Antiferromagnetic Materials: Characterisation techniques

Bryan Gallagher, Nottingham University

Experimental techniques which can be used to characterize AF materials.

Exclusive Jewellery for Pets- Combined with the power of Magnets!

MagnetAnimal Energise your pet



Dr. Bakst Magnetic Shoe Inserts



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1. Materials Growth Molecular Beam Epitaxy (MBE) Richard Campion 9.30 Friday





Molecular Beam Epitaxy

Can achieve (with regular calibrations)

- Very good epitaxy
- Very good control of stoichiometry ۲
- Accurate growth temperature control
- Monolayer by monolayer growth ٠
- Abrupt interfaces

Very slow Very expensive

In situ monitoring of crystal structure **Reflection high energy electron diffraction (RHEED) CuMnAs** [110] [110]

Good for materials structurally compatibly with commercial semiconductors⁶

Limited number of elements in a specific machine



Sputter Deposition Facilities

- Very flexible
- Relatively fast and low cost
- Can achieve close to epitaxial growth
- Very wide range of elements
- Can co-deposit from multiple sources
- Can sputter in reactive gas (O₂) or from composite targets (e.g. MgO)



Good to have access to MBE and sputtering

2.1 Structural Characterisation: X-Ray Diffraction (XRD)

- X-ray diffraction can reveal crystallographic structure.
- Want x-ray wavevector, $k \approx$ reciprocal lattice vector, $G \approx 10^{10}$ m⁻¹.
- For $k = 10^{10} \text{ m}^{-1}$ x-ray energy is $\varepsilon = 21 \text{ keV}$.
- Scattering almost elastic since ε >> phonons and magnons energies (~25meV at room temperature).



Phillips X-Pert high-resolution X-ray diffractometer

Elastic X-Ray Scattering



Bragg's Law in Reciprocal Space (Ewald Sphere)

X-ray Scattering Amplitude

$$A(Q) \propto \int \rho(r) \exp[iQ.r] dr \propto \sum_{j} f_{j}(Q) \exp[iQ.r_{j}] \sum_{T} \exp[iQ.r_{j}]$$

Q scattering vector $\rho(r)$: electron charge density $f_{j}(Q)$ atomic structure factor
T translation vectors

Inverse problem: infer real space structure from reciprocal space structure

Translational symmetries

Atom positions in basis

Atom types in basis

Order / disorder



Peak Positions

Peak Intensities

Extent of periodicity crystallite size / film thickness

X-ray diffraction from NaCl crystal



One of the first diffraction photographs taken M. von Laue in 1912

Crystal structure determined from Laue pattern by W. H. and W. L. Bragg in 1913

X-ray diffraction from protein Myoglobin

Image: ~3000 diffraction spots positions of ~ 3000 atoms in protein



Myoglobin



AF CuMnAs Grown on (100) GaAs or GaP

Structure resolution: Cu_2Sb type structure Tetragonal P4/nmm a = b = 3.820 A c= 6.318 A



Crystal quality of CuMnAs



- Narrower peaks on better lattice matched GaP substrate: Higher quality
- Relaxed mosaic block structure on GaAs
- Fully strained on GaP

Wadley, Jungwirth, Marti, Zelezny et al Nat. Commun. (13) DOI: 10.1038/ncomms3322

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FM (Ga,Mn)As Grown on GaAs



Kiessig fringes from thin films



FM / AF FeRh thin film





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X-ray reflectometry spectrum from a 25 nm thick FeRh epilayers capped with polycrystalline AI. The solid line is a fit using the FeRh density profile of the insert.

Le Graët, Marrows, et al Journal of Visualized Experiments (JoVE), no. 80, e50603. (2013)

3.2 Structural Characterisation: Transmission Electron Microscopy (TEM)

Element (Z)-resolved TEM image of CuMnAs



Remember samples ~100 nm thick.

Jaume Gasquez, Oakridge NL



CuMnAs: Anti-phase boundary defects



Arise from steps in the substrate





3.1 Magnetic Characterisation: Neutron Scattering

- Elastic neutron scattering can reveal magnetic structure.
- Inelastic neutron scattering can measure dispersion of phonons and magnons.
- Want neutron wavevector, $k_n \approx$ reciprocal lattice vector, $G \approx 10^{10}$ m⁻¹.
- For $k_n = 3 \times 10^{10} \text{ m}^{-1}$ neutron energy is $\epsilon_n = 25 \text{ meV} \approx \text{kT} @ T \approx 300 \text{K}$ (Thermal neutrons).
- Thermal neutrons have energies ≈ phonons and magnons.

X-ray Scattering

- X-rays scattered by electrons of atoms. Atomic structure factor f(Q) ~ Z, atomic number.
- Size of atoms ≈ neutron wavelength: scattering factor f (Q) decreases as
 |Q| increases.



X-rays: Scattered intensity ~ Z². Hard to 'see' light elements.

Neutron Nuclear Scattering

- Neutrons scattered by nuclei (strong force).
- Size of nuclei $\approx 10^{-5}$ x neutron wavelength.
- Nuclear scattering factor (b) for neutrons is ≈ independent of scattering wavevector q. Irregular variation with atomic number and isotope.



Neutrons: Sensitive to light elements. Isotope dependent: can vary contrast by isotope substitution.

Neutron Magnetic Scattering

- Neutrons scattered by magnetic moments.
- Spin and orbital moments of atom associated with outer electrons.
- Magnetic scattering factor for neutrons is strongly dependent on scattering wavevector Q.



Neutron Diffraction: MnO (T_N = 116 K)



Neutron Diffraction: CuMnAs

Structurally forbidden in plane (100) diffraction peak.



- AFM ordering with same dimensions as the structural unit cell
- Collinear layered antiferromagnet with spin axis in the *ab* plane
- Mn moment $\approx 3.6 \mu_B$



Neutron Diffraction: CuMnAs



3.2 Magnetic Characterisation: Magnons

Inelastic Neutron Scattering



Phonons: 1D Harmonic Diatomic Chain



Ferromagnetic Magnons / Spin Waves



1D linear response, nearest neighbour exchange.

Without anisotropy

$$\hbar\omega = 2E_{ex}(1 - \cos(ka))$$

$$\hbar\omega \approx E_{ex}a^2k^2 = Dk^2$$
 for small k

Energies per moment. D: spin wave stiffness

With uniaxial anisotropy

$$\hbar\omega \approx E_{an} + Dk^2 \text{ for small k}$$

For k = 0
$$\hbar\omega \approx E_{an}$$



Ferromagnetic Magnons





Antiferromagnetic Magnons / Spin Waves



Antiferromagnetic Magnons



Antiferromagnetic Magnons

Highly anisotropic magnon dispersion in Ca₂RuO₄: evidence for strong spin orbit coupling



Kunkemöller, et al Phys. Rev. Lett. 115, 247201, 2015

4 Magnetic Characterisation: Magnetic Resonance


Ferromagnetic Resonance (FMR): Anisotropy Energies



Ferromagnetic Resonance: Anisotropy

Angular dependence of ferromagnetic resonance frequency with a constant magnitude Applied magnetic field rotated in-plane.



Antiferromagnetic Resonance (AFMR)

 $H_{ext} \rightarrow 0$ Excited modes are magnons with k ~ 0



Resonant frequencies ~ 100 - 1000 GHz. Natural speed of dymamics

Antiferromagnetic Resonance



More than one type of Mn site : both "acoustic" and "optical" magnons

L.A. Prozorova, V.I. Marchenko, Yu.V. Krasnyak, JETP Letters, 41, 637 (1985)

3.4 Magnetic Characterisation: Remanence



Measuring Remanence. Cool in field (in 300mT). Warm in zero field

Magnetisation: AF CuMnAs



Magnetisation: AF CuMnAs



Susceptibility



From Kittle

Antiferromagnetic Susceptibility



Peak susceptibility gives Neel Temperature

Antiferromagnetic Susceptibility







Magnetic Behaviour in "Large" Fields



Normally don't see ideal behaviour because of domain formation



Dominant magneto-crystalline anisotropy in-plane for compressive strain and or out-of-plane for tensile strain strain

End Part One



The importance of avoiding stray fields 50

Welcome back



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. Vielmehr ist es eine konzennierte Gedankenkraft, die





Magnetic Behaviour in "Large" Fields



Normally don't see ideal behaviour because of domain formation



Dominant magneto-crystalline anisotropy in-plane for compressive strain and or out-of-plane for tensile strain strain

Antiferromagnets: Spin Flop Transitions

Single domain uniaxial antiferromagnet H perpendicular to easy axis



Antiferromagnets: Spin Flop Transitions Single domain uniaxial antiferromagnet. H parallel to easy axis. Small K₁ $\epsilon = J_{ex,inter} M^2 \cos(2\phi) - K_u \cos^2 \phi - \mu_0 H M \cos(\phi)$ M_1 H = 0 $H < H_{sf}$ $H > H_{sf}$ Ф M_{1} M_{2} M_{2} Ф H_K H_{K} H_K \boldsymbol{M}_{1} M_2 M_{2} Μ **Spin Flop Transition** Hsf = 0 for $K_u = 0$ $\mu_0 HM \approx \sqrt{2 K_{\mu} J_{ex} M^2}$ M Zeeman energy ~ (2 x exchange energy x anisotropy energy)^{1/2} 0 57 Hsf

Η

Antiferromagnets: Spin Flip Transitions Single domain uniaxial antiferromagnet. H parallel to easy axis. Large K_{μ} $\epsilon = J_{ex,inter} M^2 \cos(2\phi) - K_u \cos^2 \phi - \mu_0 H M \cos(\phi)$ M_1 *H* = 0 $H < H_{sf}$ $H > H_{sf}$ Φ M_{1} M_{2} M_2 M. ф H_{K} H_K H_K M_2 **M**₁ M **M**₁ **Spin Flip Transition** M_{2} 0

Antiferromagnets: Spin Flop Transitions



Spin Flop Transition seen in AFMR

If Exchange energy >> Anisotropy energy and T << T_N



Hagiwara, et al : J. Phys. C8, 7349 (1996). Nagamiya et al Adv. Phys. 4, 1 (1955). Foner Phys. Rev. 107, 683 (1957).

Torque Magnetometry: α-MnTe

Can give symmetry and strength of anisotropy

NiAs-structure Six fold symmetry



Komatsubara et al J Phys Soc Japan 18, 3 (1963)

Torque Magnetometry

monoclinic quasi-one-dimensional S = 1/2 Heisenberg antiferromagnet CuSb₂O₆



Herak et al Phys. Rev. B 91, 174436 (2015)

Zero Field NMR in Antiferromagnets



Yogi et al J. Phys. Soc. Jpn. 82, 103701 (2013)



Antiferromagnetism : ZFNMR



Applying a magnetic field of $\mu_0 H_{app}$ =0.5 T changes the five-peak ZFNMR spectrum into an unresolved broad spectrum extending.

In the applied field equivalent sites in the constituent grains experience different fields because of the distribution of angles between internal and applied fields. The total field experienced by ⁵⁵Mn nuclei takes all values between $H_{hyp}+H_{app}$ and $-H_{hyp}+H_{app}$. Barthem et al Nature Communications 4:2892 · December 2013

4.1 Critical behaviour: Specific Heat



Mamsurova et al Zh. Eksp. Teor. Fiz. 69, 666, (1975)

Antiferromagnets : Specific Heat



Maca et al J. Mag. Mag. Mater. 1606, 324, 8, (2012)

4.2 Critical Behaviour: Resistivity

For dense moment magnetic semiconductors the moment density >> carrier density. Only long wavelength spin fluctuations scatter carriers effectively [1] and the mobility has a peak at T_C / T_N with the same form as the susceptibility [2].



[1] de Gennes and Friedel, J. Phys. Chem. Solids 4, 71 (1958)
[2] Haas, Crit. Rev. Solid State Sci. 1, 47 (1970)

4.2 Critical Behaviour: Resistivity

In ferromagnetic metals [1] and dilute ferromagnetic semiconductors [2] carrier density ~moment density. Critical fluctuations produce a peak in $d\rho_{xx}/dT$ at T_c with same form as specific heat [3].



[1] Craig et al Phys. Rev. Lett. 19, 1334 (1967); Shacklette , et al , Phys. Rev. B 9, 3789 (1974)
 [2] Novák, et al Phys. Rev. Lett. 101, 077201 (2008) [3] Kim, et al Phys. Rev. B 67, 100406(R) (2003)

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Critical Behaviour: Resistivity



Hills et al JAP 2015

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AF CuMnAs with FM MnAs inclusions



4.3 Critical Exponents

Close to a second order phase transition power law relationships between thermodynamic variables exist.



Only C_V is easy to measured accurately in an antiferromagnet.
Critical Exponents

The values of the exponents close to the critical temperature often depend only on the dimensionality and symmetry of the system and belong to a small number of universality classes.

	α	β	γ
Mean Field	0	0.5	1.0
Ising	0.11	0.326	1.237
3D Heisenberg	-0.134	0.369	1.396

Determining critical exponents can give information on dimensionality of moment system and range of exchange interactions.

FM (Ga,Mn)As	??	0.366 +/-	1.47 +/-
		0.003	0.05

Three-dimensional Heisenberg critical behaviour in the highly disordered dilute ferromagnetic semiconductor (Ga,Mn)As M. Wang, R. A. Marshall, K. W. Edmonds, A. W. Rushforth, R. P. Campion, and B. L. Gallagher Physical Review B 93, 184417 (2016)

Critical Exponents of Antiferromagnets



Fitting functions used to obtain critical exponent α

 $c = B + C(T - T_{\rm N}) + A^{+}|T - T_{\rm N}|^{-\alpha}(1 + E^{+}|T - T_{\rm N}|^{0.5}) \qquad T > T_{\rm N}$ $c = B + C(T - T_{\rm N}) + A^{-}|T - T_{\rm N}|^{-\alpha}(1 + E^{-}|T - T_{\rm N}|^{0.5}) \qquad T < T_{\rm N}$

Eight free parameters plus choice of fitting temperature range

Conclude α = -0.11 +/- 0.01 3D Heisenberg value

A Oleaga¹, A Salazar¹, D Prabhakaran² and A T Boothroyd²

J. Phys.: Condens. Matter 17 (2005) 6729-6736

5. X-ray magnetic dichroism



Lab x-ray source

- fixed energy (e.g., Cu Ka)
- unpolarized

Synchrotron x-ray source

- controllable energy (sub-eV \rightarrow 100s of keV)
- high flux, high coherence
- controllable polarization (linear or circular)
- **BUT** limited availability



Peter Wadley tomorrow

X-ray Magnetic Circular Dichroism (XMCD)



- Probes unfilled local density of states around excited atom
- Combined chemical and magnetic probe
- Element-specific magnetometer
- Depth-dependent information
- Semi-quantitative (orbital and spin magnetic moments per atom)⁷⁶

X-ray Magnetic Circular Dichroism (XMCD)

FM (Ga,Mn)As $2p \rightarrow 3d$ transitions



Sum rule reference: Paolo Carra, et al Phys. Rev. Lett. 70, 694 1993

X-ray Magnetic Circular Dichroism (XMCD)



Sensitive to unpaired spin or orbital magnetic moments, *ie* **ferromagnetic order** Sensitive to electric, magnetic or structural anisotropies, *including* **antiferromagnetic order**





Source Condenser Objective **Spatial resolution** Condenser zone plate Plane mirror Pinhole ALS Bending Micro zone Soft x-ray Magnet plate sensitive CCD **1.** Scanning transmission x-ray microscopy

- powerful, but limited to thin (~200nm) samples
- 2. X-ray photoelectron emission microscopy (X-PEEM)
- collect and focus secondary electrons
- surface sensitive





Imaging exchange coupling in AF NiO/ FM Co bilayers Ohldag et al., PRL 86, 2878 (2001)

XMLD X-PEEM CuMnAs domains

40nm CuMnAs layer: uniaxial anisotropy with 180° domain walls



Uniaxial Domains

Domain Wall Profile

6 Spin-Polarised Scanning Tunnelling Microscopy (SP-STM)

Tunnelling current depends on local spin dependent densities of states



- Atomic resolution
- Sensitive to surface monolayer and few subsurface monolayers
- Need near perfect surfaces: no oxidation etc
- Usually produce sample within UHV STM system by deposition or cleavage.
- Surface properties may not reflect bulk properties: surface reconstructions, uncompensated moments etc.

SP-STM AF Mn₃N₂



Yang et al https://arxiv.org/pdf/cond-mat/0510147.pdf

SP-STM AF Mn₃N₂



SP-STM: Atomic spin structure of an antiferromagnetic wall

Deposit Iron monolayer on (001) surface of Tungsten. Iron layer antiferromagnetic

Right: Simulated (grey) and measured (colour) SP-STM signals



M. BODE, ...Wiesendanger et al Nature Materials 2006

SP-STM AF Mn₃N₂



(a)The spins of the antiferromagetic manganese surface in a spin-spiral state.

(b) Out of plane SP-STM image showing the anti-parallel spins.



Boris Wolter,....,Roland Wiesendanger, et al Phys. Rev. Lett. **109** 116102

AMR ?









5.1 Anisotropic Magnetoresistance (AMR)

"Normal" Non Crystalline AMR $R_{0}+R_{Max}$ $R_{0}-R_{Max}$ Hall Bar

$$\rho_{xx} = \rho_0 + \Delta \rho \cos 2\phi$$
 $\rho_{xy} = \Delta \rho \sin 2\phi$

Resistance depends on relative orientation of Magnetisation and current.

Only contribution for isotropic (e.g. polycrystalline) materials.

FM (Ga,Mn)As: Measured AMR

GaMnAs 5% Mn 25nm epilayer. Fixed field of 1 Tesla rotated in plane @ 4.2 K

4 Hall Bars along 4 crystal directions



Find size of measured AMR Depends on crystallographic orientation of the Hall bar



FM (Ga,Mn)As: Measured AMR

Corbino Disk. Current radial. Zero non-crystalline AMR



GaMnAs 5% Mn 25nm epilayer. 1 Tesla field rotated in plane @ 4.2 K



Measured AMR depends on relative orientation of magnetisation and crystallographic axis.

"Small" Bi-axial and uniaxial magneto-crystalline contributions

 $\frac{\Delta \rho_{xx}}{\rho_{av}} = C_I \cos 2\phi + C_U \cos 2\psi + C_C \cos 4\psi + C_{I,C} \cos(4\psi - 2\phi) + C_{I,U} \sin(6\psi - 2\phi) + \dots$

$$\frac{\Delta \rho_{xy}}{\rho_{av}} = C_I \sin 2\phi + C_{I,C} \sin(4\psi - 2\phi) + C_{I,U} \cos(6\psi - 2\phi) + \dots$$

Rushforth et al., PRL 99, 147207 (2007)

Antiferromagnetic AMR: FeRh

FeRh: AF to FM transition at ~400K.



Cool in field through the FM to AF transition temperature: Spins flop into direction perpendicular to applied field.

Antiferromagnetic AMR: α-MnTe



Kriegner, et al. Nature Commun. '16

Antiferromagnetic AMR: α-MnTe



Kriegner, et al. Nature Commun. '16

5.2 Tunnelling Anisotropic Magnetoresistance (TAMR)

Single magnetic contact. Tunnelling density of states depends on relative orientation of magnetisation and crystal axes due to spin-orbit interaction.



Antiferromagnetic TAMR

Exchange bias used to control AFM moments



Park et al. Nature Mat. 2011, PRL 2012 Wang et al. PRL 2012:

The End



The Detective Dick Tracy (1930s)