al, JMMM 165, 250(1997).

First principle calculation:

Rapid oscillations

G. H. O. Daalderop et al, PRB 41, 11919 (1990).

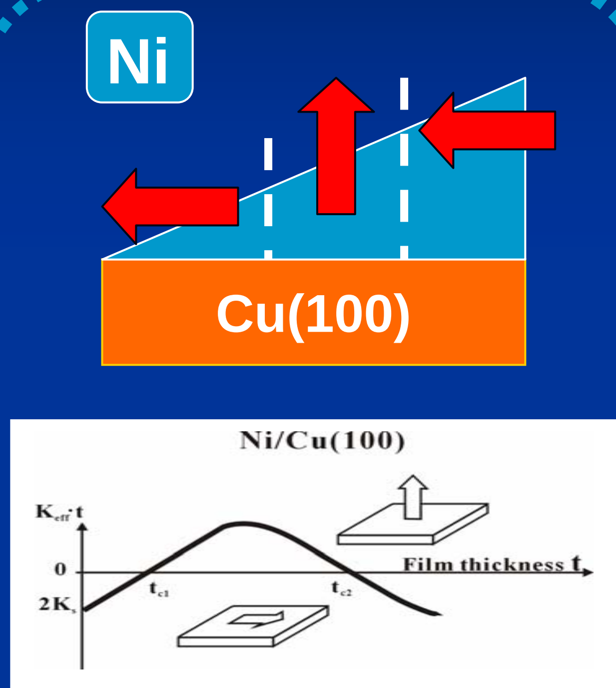
Smooth behavior

D.-S. Wang et al, PRL 70, 868 (1993).

Probe $E_{ani.}$ by monitoring SRT

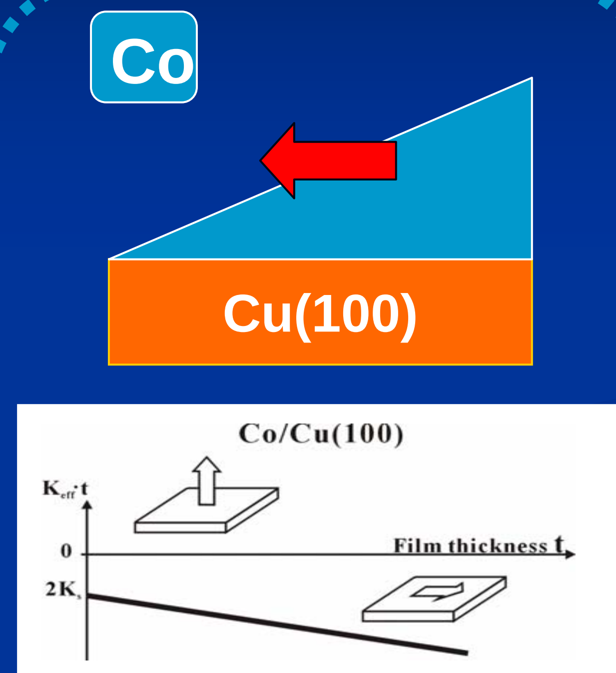
Alloy effect??

In Phenomenon:



$K_S < 0$, $K_{mag.-elastic} > 0$

+

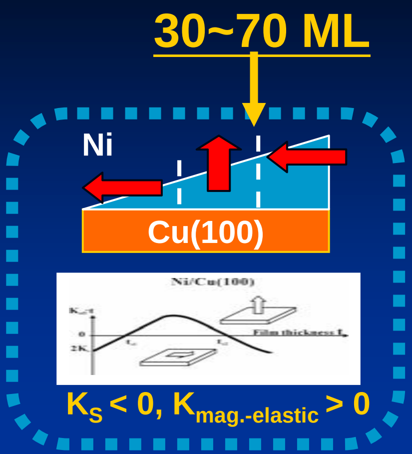


$K_S < 0$, $K_V < 0$

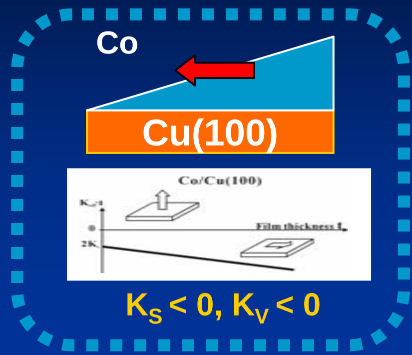
=?

Manipulation of spin orientation!!

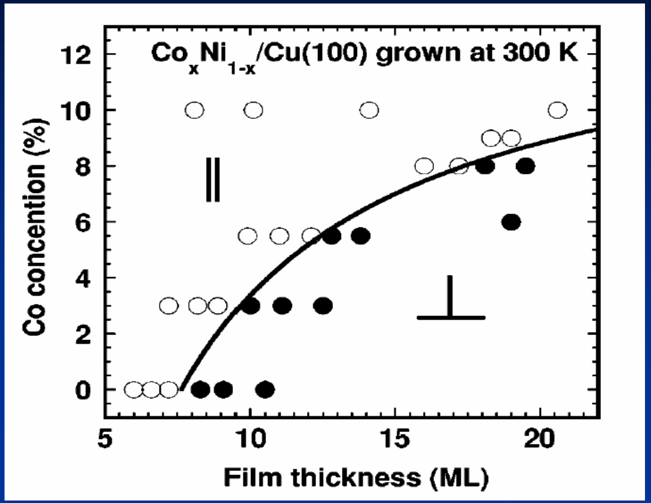
Alloy effect



+



= ?



M.-T. Lin,W.C.Lin,C.C.Kuo, and et.al,PRB, **62**, 14268 (2000).

Why $Cu_3Au(100)$?

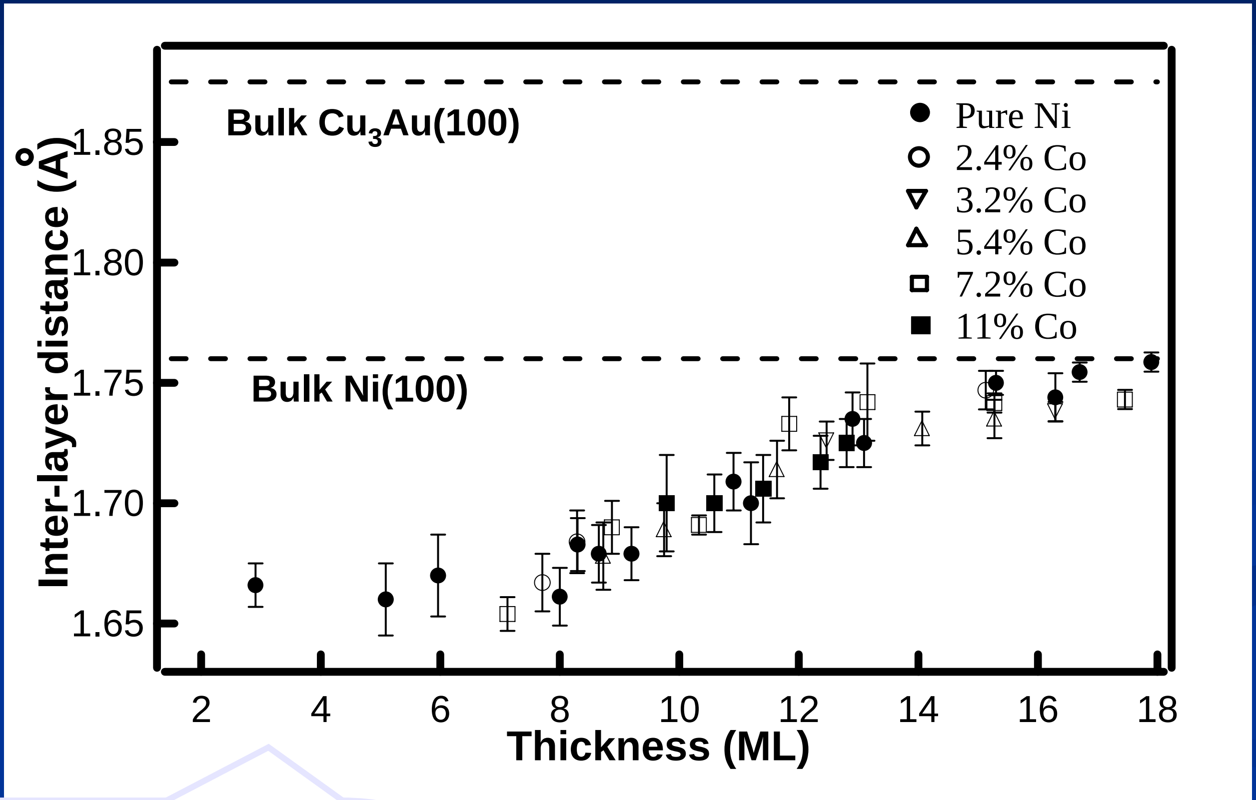
Ni/Cu(100): Lattice mismatch = -2.6 %

$Ni/Cu_3Au(100)$: Lattice mismatch = -6.1 %

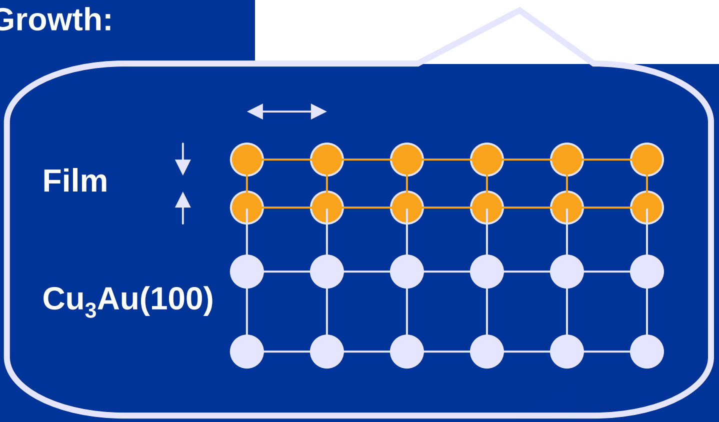
⇒ Earlier strain relaxation & the 2nd SRT

Alloy effect on the 2nd SRT?

Interlayer distance of $Co_xNi_{1-x}/Cu_3Au(100)$ ___ *at 100K*



Pseudomorphic Growth:



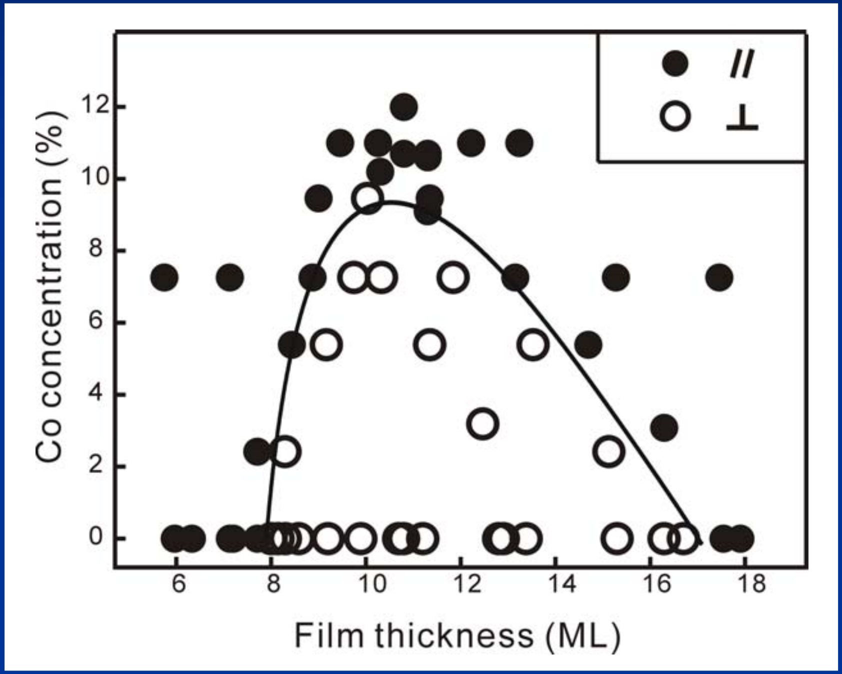
⇒ ***Vertical lattice relaxed with the increasing of thickness***

⇒ ***This relaxation process is independent of alloy composition***

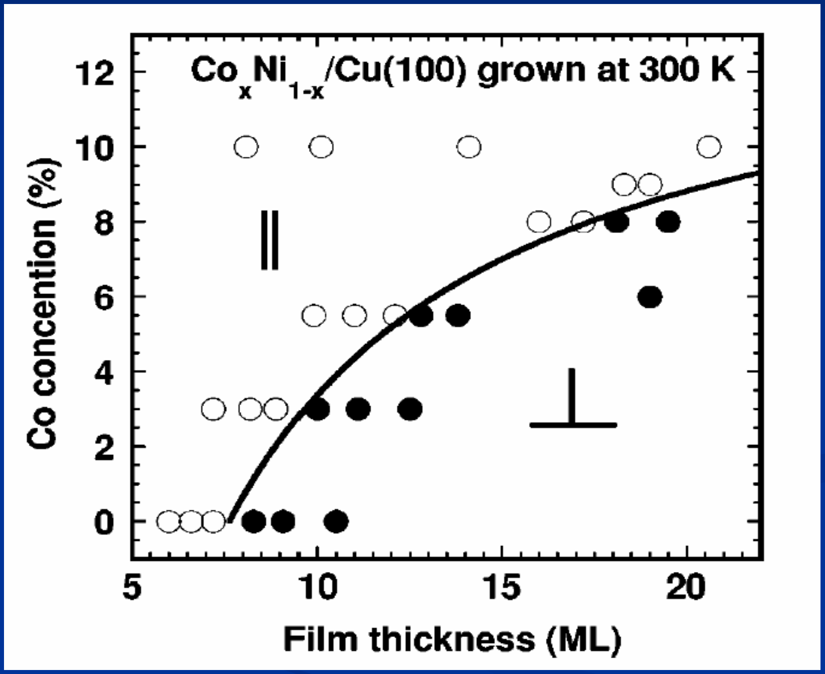
$Co_xNi_{1-x}/Cu_3Au(100)$

(grown at 300K, measured at 100 K)

M.-T. Lin, W.C.Lin,C.C.Kuo et.al,Phys. Rev.B, 62, 14268 (2000).



W.C. Lin, B.Y. Wang, Y.W. Liao, K-J Song, M-T Lin, *PRB 71, 184413 (2005)*

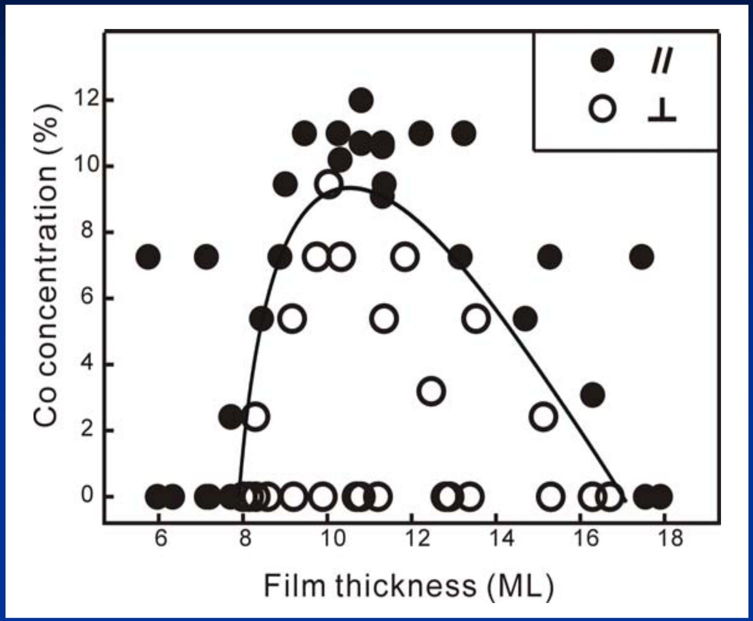


Larger mismatch for Co-Ni/Cu_3Au(100) => earlier strain relaxation & 2^nd SRT

=> Alloy effect on the 2^nd SRT can be observed clearly

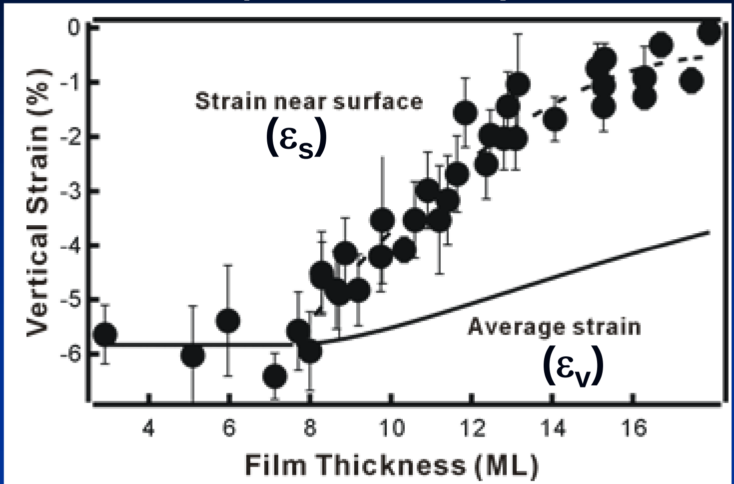
$Co_xNi_{1-x}/Cu_3Au(100)$

(grown at 300K, measured at 100 K)



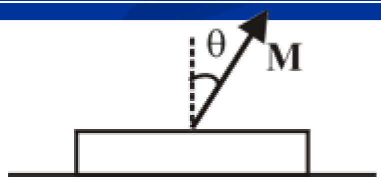
Vertical strain

(from LEED-I/V)



$$\varepsilon_v(d) = \left(\int_0^d \varepsilon_s \cdot dt\right)/d$$

$$E = K_{eff}\sin^2\theta = (K_V + 2K_S/t)\sin^2\theta$$



$$= [(B_V \cdot \varepsilon_V - 2\pi \cdot M^2) + (K_s + B_s \cdot \varepsilon_s)/t]\sin^2\theta$$

Change with the alloy composition

B_v of 3*d* alloys: Peter James et al, Appl. Phys. Lett. 76, 915 (2000).
A. Lessard et al, Phys. Rev. B 56, 2594 (1997).

Low dimensional systems:

□ *2-dimensional: Ultra-thin films*

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- **$Mn/Cu_3Au(100)$: Artificial AFM structure**
- Fe/Fe_xMn_{1-x} on $Cu_3Au(100)$ & Cu(100): Enhanced H_{ex}
- Cu(100): Spin-polarized multi-photon photoemission

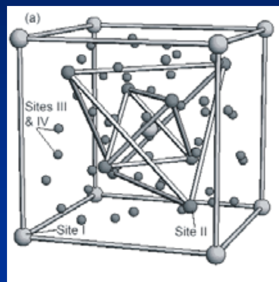
□ *0~1-dimensional: Aligned nanoparticles*

- nano-dots/Al_2O_3/NiAl(100) : Magnetic nanostructures

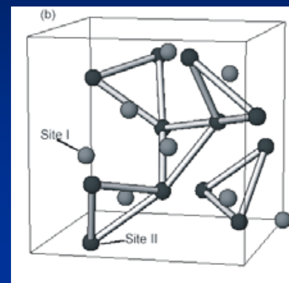
Motivation:

Mn atom: ↓↑ (4s) ↑↑↑↑↑ (3d)

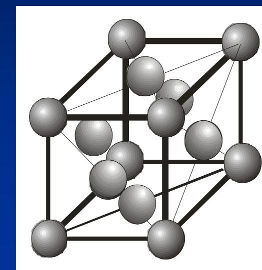
α - Phase
58 atoms/unit cell



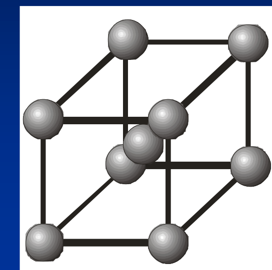
β -Phase
20 atoms/unit cell



γ -Phase (f.c.c.)



δ -Phase (b.c.c)



Bulk Mn

↔ 1000 K ↔ 1368 K ↔ 1406 K ↔

AF.
$T_N < 100$ K

Para.

γ -Phase (f.c.c.)
Para.

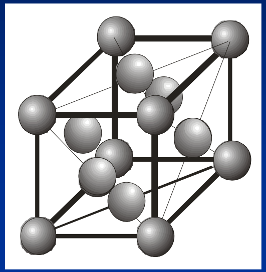
Para.

Motivation:

Search for stable γ-phase Mn at RT.

How about its magnetic property at RT??

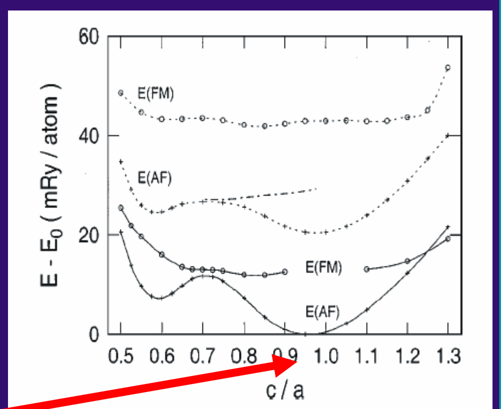
γ -Phase (f.c.c.)



1368 K ⟷ 1406 K

γ -Phase (f.c.c.)
Para.

Theoretical calculation



Ground state: AFM
c/a=0.96

S.L. Qiu, P.M. Marcus, PRB 60, 14533(1999)

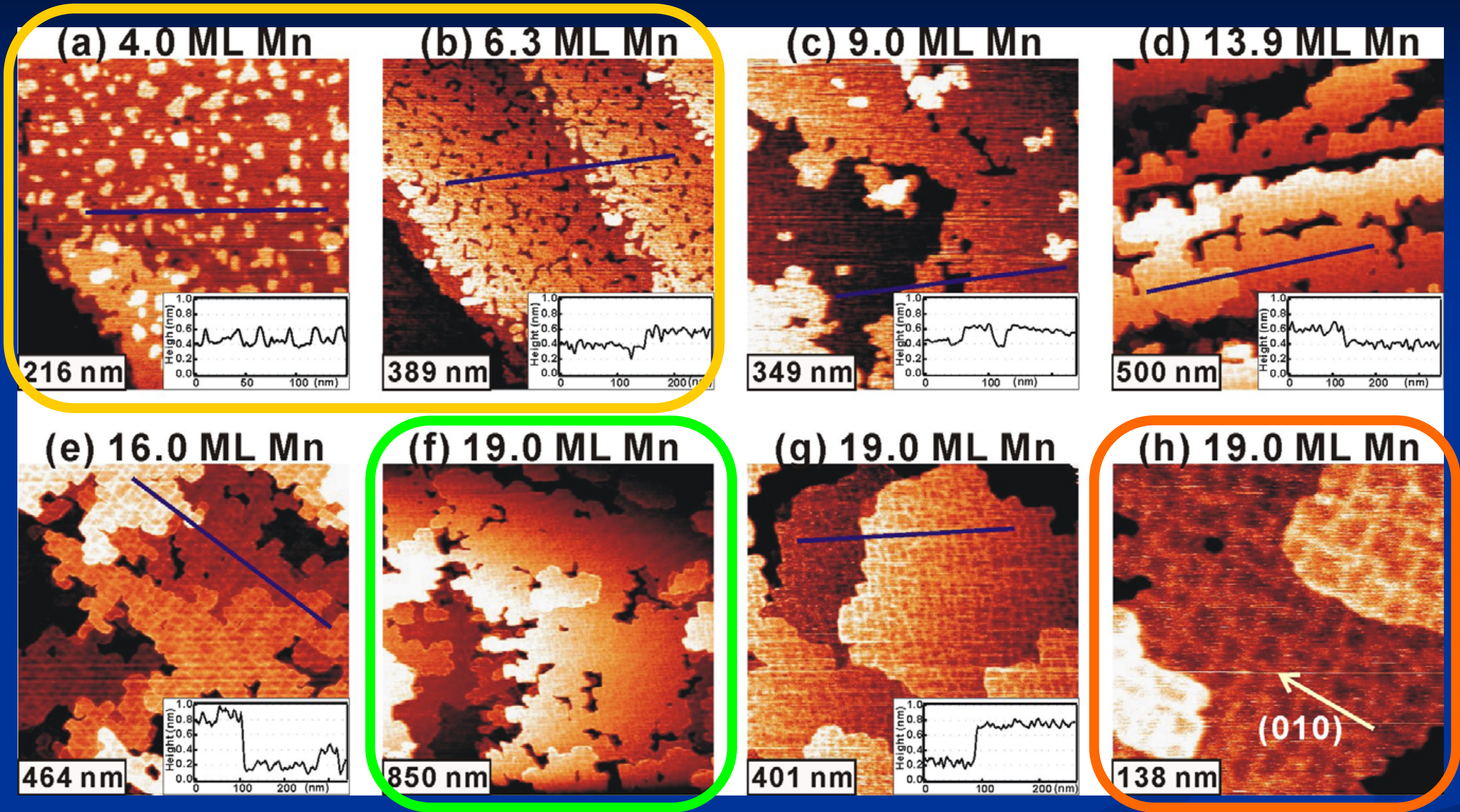
a. fcc-Mn/$Cu_3Au(100)$

γ -Mn (bulk alloy):	2.60 ~ 2.68	Å
$Cu_3Au(100)$:	2.65	Å

$\Rightarrow$ mismatch = (-1.9) ~ 1.1 %

STM of $Mn/Cu_3Au(100)$

Layer-by-layer growth

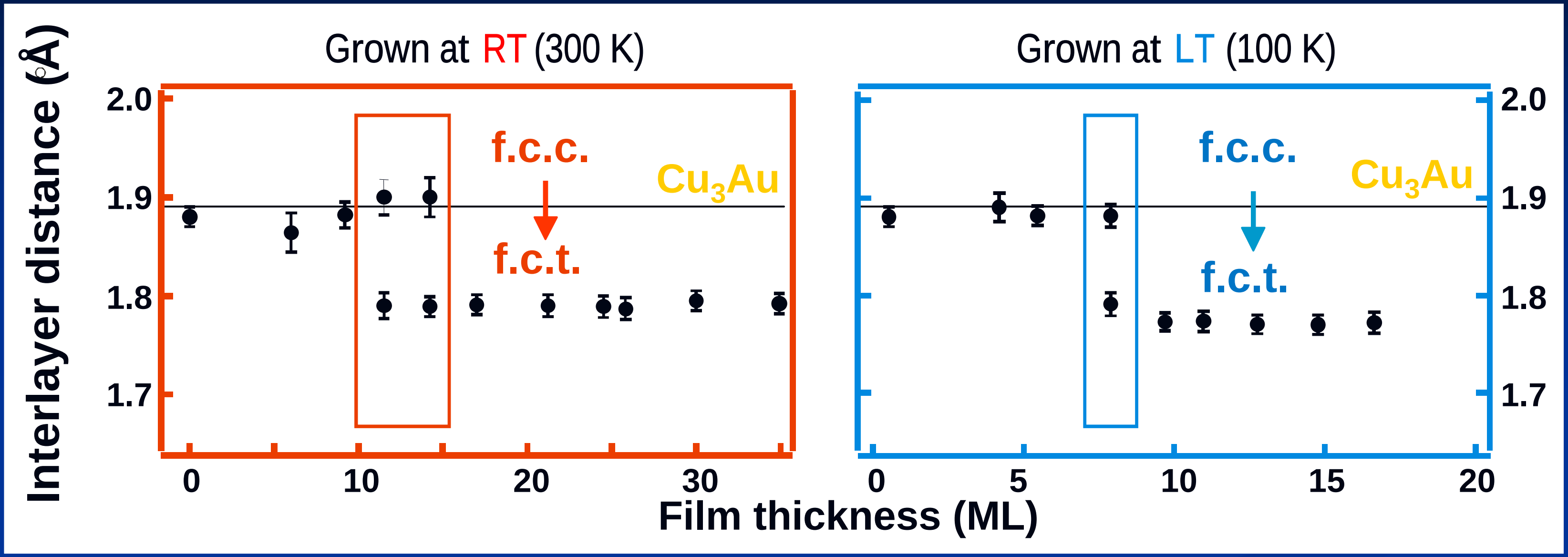


Large terraces

Plaided pattern:

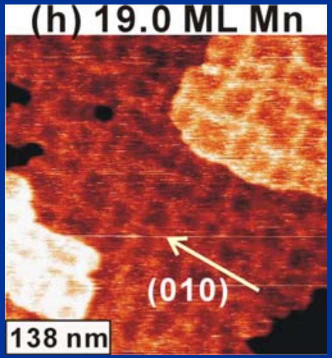
- Interesting patterns after 9 ML ***(Size: 10~20 nm. Line direction // (010) & (001).)***
- Large terraces during 4~19 ML

f.c.c. to f.c.t. Structural transition



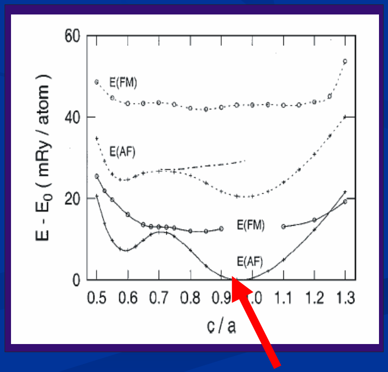
- Structure transition from **fcc**(c/a~1) to **fct**(c/a~0.96): RT 11~14 ML, LT 7~8 ML

Plaided pattern after 9 ML



misfit ~1 %

$\Rightarrow$ (1/1%)*2 Å = 20 nm

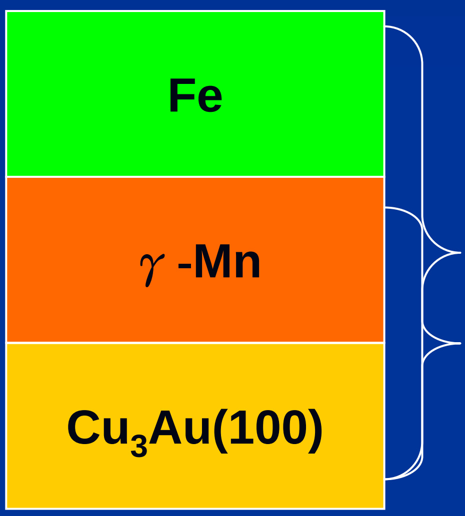


AF is most stable, c/a = 0.96

S. L. Qiu, P.M. Marcus, Phys. Rev. B, **60**, 14533(1999)

Magnetic property ??

Exchange Bias



If Mn is **AFM**

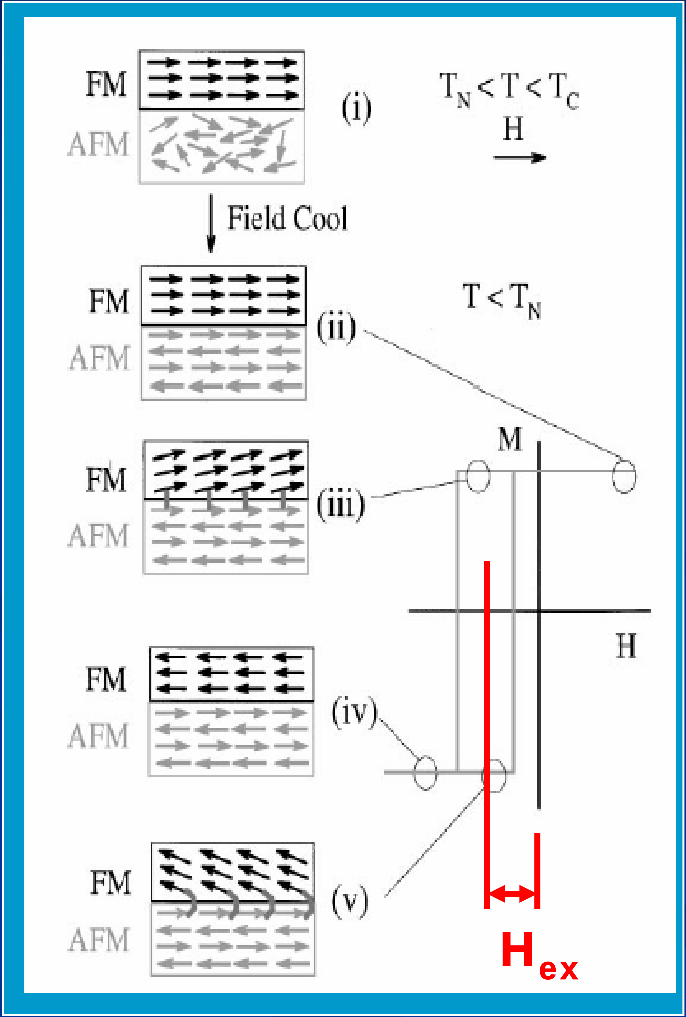
No Kerr hysteresis

⇔ **Exchange Bias??**

loop observed!

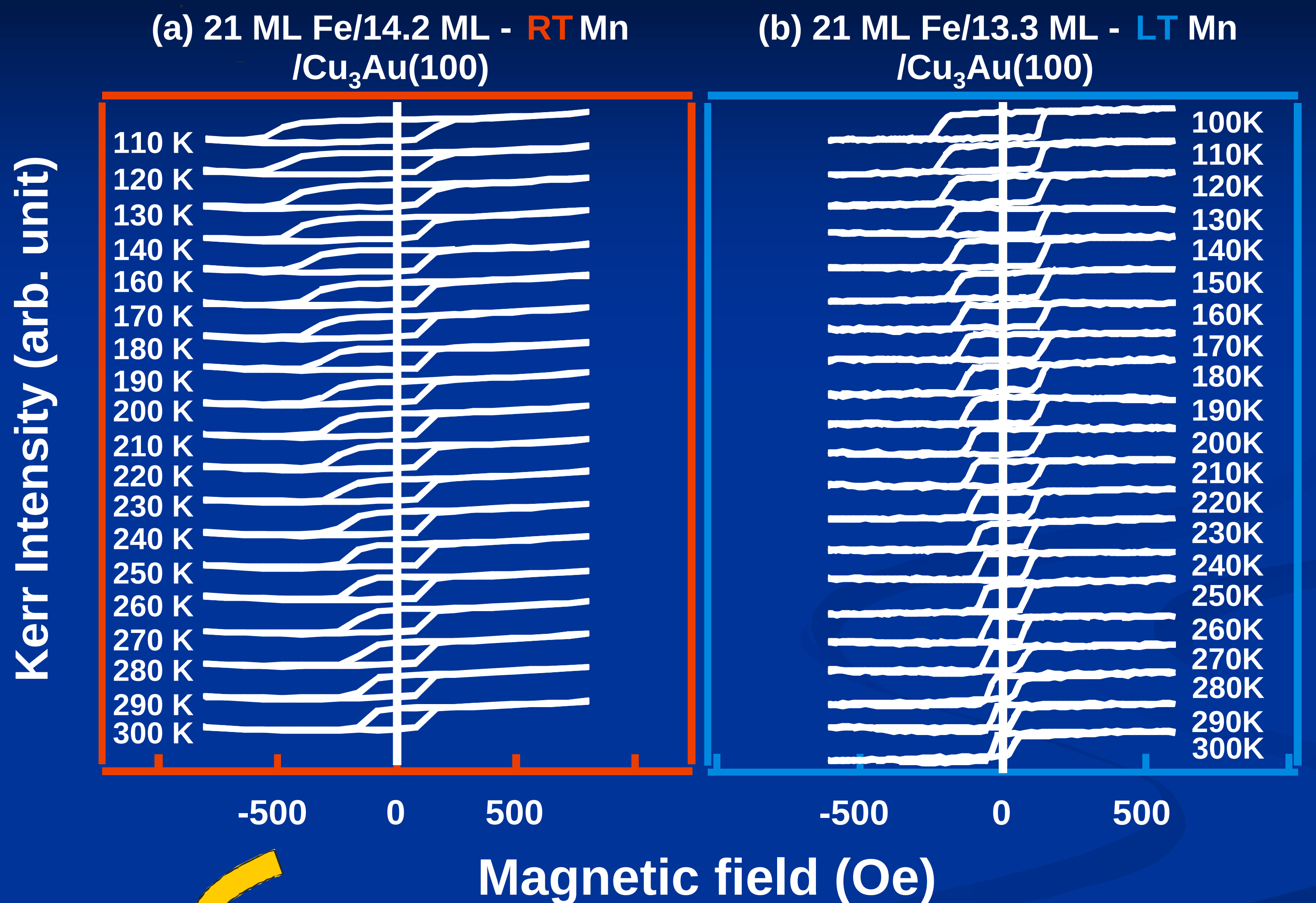
⇒ **Not FM**

⇒ **AFM??**



J. Nogues, Ivan K. Schuller,
J. Magn. Magn. Mater. ***192****(1999) 203*

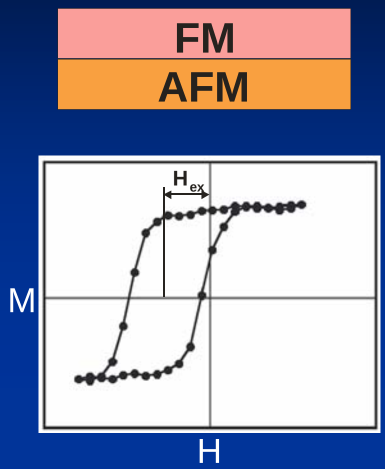
Large exchange bias in Fe/Mn bilayers



Antiferromagnetic γ -Mn!!

W.C. Lin, T.Y. Chen, L.C. Lin, B.Y. Wang, Y.W. Liao, K.-J. Song, and M.-T. Lin, PRB 75, 54419 (2007)

b. Enhanced exchange bias coupling in Fe/Fe_xMn_{1-x} on $Cu_3Au(100)$

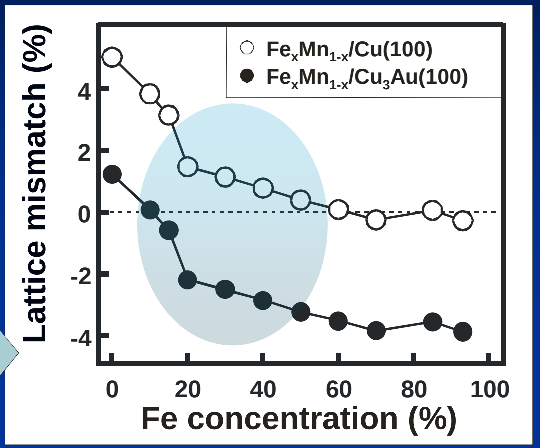


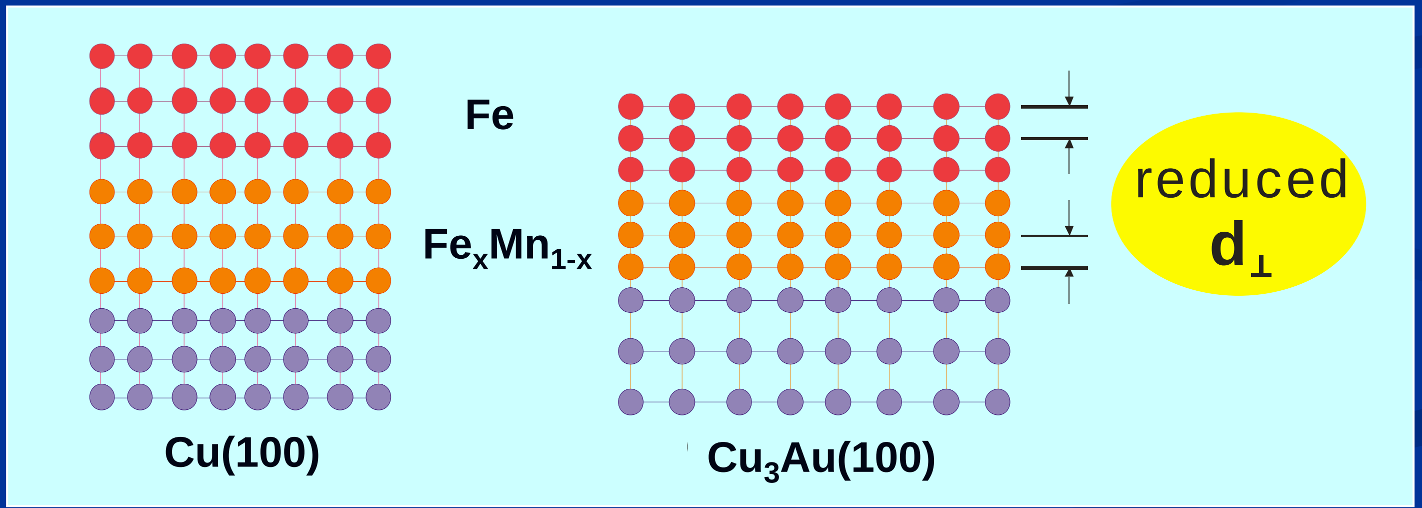
How to increase H_{ex} ??

Modulate $d_\perp$

Cu_3Au: a_0=3.75 Å

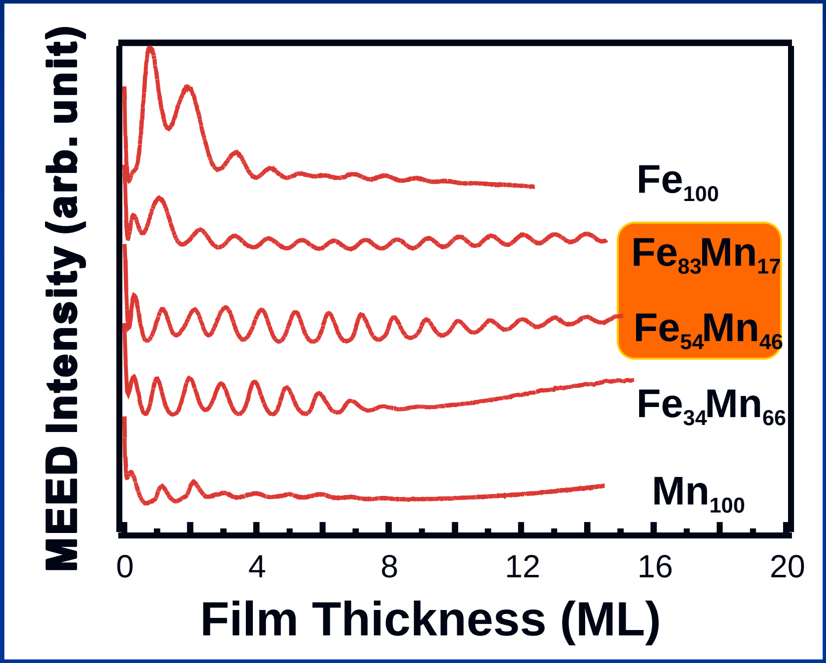
Cu: a_0=3.61 Å



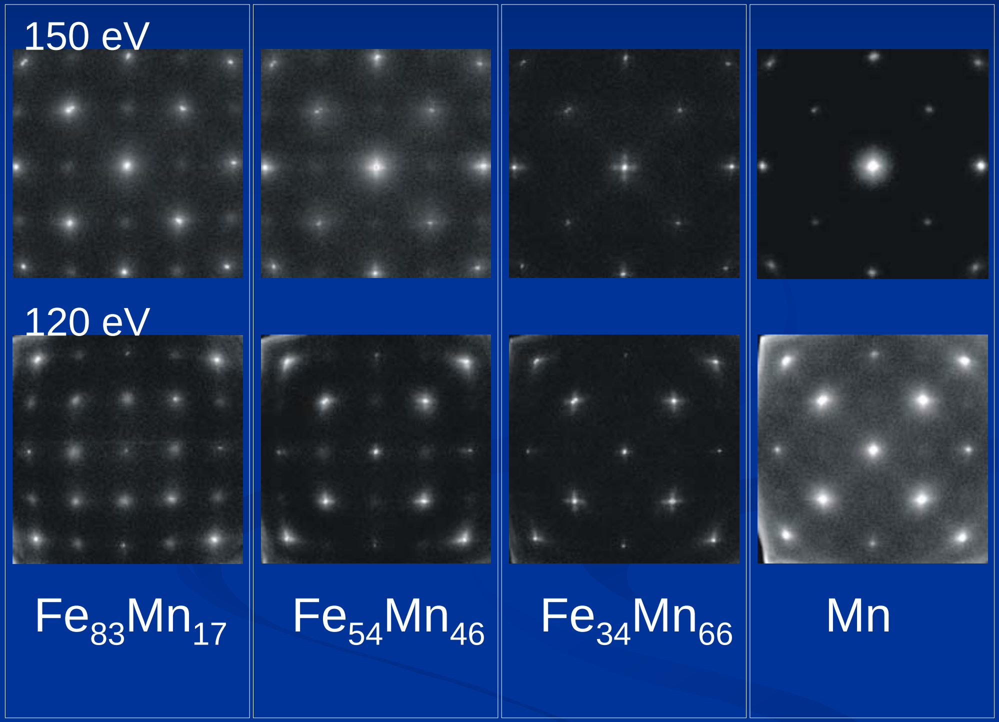


15 ML $Fe_xMn_{1-x}/Cu_3Au(100)$

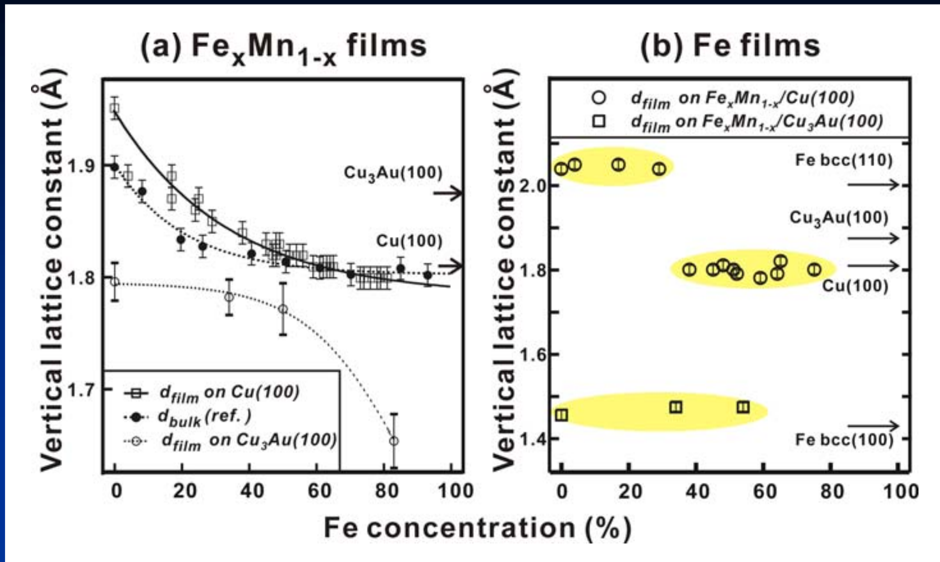
MEED



LEED



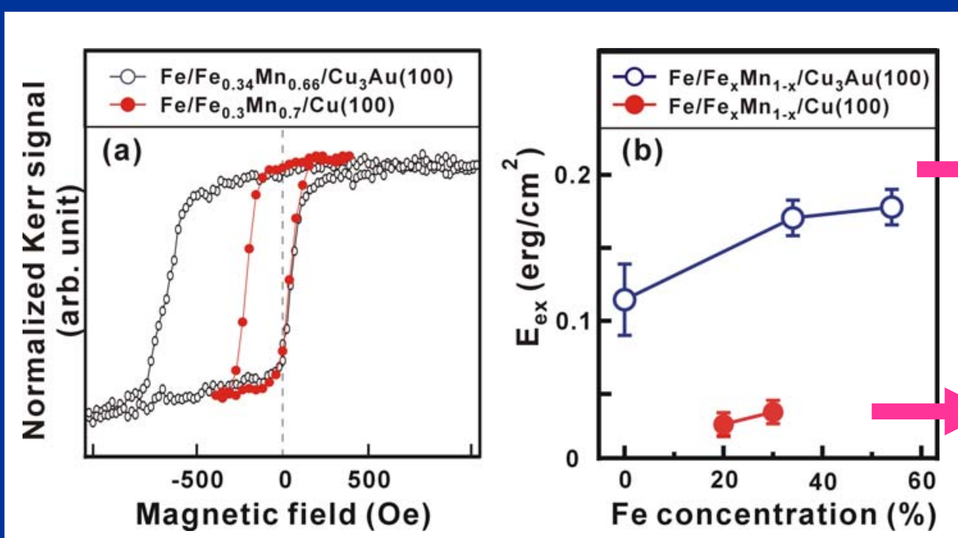
- Fe_xMn_{1-x}, x=83~54 % => good layer-by-layer growth up to >15 ML.
- Clear LEED patterns.



$d_\perp \downarrow$ in Fe/Fe_xMn_{1-x} on Cu_3Au(100)

Interface exchange bias coupling energy: $E_{ex} = M \cdot t \cdot H_{ex}$

M, t : moment and thickness of Fe layer



3-4 times E_{ex} in Cu_3Au system: E_{ex} ~ 0.17 erg/cm^2

W.C. Lin, B.Y. Wang, T.Y. Chen, L.C. Lin, Y.W. Liao, W. Pan, N.Y. Jih, K.-J. Song, M.-T. Lin, APL 90, 52502 (2007)

NiFe/fcc-$Fe_{50}Mn_{50}$: E_{ex}~ 0.04 -0.07 erg/cm^2

J. Nogues, I. K. Schuller, J. Magn. Magn. Mater. **192** 203 (1999).

Low dimensional systems:

□ *2-dimensional: Ultra-thin films*

- $Co_xNi_{1-x}/Cu_3Au(100)$: Manipulation of spin orientation
- $Mn/Cu_3Au(100)$: Artificial AFM structure
- Fe/Fe_xMn_{1-x} on $Cu_3Au(100)$ & Cu(100): Enhanced H_{ex}
- Cu(100): Spin-polarized multi-photon photoemission

□ *0~1-dimensional: Aligned nanoparticles*

- **nano-dots/Al_2O_3/NiAl(100) : Magnetic nanostructures**

What do we expect
in magnetic nanoparticle assembly?

- size uniformity ??
- ordered alignment ??
- high thermal stability ??
- suitable for various materials ??
- capability of manipulation ??
- enhanced Tc ??
- electronic structure ??
- other new phenomenon ??

Structured template

- Al_2O_3/NiAl(100)

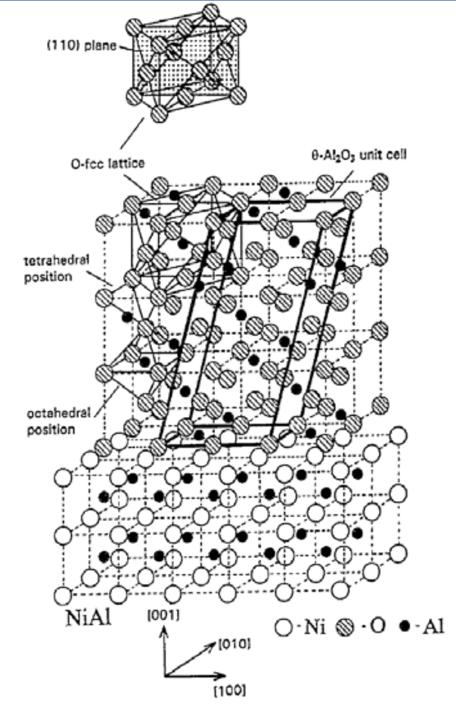
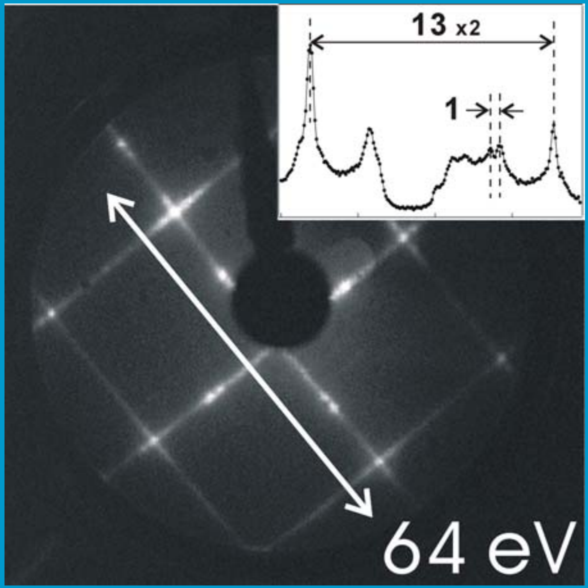
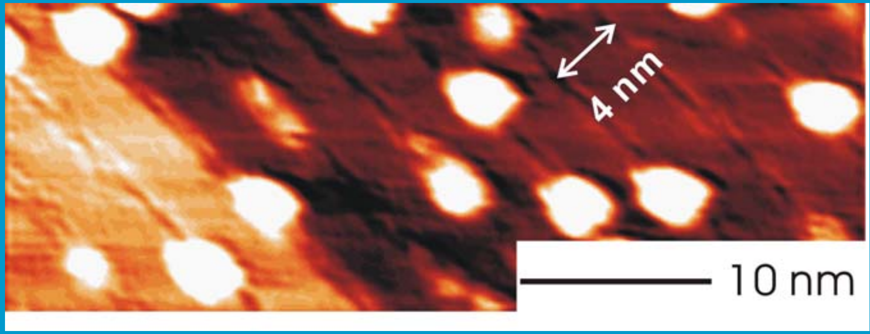


Fig. 11. Structure model for θ-Al_2O_3/NiAl(001); it illustrates the relationship between the oxygen-fcc-sub-lattice and the NiAl(001) (bcc-structure) substrate.

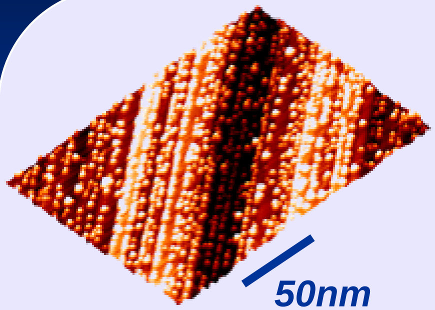
P. Gassmann, R. Franchy, H. Ibach
Surf. Sci. **319** (1994) 95-109.



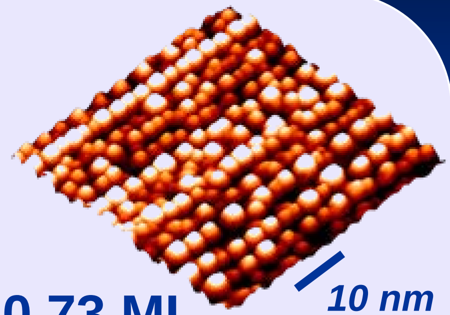
13 × 2.89 Å ~ 38 Å



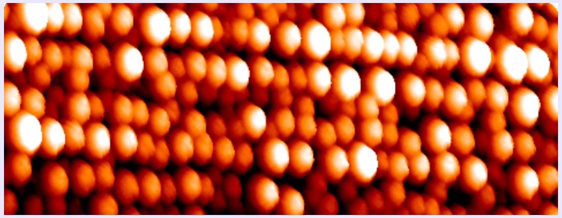
Aligned Co particles chains



0.13 ML



0.73 ML

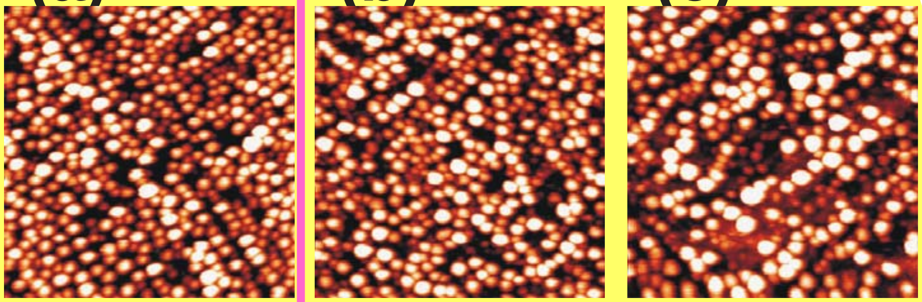


20 nm

2.2 ML

Uniform size distribution
Height ~ 1 nm
Diameter ~ 2.7 nm

High thermal stability



700 K | 750 K | 800 K

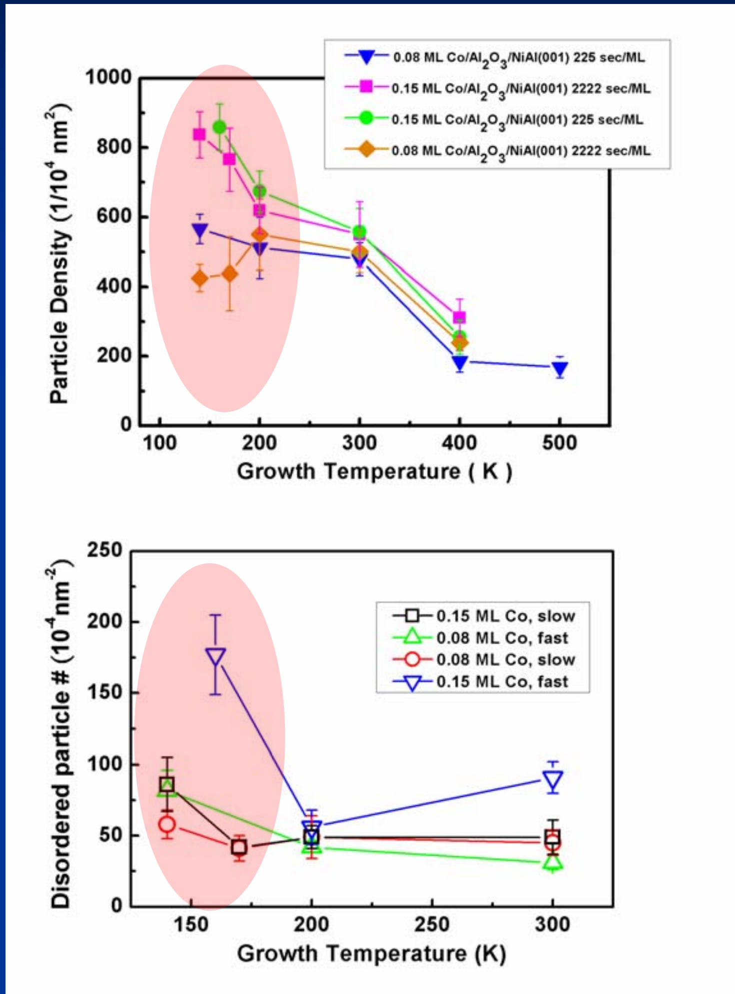
2.2 ML Co annealed for 10 mins.
(100 X 100 nm)

W.C. Lin, C.C. Kuo, M.F. Luo, K-J Song, Minn-Tsong Lin, APL 86, 043105 (2005)

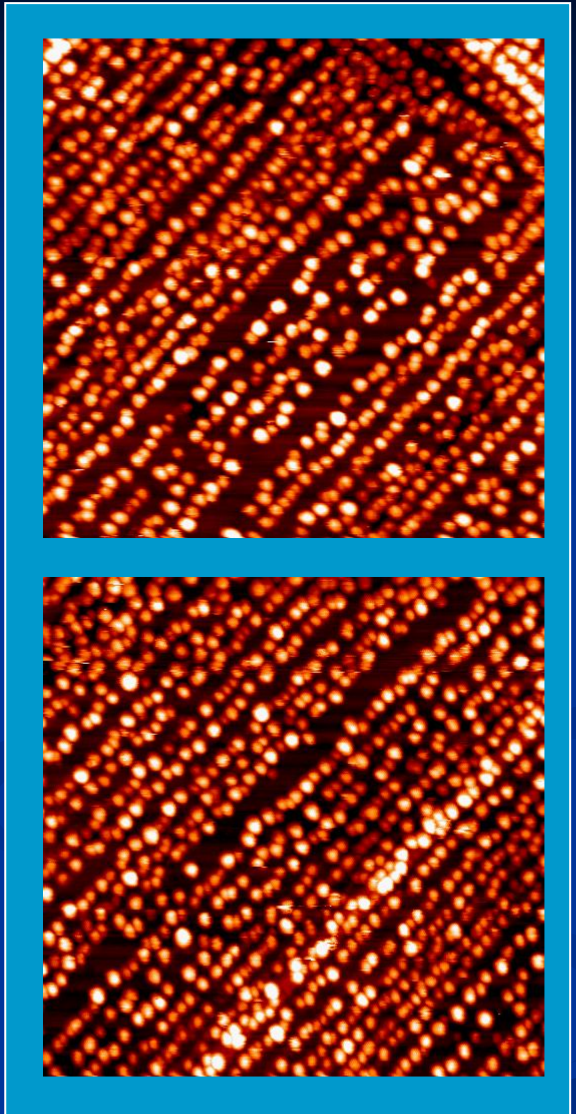
Controlled Growth:

Growth temperature, annealing, deposition rate …

⇒ high density & good alignment



0.15 ML Co grown at 170 K



100 × 100 nm^2

W.C. Lin, S.S. Wong, P.C. Huang, C.B. Wu, B.R. Xu, C.T. Chiang, H.Y. Yen, Minn-Tsong Lin, APL 89, 153111 (2006)

Superior template for magnetic nanostructures: Single-crystalline Al_2O_3/NiAl(100)

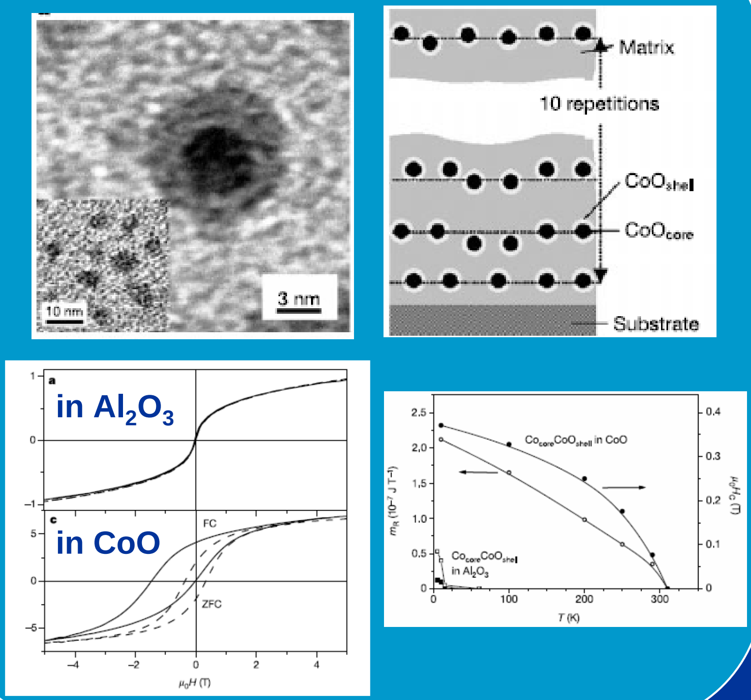
- ☑ **size uniformity** (D~3 nm, H~1nm)
- ☑ **ordered alignment** (L: 100~300 nm)
- ☑ **high thermal stability** (~700 K)
- ☑ **suitable for various materials** (Fe, Co, Mn, Cu etc.)
- ☑ **capability of manipulation** (by T_{growth})
- ☐ **Magnetic behavior??**
- ☑ **electronic structure (XPS):**

  (a) shift of Co^{3p} & Al^{2p} levels. (b) evolution of valence band

In magnetism: How to enhance T_c ??
Other magnetic coupling ??

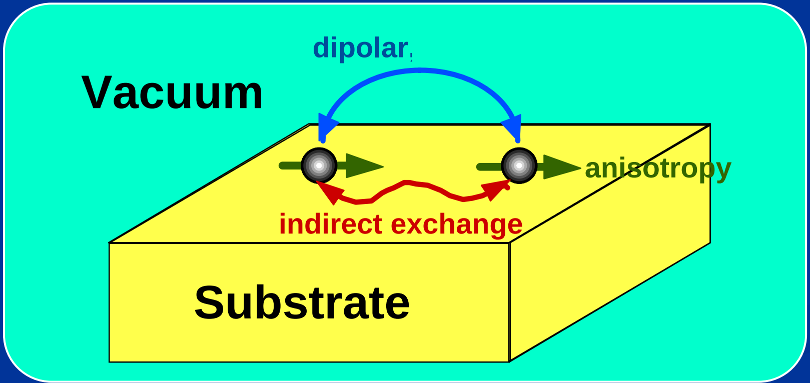
Beating the superparamagnetic limit with exchange bias

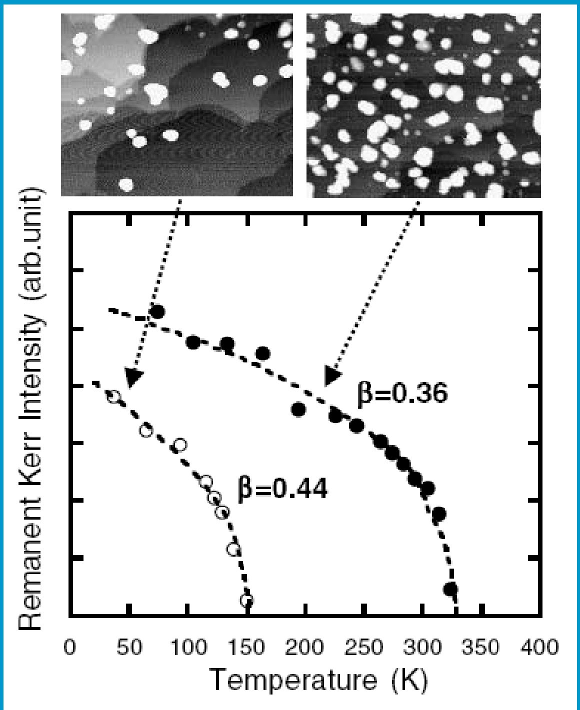
$Co_{core}CoO_{shell}$



V. Skumryev, S. Stoyanov, Y. Zhang, G. Hadjipanayis, D. Givord and J. Nogués, Nature **423**, 850-853 (2003)

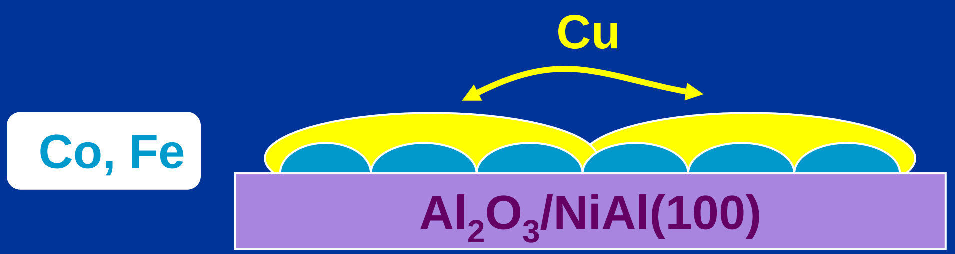
indirect exchange coupling via the Cu(111) substrate





J.P. Pierce, M.A. Torija, Z. Gai, Junren Shi, T.C. Schulthess, G.A. Farnan, J.F. Wendelken, E.W. Plummer, and J. Shen, Phys. Rev. Lett. **92**, 237201-1 (2004).

Magnetic coupling provided by Cu capping layer ??

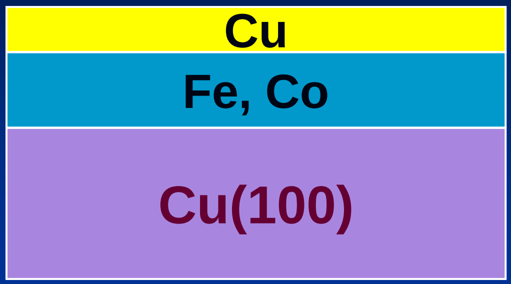


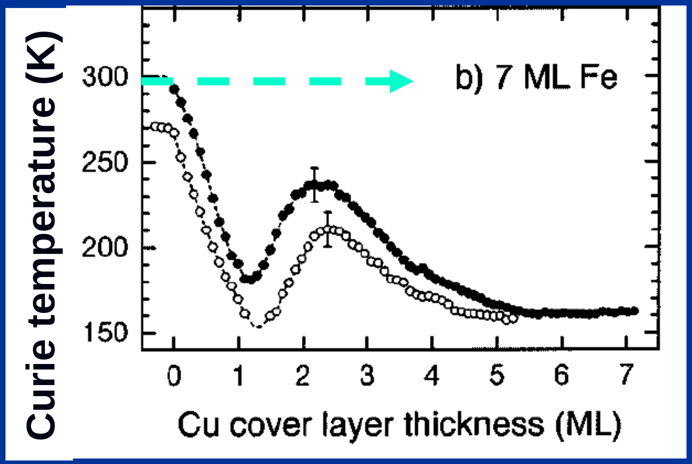
Crucial issue

for further "*ex situ*"

applications and measurements !!

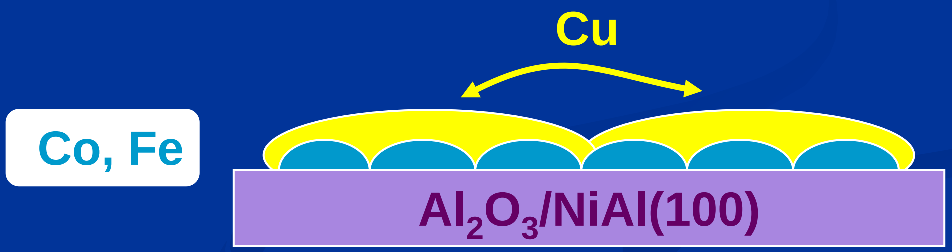
$T_c \downarrow$ in thin films *(alloy formation & modification of surface anisotropy)*





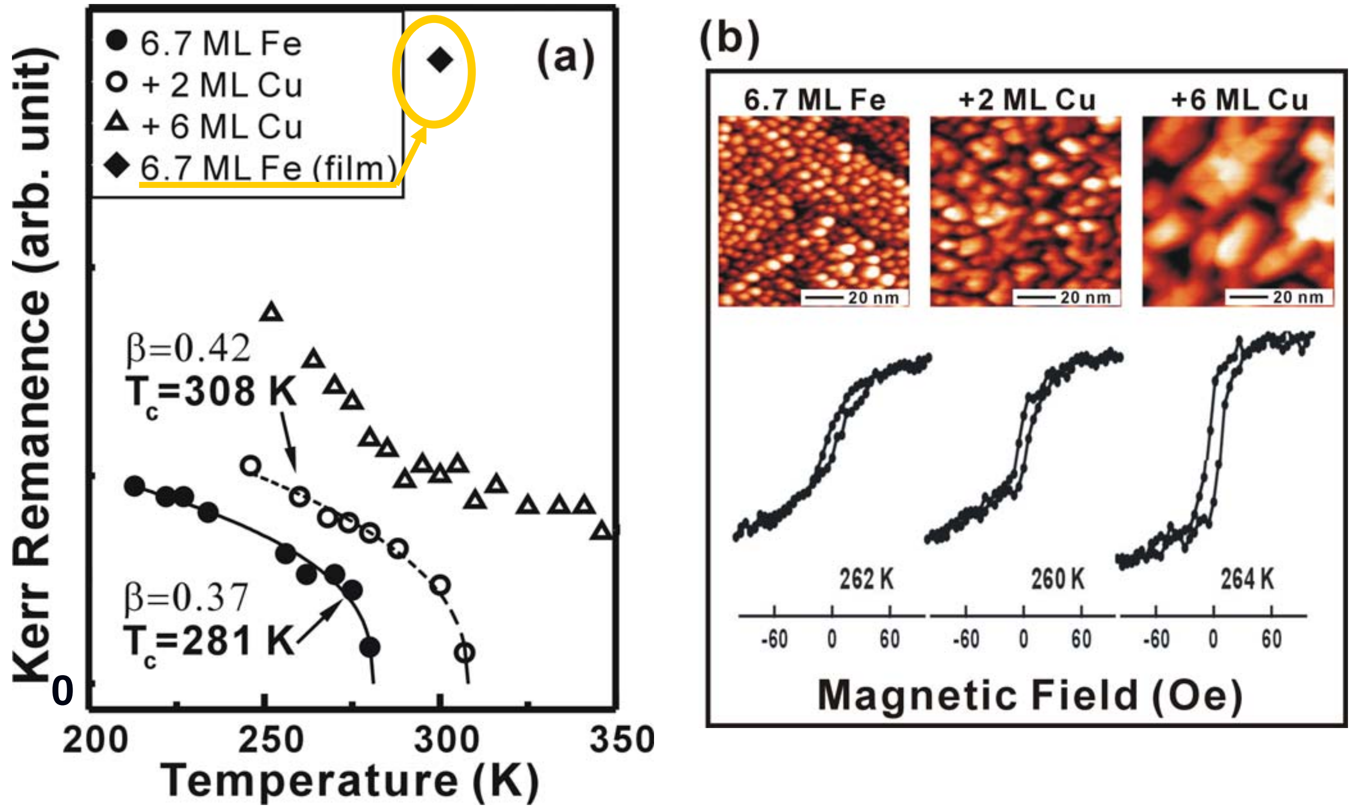
$T_c \uparrow$ or $T_c \downarrow$

in nanoparticle assembly ??



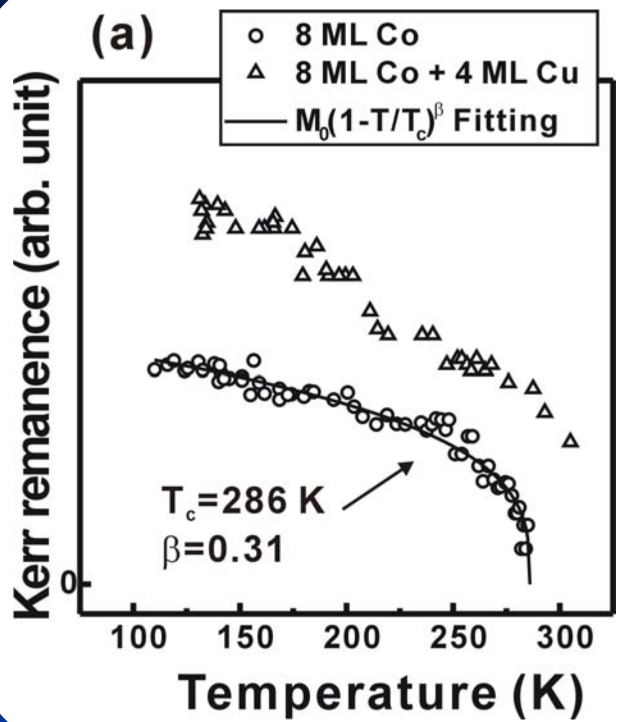
R. Vollmer, S. van Dijken, M. Schleberger, and J. Kirschner, Phys. Rev. B **61** 1303(2000).

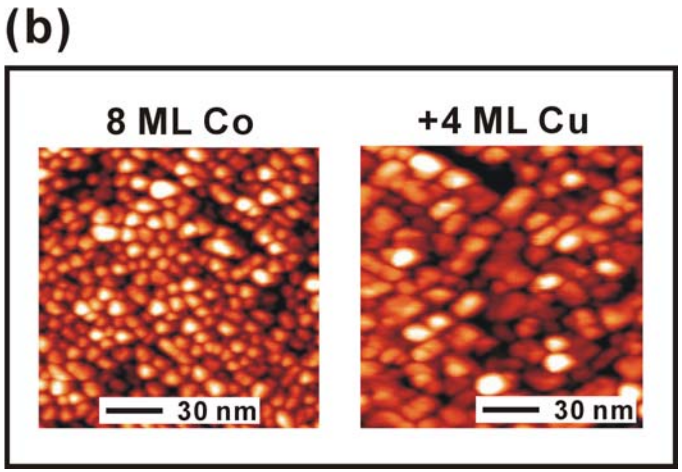
Enhanced T_C in Fe nanoparticle assembly



Cu capping layer: Provide connections between the Fe nanoparticles.

Enhanced T_C in Co nanoparticle assembly





Cu capping layer:

Provide connections between the Co nanoparticles.

W.C. Lin, P.C. Huang, K-J Song, Minn-Tsong Lin, APL 88, 153117 (2006)

Magnetic Domain Imaging of Fe Nanoparticle Assemblies Using SEMPA

Why magnetic domain imaging of nanoparticle assemblies?

Not only dipole-dipole interaction….

- **Multipole interaction might be stronger**

N Mikuszeit, E Y Vedmedenko, and H P Oepen, J. Phys: Condens. Matter **16**, 9037 (2004)

- **Inter-particle distance is crucial to collective behavior**

S. Tomita, K. Akamatsu, H. Shinkai, S. Ikeda, H. Nawafune, C. Mitsumata, T. Kashiwagi and M. Hagiwara, PRB 71, 180414 (2005)

- **Various phases of collective states:**

  superparamagnetic (SPM),
  superspin glass (SSG),
  superferromagnetic (SFM),

interaction strength $\Rightarrow$ sensitive to density, inter-distance

O. Petracic, X. Chen, S. Bedanta, W. Kleemann, S. Sahoo, S. Cardoso, P.P. Freitas, J. Magn. Magn. Mater. **300**, 192 (2006)
M. R. Scheinfein, K. E. Schmidt, K. R. Heim, and G. G. Hembree, PRL **76**, 1541 (1996)

S. A. Koch, R. H. te Velde, G. Palasantzas, and J. Th. M. De Hosson, APL **84**, 556 (2004)

$\Rightarrow$ Collective behavior??

⇒ Collective behavior ?? Domain Imaging??

Up to now:

- ***Neutron scattering*** ⇒ indirect method

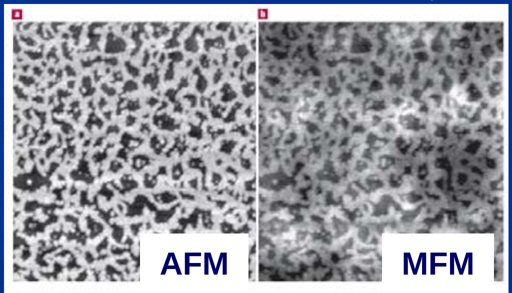
Jörg F. Löffler, Hans-Benjamin Braun, and Werner Wagner, PRL **85**, 1990 (2000)

- ***MFM***

⇒ interference with morphology, magnetized by tip

S. A. Koch, R. H. te Velde, G. Palasantzas, and J. Th. M. De Hosson, APL **84**, 556 (2004)
V. F. Puntes, P. Gorostiza, D. M. Aruguete, N. G. Bastus and A. P. Alivisatos, Nature material **3**, 263 (2004)

Incomplete layer: 12 nm NP, 2x2μm



- ***SP-STM***

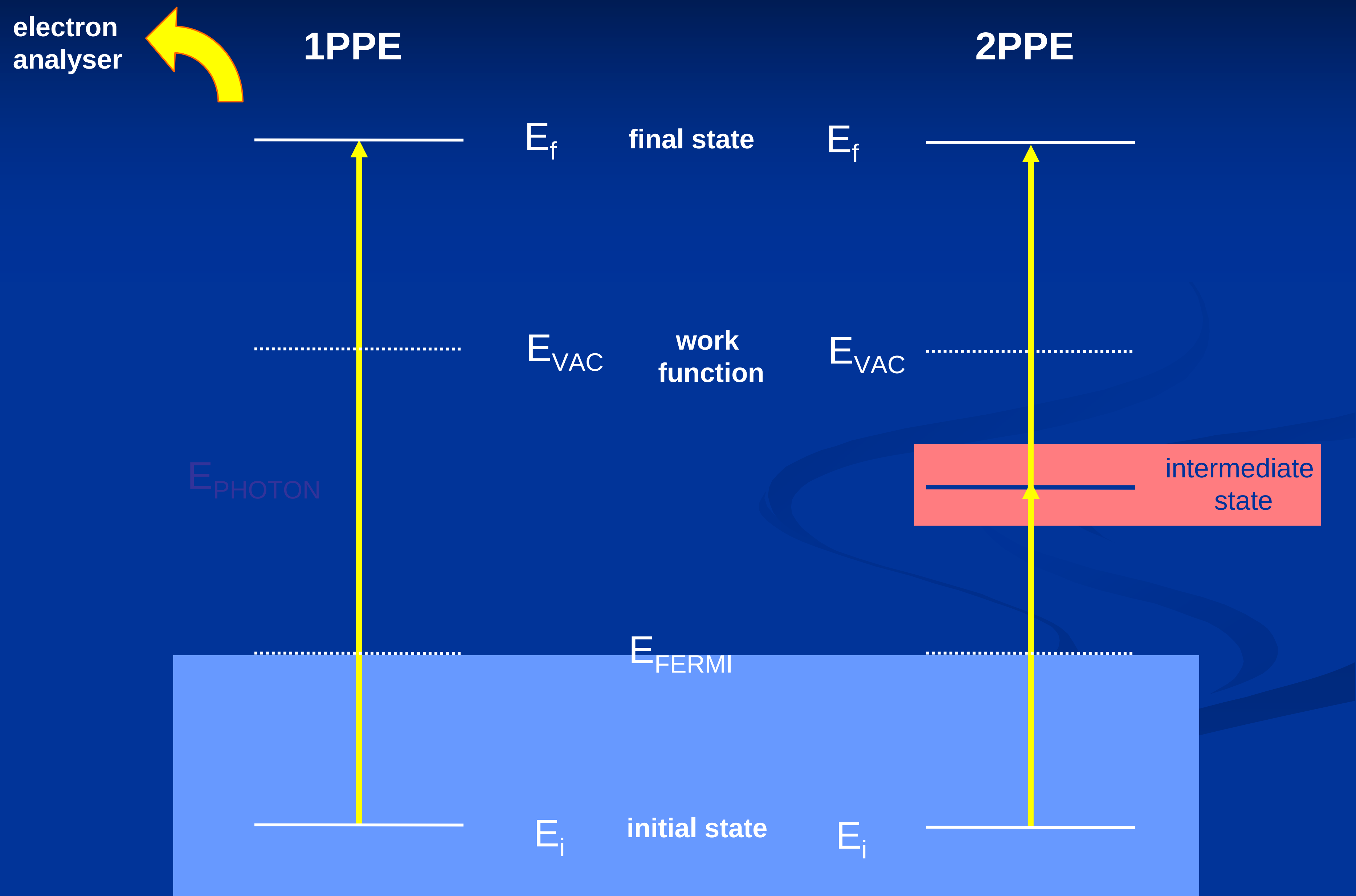
⇒ interference with morphology, only contrast

SEMPA:

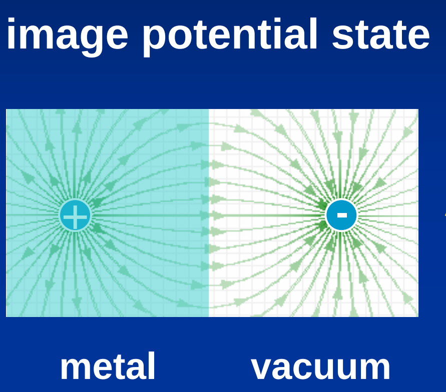
1. *In-situ* measurement
2. Surface sensitive
3. **Vector-analysis** ⇒ more detailed domain structure
4. **Field-dependent**……

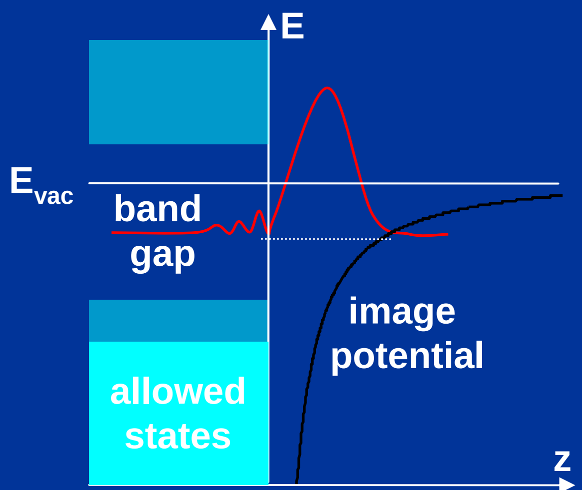
Multi-photon photoemission at Cu(001) surface with spin analysis

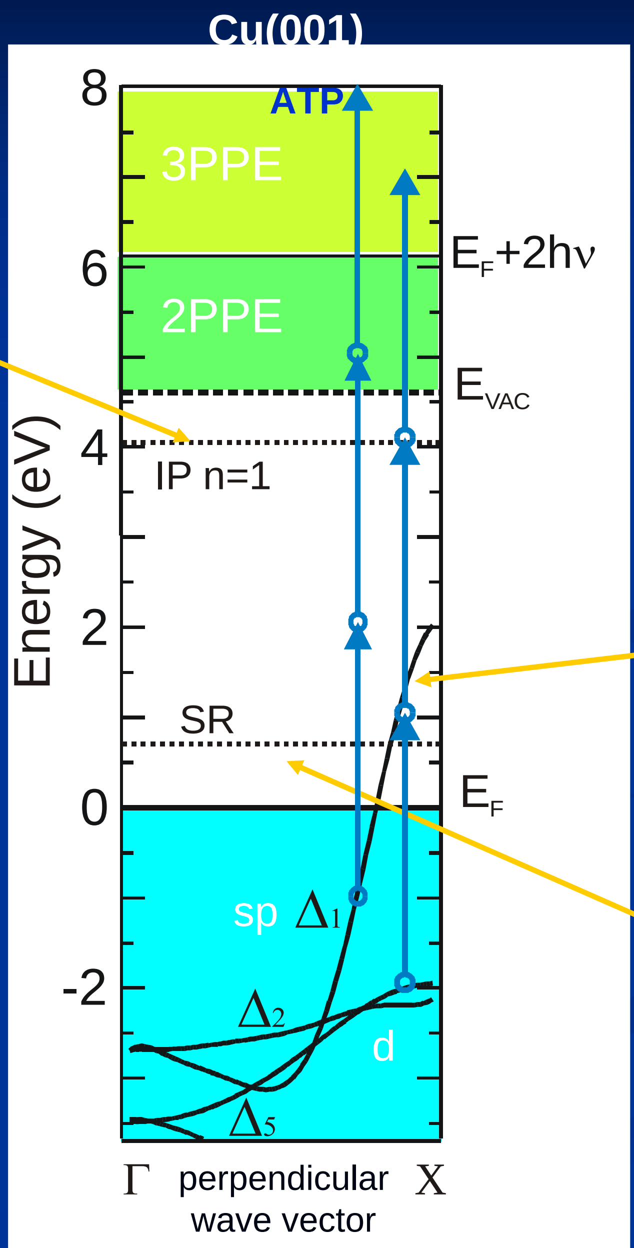
Photoemission

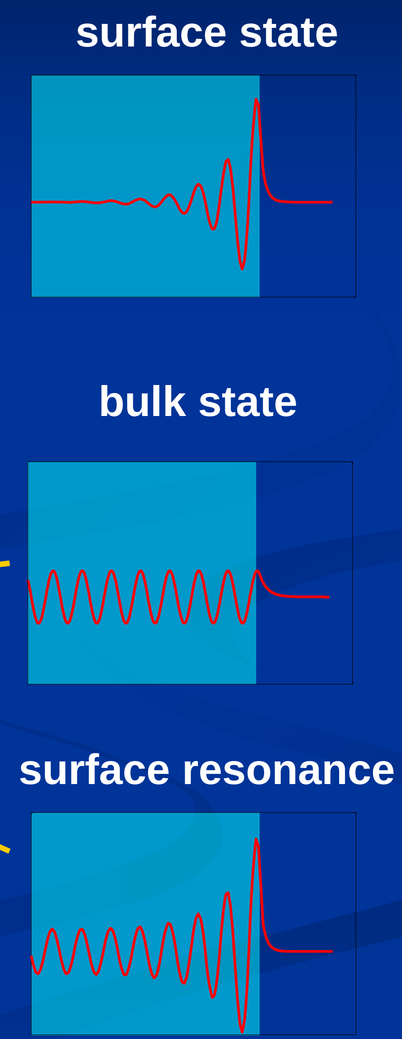


Unoccupied states and Cu band structure

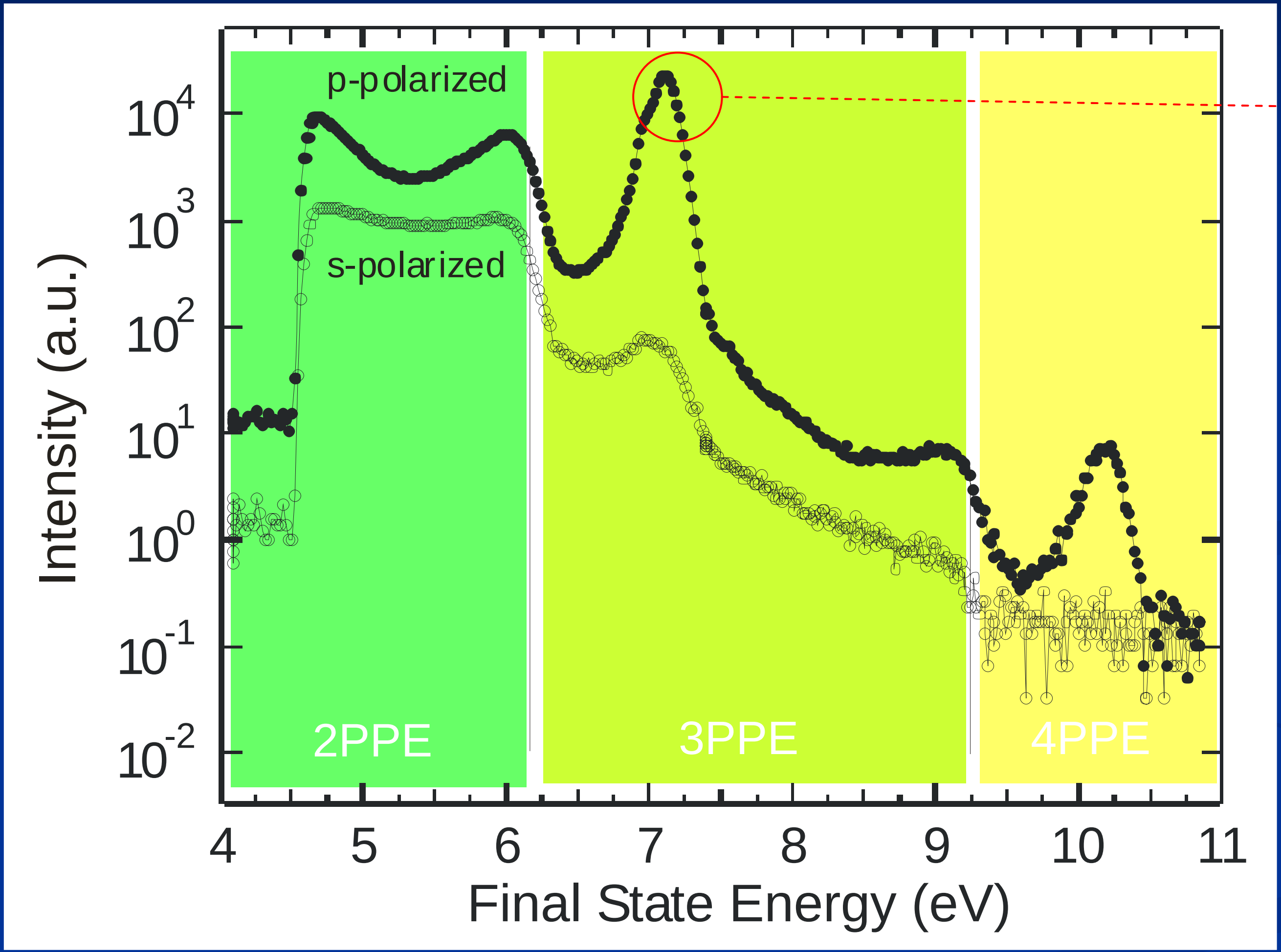


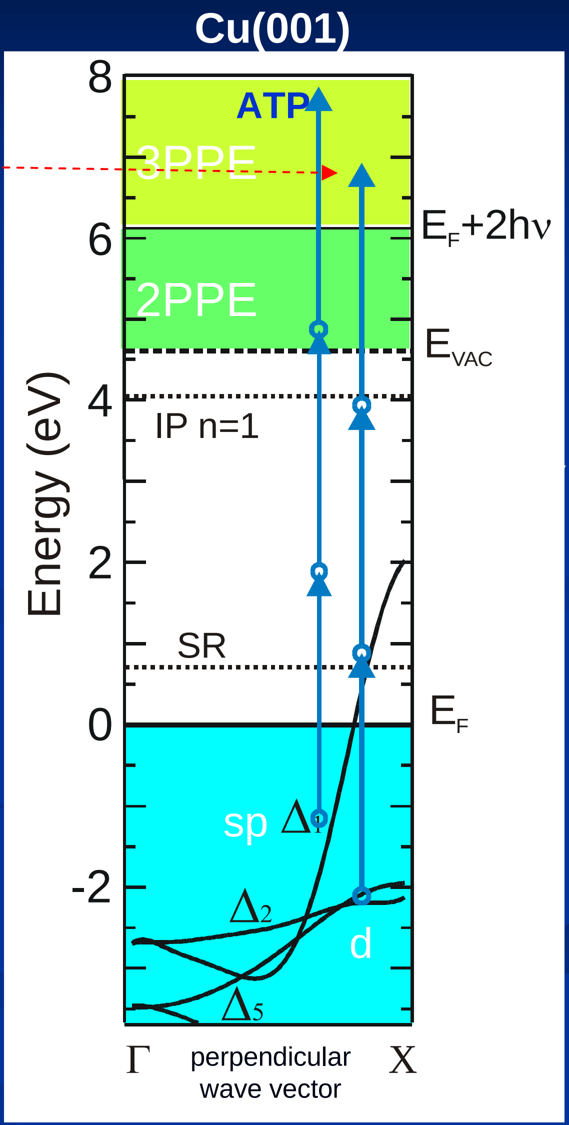






Multi-photon photoemission spectrum from Cu(001)

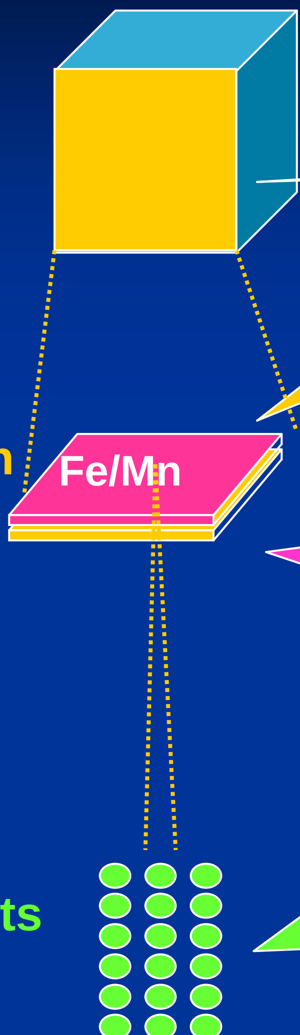




F. Bisio *et al.* Phys. Rev. Lett. **96**, 087601 (2006)

Summary

Bulk



Cu(100): Spin injection into images states by multi-photon photoemission

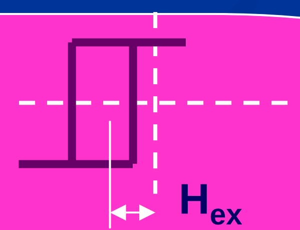
Ultrathin film

Co_xNi_{1-x} films: strain relaxation & the 2nd SRT

⇒ Manipulation of Spin orientation

W.C. Lin, B.Y. Wang, Y.W. Liao, K-J Song, M-T Lin, PRB **71**, 184413 (2005)
B.Y. Wang, W.C. Lin, Y.W. Liao, K-J Song, M-T Lin, Surf. Sci. **600**, 4517 (2006)

- **AFM fcc & fct Mn:**
  // & ⊥ exchange bias coupling
- **Enhanced H_{ex} by reducing $d_{\perp}$**



W.C. Lin, B.Y. Wang, T.Y. Chen, L.C. Lin, Y.W. Liao, W. Pan, N.Y. Jih, K.-J. Song, M.-T. Lin, APL **90**, 52502 (2007)
W.C. Lin, T.Y. Chen, L.C. Lin, B.Y. Wang, Y.W. Liao, K.-J. Song, and M.-T. Lin, PRB **75**, 54419 (2007)

Nanodots

size uniformity, alignment,
high thermal stability,
various materials, manipulation

T_c ↑ : inter-particle coupling

Flux-closure in magnetic domain

W.C. Lin, C.C. Kuo, M.F. Luo, K.-J. Song, M.-T. Lin, APL **86**, 043105 (2005)
W.C. Lin, P.C. Huang, K.-J. Song, M.-T. Lin, APL **88**, 153117 (2006).
W.C. Lin, S.S. Wong, P.C. Huang, C.B. Wu, B.R. Xu, C.T. Chiang, H.Y. Yen, M.-T. Lin, APL **89**, 153111 (2006)