Nobel Laureates 2007

Physics: Prof. Peter Grünberg, FZ Jülich and Prof. Albert Fert, Paris





 Φ Deutsche Physikalische Gesellschaft

Chemistry: Prof. Gerhard Ertl, Fritz Haber Institut der MPG, Berlin

Giant Magneto Resistance: GMR Electrical resistance of stacked magnetic layers FAST transition discovery - application



P. Grünberg, FZ Jülich US Patent 4,949,039 1990





A. Fert, Paris

Magnetic Anisotropy and How it can be controlled

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Stress and magnetism: Magnetic anisotropy

Co / Cu(111)



40x40 nm² Spin-STM Magnetic switching Spin-polarization

Surface stress, Film stress, magnetoelastic stress

Acknowledgment





Jürgen Kirschner



Hirofumi Oka Guillemin Rodary Zhen Tian Sebastian Wedekind Nicole Kurowsky

Magnetism is everywhere!



Magnetic anisotropy

decisive for applications, and demanding for theory:

Easy magnetization direction

Remanent magnetization in view of temperature and stray fields





What will be covered?

Experimental evidence for magnetic anisotropy and why do we worry...

Typical energy scales involved

Contributions to the magnetic anisotropy dipolar interactions spin-orbit-coupling

How to quantify magnetic anisotropy Hard-axis magnetization loops Magnetoelastic coupling Magnetic switching and thermal stability (?)

How to control the magnetic anisotropy crystalline order film thickness, lattice strain adsorbate coverage, temperature

Ferromagnetic nanostructures

• $L_{sample} \sim L_{exch} \sim L_{domain wall}$ monodomain (Stoner-Wohlfarth switching ?)

Bonet et al., PRL 83, 4188 (1999)

Temperature could overcome anisotropy *kT ~ KV* superparmagnetism
Bean et al., JAP 30, 120S (1959)
Néel, Ann. Geophys. 5, 99 (1949)
Atoms with low coordination *K*_{surface} and / or *M* could be very high
Gambardella et al.,
Science 300, 1130 (2003)

we study: Co / Cu(111)



Quantum effects (discrete states, collective tunneling)

Bernand-Mantel et al., APL 89, 062502 (2006) Wernsdorfer et al. ,PRL 79, 4014 (1997)

Reminder about units: magnetic moment, magnetization, magnetic field



Current loop and its magnetic moment *m*: $m = I A [A m^2]$

 $m = \frac{e\ell}{2m_{\rm e}} = \frac{e\hbar}{2m_{\rm e}} = \mu_{\rm B}$ $= 9.27 \times 10^{-24} \,\mathrm{A} \,\mathrm{m}^2$

Natural unit of *m*: Bohr magneton $\mu_{\rm B}$

Note: [A m²] = [J T⁻¹]

 $B = \frac{\mu_0 I}{2\pi r} \left(H = \frac{1}{\mu_0} B [A/m] \right)$ $\mu_0 = 4\pi 10^{-7} [T \frac{m}{A}]$ $1 T = 7.96 \times 10^5 A / m$

Magnetization *M*: total magnetic moment per volume M: [A m⁻¹] = [J m⁻³ T⁻¹]

microscopic view: electron orbit with orbital moment

Magnetic field *B* of induced by current *I* through wire: Custom: x-scale of hysteresis loop: $\mu_0 H$ [T] Note: energy density $\int \mu_0 H \, dM : [J/m^3]$

Contributions to the magnetic anisotropy energy

dipolar origin:

spin-orbit interaction:

Μ

[001]



magnetocrystalline anisotropy



magnetization [001] epitaxial lattice contraction [001]: polar magnetization

contraction upon

magnetostriction

 $\Delta 1$

B1= 650 µeV / atom



 $K1 = 0.4 \mu eV / atom$

11 µeV / atom

lattice strain: decisive for anisotropy

Physical origin of magnetic anisotropy spin-orbit interaction

Exchange energy refers only to the angle between spins, but NOT to the absolute orientation $H \sim I_{CC}$

Relativistic quantum mechanics:

spin-orbit interaction:

 $H_{exchange} \sim J_{ij} s_i s_j$

 $H_{\rm SOC} \sim \xi \ \ell \cdot s$ Spin-orbit constant: ξ (3d: 50 – 100 meV)

electron spin s interacts with the magnetic moment of its own orbital motion /

the orbital motion interacts with the crystal structure by electrostatic fields

However, the orbital angular momentum is largely quenched in cubic crystals Electrons: hybrids of wavefunction of opposite m_i

Small magnetic anisotropy: cubic systems (µeV / atom), large anisotroy: reduced symmetry, e.g. hexagonal or strained systems (meV / atom)

Dipolar crystalline anisotropy: (NOT shape anisotropy) hcp and strained cubic: neglible, as compared to SOC

Energy scales in magnetism and magnetic anisotropy

Magnetic anisotropy energy scales are very small (µeV) as compared to bond energies, elastic energies

 $f_{\text{cubic}} = K_1(\alpha_1^2 \alpha_2^2 + \alpha_2^2 \alpha_3^2 + \alpha_1^2 \alpha_3^2) + K_2(\alpha_1^2 \alpha_2^2 \alpha_3^2) + \dots$

 $f_{\text{hex}} = K_1 \sin^2 \theta + K_2 \sin^4 \theta + \dots$

		bcc-Fe 273 К	hcp-Со 275 К	fcc-Ni 296 K
K_1	$(MJ m^{-3})$	0.048	0.513	-0.006
K_2	(MJ m^{-3})	0.0033	0.033	-0.0004 -0.003
T _C	(meV/atom) (K)	0.000 07 1044	0.000 07 1360	-0.0002 627
	(meV/atom)	90	11/	54

 α_i : Direction cosine with respect to cubic axes

$$\theta$$
: Angle M, c-axis

D. Sander JPCM 16 (2004)R603

Dipole-dipole interactions

Shape anisotropy and demagnetizing field

Phanomenological picture:

magnetic surface charges, *outside*: sources of stray field Inside: H_{dem} oriented antiparallel to M demagnetizing field

		bcc-Fe 286 К	hcp-Co 287 K	fcc-Ni 287 K
M _s	$(kA m^{-1})$	1717	1447	493
$\mu_0 M_{ m s}$	(T)	2.16	1.82	0.62
$\frac{1}{2}\mu_0 M_{\rm s}^2$	$(MJ m^{-3})$	1.85	1.32	0.15
	(meV/atom)	0.14	0.09	0.012

D. Sander JPCM 16 (2004) R603



Stress: from films to surfaces

900 nm Cr / glass



Strain and its impact on magnetic anisotropy needs to be considered

Specific experimental equipment at the MPI Halle

In-stitu preparation and magnetic measurements (separate: spin-STM)



Auger electron spectroscopy Low energy electron diffraction lon gun Evaporators Magneto-optical Kerr-effect Crystal curvatre stress measurements



Stress measurements



magneto-elastic stress:

magnetization reversal



Magnetostriction

On the Effect of Magnetism upon the Dimension of Iron and Steel Bars J. P. Joule, Phil. Mag. 30 (1847)225



James Prescott Joule (1818 - 1889)

... the experiments were very troublesome... the experiments had to be carried out after eight o'clock P.M. It was impossible to make an observation when a cart was passing ... nor could anything be done when wind was blowing...

Magnetostriction and magneto-elastic stress



$$f_{ME}(\varepsilon,\alpha) = B_1(\alpha_1^2\varepsilon_1 + \alpha_2^2\varepsilon_2 + \alpha_3^2\varepsilon_3) + B_2(\alpha_1\alpha_2\varepsilon_6 + \alpha_1\alpha_3\varepsilon_5 + \alpha_2\alpha_3\varepsilon_4) + \dots$$

 $B_1(Fe) = -3.43MJm^{-3}(MPa!)$



Simultaneous "magnetostriction" and MOKE



Experimental evidence of magnetic anisotropy Hard-axis magnetization loops (1)



Quantitative analysis of $K_{\rm eff}$ possible

$$f_{\rm anis} = K_{\rm eff} = \int_0^{M_{\rm S}} \mu_0 H \ dM$$

Alternative description:

Anisotropy field H_{anis}

$$K_{\rm eff} = \frac{1}{2} \mu_0 H_{\rm anis} M_{\rm S}$$

Here: $K_{eff} = 0.26 \text{ MJ} / \text{m}^3$ $\mu_0 H_{anis} = 0.3 \text{ T}$

Compare bulk Fe: 0.048 MJ / m³ (3.5 µeV / atom)

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Change of K: Fe thickness, temperature

Quantitative analysis: hard-axis magnetization loops (2)

Trick:



D. Sander JPCM 16 (2004)R603 small constant field (2 mT) along easy direction (e.g. sample length) small magnetizing field along sample width Weber et al., APL 70 (1997) 520. "hard-axis loop" can be obtained

Here: 2 mT along sample length Hysteresis loops with H along sample width

Slope:
$$s = \frac{\Delta M}{\Delta \mu_0 H}$$

 $\mu_0 H_{\text{anis}} = M_{\text{S}}/s$
 $K_{\text{eff}} = \frac{1}{2} \mu_0 M_{\text{S}}^2/s = 58 \text{ kJ/m}^3$

Experimental determination of magnetic anisotropy (1)

Fe / W(001): a combined MOKE and stress study

Total energy density:

$$F = K_4(\alpha_1^2 \alpha_2^2 + \alpha_2^2 \alpha_3^2 + \alpha_1^2 \alpha_3^2) + 2K_2 \alpha_3^2 / t_F$$

+ 1/2c_{11}(\epsilon_1^2 + \epsilon_2^2 + \epsilon_3^2) + c_{12}(\epsilon_1 \epsilon_2 + \epsilon_2 \epsilon_3 + \epsilon_1 \epsilon_3)
+ 1/2c_{44}(\epsilon_4^2 + \epsilon_5^2 + \epsilon_6^2) + B_1(\epsilon_1 \alpha_1^2 + \epsilon_2 \alpha_2^2 + \epsilon_3 \alpha_3^2)
+ B_2(\epsilon_4 \alpha_1 \alpha_2 + \epsilon_5 \alpha_2 \alpha_3^2 + \epsilon_6 \alpha_1 \alpha_3 + 1/2 \mu_0 M_s^2 \alpha_3^2

Stress and magnetoelastic coupling:

$$\partial F/\partial \epsilon_i = c_{11}\epsilon_{\parallel} + c_{12}(\epsilon_{\parallel} + \epsilon_{\perp}) + B_1\alpha_i^2 = \tau_i, \quad i = 1,2$$

$$\partial F/\partial \epsilon_3 = c_{11}\epsilon_{\perp} + 2c_{12}\epsilon_{\parallel} + B_1\alpha_3^2 = 0.$$

 $f_{\parallel} = K_4/4$ From in-plane measurements with small field

$$f_{\perp} = -B_1 \epsilon_0 (1 + 2c_{12}/c_{11}) + 2K_2/t + \mu_0 M_s^2/2$$
 For info

Enders, Sander, Kirschner, JAP 85 (1999) 5279.

Fairly complete extraction of magnetic anisotropy

(2)



· 2×10^t magnetoelastic coupling $B_{1,eff}$ (J/m³) magnetostriction B_{1 eff}, from eq. (4): $B_{1,eff}(\varepsilon) = -3\frac{MJ}{m^3} + 1000\frac{MJ}{m^3} \cdot \varepsilon_{\parallel n}$ 1×10⁶ change in sign at t _{Fe}= 20 nm -1×10[€] 20 0 4∩ 60 Fe thickness $t_{\rm F}$ (nm) (kJ/m³) 80 $\Delta K = 17 \text{ kJ/m}^3$ plane anisotropy K₄ 60 $K_A^{\text{bulk}} = 58 \text{ kJ/m}^3$ 40 $K_4 = K_4^V + \frac{2K_4^S}{2K_4^S}$ 20 ⊒. 0 0 20 40 60 Fe thickness (nm)

Enders, Sander, Kirschner JAP 85 (1999) 5279

Lattice strain in thicker films: deviation of K₄ from bulk Magnetoelastic coupling changes with strain

Stranski-Krastanov layers of Fe: in-plane SRT



Rep Prog Phys 62 (1999) 809

Film morphology, structure and stress: Fe / W(110)



Shape matters, but strain also ...





Shape favors M along [001] Strain reduction also favors M along [001], in-plane SRT from [110] to [001] also for flat films

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Strain-modified magneto-elastic coupling

Implication for magnetic anisotropy

What about theory?





PRB 68 (2003) 155421

Orbital occupation vs. lattice strain

Calculations for distorted bcc Fe:

Strain induced change of occupation of different d orbitals of Fe, driven by the strain-induced shift of energy positions of d-states

Spin-orbit coupling is modified, and modified magneto-crystalline anisotropy results



Figure 3. Calculated change of electron density of the 3d-states of bulk Fe, due to a compression along the *z*-axis. A net charge transfer from the $d_{x^2-y^2}$ -state to the d_{z^2} -state is calculated. This induces an easy magnetization direction along the in-plane *x*-*y*-plane [38].

From: Wu, Chen, Shick, Freeman, JMMM 177-181 (1997) 1216.



O-mediated surfactant growth of Ni / Cu(100)



Phys. Rev. Lett. 99 (2007) 116101

H-induced reversible switching of the magnetic anisotropy



Adsorbate-induced SRT and structural change?



Adsorbate coverage from stress measurements





parameters from H / Ni(001) Christmann, Schober, Ertl, Neumann J. Chem Phys. 60 (1974) 4528.

1) assumption $\Delta \tau(t) \sim \Delta \theta(t)$ seems justified

2) VERY small H-induced stress: 0.25 S / Ni(001): -1 N / m 0.25 O / Ni(001): -1.2 N / m 0.25 C / Ni(001): -4.2 N / m Surf. Sci. 272 (1992) 318.

Theory: layer relaxation and layer-resolved magnetic anisotropy



calculated layer spacing: Maca, Shick, Redinger, Podlucky, Weinberger Czech. J. Physics 53 (2003) 33

> calculated layer-resolved anisotropy: Uiberacker, Zabloudil, Weinberger, Szunyogh, Sommers Phys. Rev. Lett. 82 (1999) 1289



FIG. 2. Layer resolved band energy differences ΔE_b^n for six (top), nine (middle), and twelve (bottom) Ni layers on Cu(100). Triangles, squares, and circles refer in turn to a uniform relaxation by 0%, -2.5%, and -5.5%, i.e., to a c/a ratio of 1, 0.975, and 0.945.

Interfaces are decisive

Electron confinement, magnetic switching, and Spin-polarization: LT-spin STM studies



Cr / W tip







 $V_s = +0.04 \text{ V}$



dl/dV maps



dl/dV asymmetry



How does a STM work?





Heinrich Rohrer Gerd Binnig IBM Zürich, Nobelprize 1986 (with Ernst Ruska)

Tunneling through a vacuum barrier: occupied vs. unoccupied electron states



Hamers, Ann. Rev. Phys. Chem. 40 (1989) 531

Zero voltage Ugap No net tunneling current

positive voltage UgapTunneling from occupied tip statesinto empty sample states

negative voltage Ugap Tunneling from occupied sample states into empty tip states

Arrows indicate tunneling probability

Low Temperature STM with vertical field



Tip Carrier





Cu(111)

Low Temperature: 7 K High Magn. Field : 8 T

Scanning Tunneling Spectroscopy (STS)



 $\frac{\text{Lock-in}}{\text{Amplifier}} \rightarrow \frac{dI}{dV}$

$$\frac{\mathrm{d}I}{\mathrm{d}V} \left(U_{gap} \right) \propto \mathrm{LDOS}_{sample}$$

Kaiser, Jaklevic, IBM J. Res. Develop. 30 (1985) 411; Fiete, Heller, Rev. Mod. Phys. 75 (2003) 933

High stability, low noise ...

factor 50 better than specs!

atomic resolution and standing wave modulation

dI / dU raw data, STS-movie 250 x 250, acquisition time: 14 h





5 x 5 nm² Cu(111) 7 K

low noise: < 200 fm_pp low drift: < 1 nm / 24 h

30 x 30 nm² Ugap: -0.5 V... + 0.5 V Cu(111) 200 fm_pp 7 K nm / 24 h

Co islands on Cu(111)



Co DL islands on Cu(111)



40 x 40 nm², +0.225 V, 1 nA 7 K, STS, dl/dV

> LDOS modulation due to Co sp majority electrons

Theory:

Diekhöner, Schneider, Baranov, Stepanyuk, Bruno, Kern Phys. Rev. Lett. 90 (2003)236801

Theory: spin-polarized Co state Spectroscopy by LT-STS



k (nm⁻¹)

2.0

2.5

3.0

3.5

-0.2

1.0

1.5

... towards Spin-STM...



PhD thesis U. Schlickum, 2005 MPI Halle

Pietzsch, Kubetzka, Bode, Wiesendanger PRL 92 (2004) 057202 Also: Co/Au/W tip: Prokop, Kukunin, Elmers, PRL 95 (2005)187202 Cr/W: Rusponi, Weiss, Cren, Epple, Brune, APL 87 (2005) 162514

Magnetic contrast in spin-STM

Spin-STM: Bode et al, PRL 81, 4256 (1998); Wulfhekel, Kirschner, APL 75, 1944 (1999)

Co / Cu(111): Pietzsch, Kubetzka, Bode, Wiesendanger, PRL 92 (2004) 057202.

dl/dV mapping



W tip with 40 ML Cr



Point spectroscopy





Magnetic switching field H_{sw} of *individual* Co islands influence of temperature and island size

T increases

size increases

Hsw decreases with T at fixed island size Hsw changes non-monotonic with island size at fixed T

Size and T-dependence of the switching field H_{SW} $H_{SW}(T,V)$: all curves Néel-Brown model

1: Hsw = 0 T; superparamagnetic regime

thermally assisted switching

2: Hsw increases with size: blocked magnetization

3: Hsw decreases with size: additional reversal mechanisms

//

superparamagnetic – blocked magnetization state Failure of the Néel-Brown model

Simplistic, but *questionable* view: nm small particle – single domain – magnetization reversal by coherent rotation stable = blocked magnetization implies a timescale, here τ = 100 s $\Delta E = KV$ $\tau^{-1} = f_0 \exp\left(-\frac{KV}{k_{\rm B}T}\right), \quad f_0 = 10^9 \dots 10^{12} \,{\rm s}^{-1}$ Dickson et al., JMMM125(1993)345 $K = 233...297 \text{ kJ/m}^3$, $V_{1200 \text{ atoms}} = 12 \text{ nm}^3$, T = 8.3 KSURPRISE: small K (hcp-Co: 513 kJ/ m³) *maximum* switching field: $\frac{2K}{M_s} = 0.3...0.4 \text{ T}$ CONFLICT: we observe 2 T

Theory: K(2 AL Co): 2.2 MJ / m³ (0.150 meV / atom) C. Etz, MPI Halle

Limitations of the Néel-Brown model of thermally assisted switching

Extension of the Stoner-Wohlfarth model to finite T is not valid here macrospin model does not work

we have *no bulk sample*: all interface atoms coordination reduced and varies possible complications: reduced exchange constant, variation of K, inhomogeneous M

> *Limitations of the macrospin model:* Rohart, Repain, Thiaville, Rousset, PRB76(2007) 104401 Wirth, Field, Awschalom, v. Molnár, PRB 57(1998)R14028

> > Non-collinear spin state Strong reduction of switching field





more complicated than coherent rotation ^{5 nm diam.} 1 AL Co reversal modes need to be considered

Conclusion Spin-STM study of magnetic reversal

Magnetization reversal of nm small Co islands:

Coherent rotation of a macrospin is not supported by our experiments

Large switching fields: large anisotropy (0.150 meV / atom)



Magnetization reversal by nucleation feasible: combination of reduced coordination and large K linear dimension more decisive than volume

Conclusion and outlook

stress measurements

surface stress, adsorption, reconstruction, growth mode, structural transitions

structural relaxation and SRT





complex magnetic switching and tip behavior

electron confinement and spatial modulation of spin-polarization



