SURFACE, MOLECULAR AND INTERFACIAL MAGNETISM

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Contents

Surfaces and interfaces

- Dimensionality effects on ordering
- Thermal excitations
- Surface magnetic anisotropy
- Exchange bias

Molecular magnetism

- Coordination compounds: Prussian Blue derivatives
- Single-molecule magnets





Effect of dimensionality on magnetic ordering

At surfaces (or interfaces!), the coordination with other magnetic atoms is reduced.

Thermal disorder effects gain importance against ferromagnetic ordering.

This effect can be observed by solving statistical mechanical models (e.g., Ising, Heisenberg, Potts, etc.).

2D magnetization curves fall off near T_{c} more abruptly than in 3D.

$$M \sim [1 - (T/T_c)]^{\beta}, \quad T \rightarrow T_c$$







Experiment:

measurements on Fe(100) using probes sensitive to magnetization but with different penetration depths:

- a) Magneto-Optic Kerr Effect
- b) Secondary electron emission
- c) Neutralization of grazing $\mathrm{He}^{\scriptscriptstyle +}$

The solid lines are mean-field calculations for different penetration/escape depths.



Pfandzelter & Polthoff, PRB 64, 140405 (2001)





Magnetization in 2D – Thermal disorder



Huang et al., PRB **49**, 3962 (1994)

Li & Baberschke, PRL **68**, 1208 (1992)

Crossover 3D \rightarrow 2D related to spin-wave spectrum: spin waves are quantized within a thin film, with energy spacing increasing as the film thickness decreases. When it exceeds $k_{\rm B}T$, only the lowest state is thermally accesible and the film becomes 2D.

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Magnetization in 2D – Thickness dependence



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SMOKE measurements on thin films:

 $T_{\rm c}$ also depends on thickness.

Huang et al., PRB 49, 3962 (1994)

TABLE I. Experimental values of transition temperature T_c and power-law exponent β for three different systems: Ni/Cu(100), Ni/Cu(111), and Co/Cu(111). The estimated errors for β are included based upon the noise level, finite-size rounding, and interdiffusion effects.

	Ni/Cu(100)			Ni/Cu(111)			Co/Cu(111)	
n (ML)	β	T_C (K)	n (ML)	β	T_C (K)	n (ML)	β	T_C (K)
3.0	0.25(6)	210	1.8	0.27(7)	197	1.0	0.17(9)	207
4.1	0.23(5)	284	2.2	0.26(7)	253	1.1	0.27(9)	283
5.0	0.25(5)	325	2.9	0.29(7)	329	1.3	0.30(9)	380
6.2	0.24(5)	388	3.0	0.30(7)	340	1.5	0.15(8)	460
7.2	0.38(4)	425	3.6	0.28(7)	382	1.7	0.15(8)	500
8.2	0.41(4)	456	4.4	0.29(7)	431			
10.0	0.41(4)	485	5.1	0.26(7)	462			
12.4	0.39(4)	514	6.0	0.30(7)	483			
16.0	0.43(4)	540	7.3	0.30(7)	519			
			8.5	0.35(6)	529			
			9.5	0.39(6)	554			
			10.5	0.45(8)	559			
			13.1	0.49(8)	591			
			16.7	0.48(8)	603			



Effect of dimensionality on magnetic ordering

The reduction of T_c in thin films reflects the cooperative nature of ferromagnetism. Using finite size scaling theory:

$$\left[\frac{T_{c}(n)}{T_{c}(\infty)}\right] = 1 - \left(\frac{n_{0}}{n}\right)^{\lambda} \quad n \to \infty \qquad \text{Domb, J. Phys. A 6, 1296 (1973)}$$

 $\lambda = 1.56$ and $\lambda = 1.49$ are the predictions from the 3D Ising and XY models, respectively. The films become paramagnetic below a certain thickness n_0 .



Magnetism in 2D – Thermal disorder

Many experimental results hint that T_{c} (1 ML) = 0.



Mermin-Wagner theorem

ABSENCE OF FERROMAGNETISM OR ANTIFERROMAGNETISM IN ONE- OR TWO-DIMENSIONAL ISOTROPIC HEISENBERG MODELS*

N. D. Mermin[†] and H. Wagner[‡] Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York (Received 17 October 1966)

It is rigorously proved that at any nonzero temperature, a onc- or two-dimensional isotropic spin-S Heisenberg model with finite-range exchange interaction can be neither ferromagnetic nor antiferromagnetic. The method of proof is capable of excluding a variety of types of ordering in one and two dimensions.

Mermin & Wagner, PRL 17, 1133 (1966)

• Long range order is excluded at finite temperatures in an **isotropic**, purely 2D system (for the Ising model there is the classic Onsager solution at T = 0);

• Anisotropies can induce order at $T \neq 0$ in 2D.

In 1D systems theory predicts that even stronger anisotropies might be unable to produce a zero-field equilibrium spontaneous magnetization.

Newell & Montroll, Rev. Mod. Phys. 25, 159 (1953)





Quasi 1D systems also display magnetic behavior at finite temperatures; dependent on growth parameters (morphology and structure)



FIG. 3. As Fig. 1, but for films prepared at 570 K. (a) $\theta =$ 0.14; (b) $\theta = 0.52$. The strong contrast marks the edge of the Fe layer; the faint contrast (straight line, indicated by arrows) the transition from W to Fe at the same level, at W steps.

High T: step-flow growth;

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Low T: island growth, percolation



FIG. 1. STM images of Fe(110) films, prepared at RT on W(110), all 70 nm \times 70 nm in size, with [001] horizontal. (a) $\theta = 0.23$; (b) $\theta = 0.53$; (c) $\theta = 0.66$; (d) $\theta = 0.85$. Upper levels (Fe) bright; lower levels (W) dark.



Magnetization in 1D



Fe stripes grown on vicinal Cu(111); $\Theta_{Fe} = 0.8$ ML. The magnetization is temperature and time-dependent.



Shen et al., PRB 56, 2340 (1997)





An Ising (or any anisotropic) chain is nonmagnetic in equilibrium

- single, isolated chains
- Interactions (magnetostatic, RKKY, substrate-mediated, ...) in a system of parallel chains ("wires") might stabilize magnetic order.

If the interactions between wires can be neglected, the equilibrium state of the system must be **superparamagnetic**:

- correlated blocks of spins with parallel orientation,
- long-range order destroyed by thermal fluctuations.

Magnetic order can still be kinetically frozen or "blocked".

The **blocking temperature** $T_{\rm B}$ can be estimated from the disappearance of the coercivity.

Above T_{B} the system behaves like a **paramagnet** with no hysteresis but with the same saturation magnetization M_{s} in an external field.





Magnetization in 1D



Kinetic limitations also imply time-dependence.

Wires made up of segments (spin blocks) connected through constrictions.

Magnetization switching is energetically favorable at those points.



Shen et al., PRB **56**, 2340 (1997)





Magnetization in 1D



 $T_{\rm C}$: gaussian distribution, $\Delta T_{\rm C}$ = 1.7 K, β = 0.32 0.5 ML Fe/vicinal W(110) 250 nm × 250 nm $T_{\rm C}$ = 179 K

Magnetization perpendicular to stripes interstripe coupling! Above T_C, typical superparamagnetic behavior:

$M(H) = M_s \tanh (H/H_s)$



Hauschild et al., PRB **57**, R677 (1998)





OD systems

Superparamagnetic limit: the energy barrier ΔE between two stable magnetizations along the easy axis becomes comparable to $k_{\rm R}T$.

The flip rate *R* is a thermally-activated process:

 $R = v \cdot \exp(-\Delta E/k_{\rm B}T)$

 ΔE can be estimated from the energy of the total magnetic moment of the particle in the demagnetizing field:

$$\Delta E = \frac{1}{2} M_{\rm s} V H_{\rm d}$$



For Fe, $M_{\rm s} = 2.2 \ \mu_{\rm B} = 1700 \ {\rm erg/G} \cdot {\rm cm}^3$; V is the particle volume, and $H_{\rm d} = 2\pi M_{\rm s}$ for uniform rotation; more realistically, $H_{\rm d} \simeq M_{\rm S}$.



Braun, PRB **50**, 16501 (1994)





OD systems

For v, we use the Larmor frequency:

$$v \simeq v_L = \omega_L / 2\pi = eH_d / 4\pi mc = 2.4 \times 10^9 s^{-1}$$

If $V = (10 \text{ nm})^3$, the flip probability per attempt is $\sim e^{-35} = 7 \times 10^{-16}$

Multiplied by the frequency, $R \sim 1$ per week.

If $V = (20 \text{ nm})^3$, the flip rate rises to once every 10^{104} years.





0D systems

Co/Au(111): Islands with double atomic height nucleate at the elbows of the herringbone reconstruction.





O. Fruchart et al., PRL 83, 2769 (1999)

Dürr et al., PRB 59, 701 (1999)

Superparamagnetic blocking temperature:

$$T_{\rm B} = 224$$
 K, for $N_{\rm atom} = 12000$

$$T_{\rm B} = 30 \, {\rm K}, \, {\rm for} \, N_{\rm atom} = 300$$

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Fe/CaF₂/Si(111)

Different magnetic phases depending on island radius *R*:

- R < 1.5 nm: perpendicular random AF
- 1.5 < R < 3 nm: in-plane superparamagnet</p>
- R > 3 nm: in-plane ferromagnet

TABLE I. Summary of Fe particle structure as a function of Fe deposited on the $CaF_2/Si(111)$ surface. SP and F indicate superparamagnetism and ferromagnetism, respectively.

Fe coverage (ML)	CaF ₂ surface coverage (%)	Average island radius (nm)	Average Fe height (nm)	Number of islands per area (10 ⁻² island/nm ²)	Magnetic state
3.3	19 ± 2	0.95 ± 0.08	1.94 ± 0.10	8.33 ± 0.44	SP
6.7	29 ± 2	1.38 ± 0.10	3.20 ± 0.10	4.83 ± 0.44	SP
8.9	42 ± 2	2.20 ± 0.20	2.90 ± 0.20	2.82 ± 0.43	SP
13.4	48 ± 5	3.34 ± 0.70	3.40 ± 0.40	1.55 ± 0.46	F
21.4	62 ± 2	Single island	>3.40	Continuous	F





Scheinfein et al., PRL **76**, 1541 (1996)

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The magnetic characteristics of any kind of atoms are altered whenever their environment is modified with respect to bulk. At surfaces:

- coordination is reduced;
- symmetry is broken;
- there may appear surface states, which can also be spin-polarized.

Electronic effects also play an important role: hybridization of bands, polarization of electronic clouds, etc.

When atoms with half-filled *d*-shell in a given material approach the dilute (single-atomic) limit, their magnetic moment is maximized according to Hund's first rule. Due to Pauli's principle, in order to have the same spin, the spatial wave functions must be different. Increasing their separation helps the electron reduce their Coulomb repulsion.

The exchange integral *I* depends on the overlap of the *d*-wavefunctions of the transition metals, which decreases from *3d* to *5d* elements. In general:

$$I_{3d} > I_{4d} > I_{5d}$$





Stoner criterion for the existence of ferromagnetism

 $I \cdot D'(E_F) > 1$

where

$$D'(E_F) = \frac{V}{2N}D(E_F)$$

is the density of states per atom and spin.

Physical meaning: when both the DOE at the Fermi level and the exchange integral have high values, the system can lower its energy by splitting the bands and shifting downwards the majority electrons.







For the 4*d* elements, the DOE and the Stoner parameter are too low for ferromagnetism, but still the magnetic susceptibility is strongly enhanced.

a) $D'(E_{F})$

b) Atomic exchange integral I

c) Product $I \cdot D'(E_{F})$

Elements with a product > 1 are ferromagnetic; those slightly below 1 can become FM in thin films and multilayers.









The density of states at the Fermi level depends on the width of the *d*-band roughly like:

$$N(E_F) \sim (W_d)^{-2}$$

with

$$W_d \propto 2\sqrt{z}h_d$$

z: coordination number, h_d : hopping matrix element of the *d*-electrons nearest neighbours.



 h_{d} depends on the transition metal and scales reciprocal with the localization of the wave function:

 $h_{3d} < h_{4d} < h_{5d}$

Therefore, for equal coordination:

$$W_{3d} < W_{4d} < W_{5d} \Rightarrow N(E_F)_{3d} > N(E_F)_{4d} > N(E_F)_{5d}$$





We can decrease W_d by reducing the coordination number.

Characteristic values for *z*:

	bulk	surface	Isolated film
fcc	12	8	4
bcc	8	6	4
SC	6	5	4

For an fcc 3*d* metal the density of states at the Fermi-level increases with reduction of *N*:

 $N(E_{\rm F})_{\rm ML}$: $N(E_{\rm F})_{\rm 001-surface}$: $N(E_{\rm F})_{\rm bulk} = 1.73 : 1.22 : 1$

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This affects the magnetic moment.

Example: Ni (using always the same nearest neighbour distance):

z	<i>m</i> (μ _Β)
12	0.58
8	0.72
4	0.85





Isolated monolayers



Calculated moments for some examples of monolayers, assuming bulk interatomic distances:

	structure	<m>_{bulk} (μ_Β)</m>	<m>_{ML} (μ_B)</m>
Fe	bcc	2.2	3.4
Ni	fcc	0.6	0.85





Magnetic monolayer on a non-magnetic substrate

Two effects:

- reduction of band width due to low coordination;
- hybridisation with the substrate



Hybridisation usually causes band expansion \Rightarrow decreased density of states at $E_{\rm F}$.

Hybridisation of magnetic monolayers on noble metal substrates is weak: the *d*-band of the latter lies several eV below the Fermi level.

Therefore, magnetic monolayers on Cu, Ag, and Au behave (theoretically) similar to isolated monolayers.





Ferromagnetism of transition metal ML's on noble metal (Ag) substrates



Even 5d elements could become magnetic!



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Blügel, PRL 68, 851 (1992)

Ferromagnetism of transition metal ML's on noble metal substrates:



- $3d \rightarrow 5d$: increasing overlap of the d orbitals within the ML
- Controlling parameter: sp-d hybridization between ML and substrate
- Au d-band higher than Ag

Blügel, PRL 68, 851 (1992)





Pd is almost ferromagnetic due to the very high density of states at $E_{\rm F}$. Highly polarizable.

A strong hybridisation between the Pd 4*d* band and the 3*d* metals can be expected.

Oscillatory induced magnetic moment in Pd layers within Fe/Pd multilayers: RKKY-type interaction.

Fe has the same magnetic moment as in a single film.



Li et al., PRB **50**, 10323 (1994)





Vanadium is another typical example of an element close to being ferromagnetic:

Scherz et al., PRB 68, 180407 (2001)

Schwickert et al., PRB 57, 13681 (1998)

TABLE I. Total magnetic moment m_{tot} measured by VSM and normalized to the number of Fe atoms only, Fe moment m_{Fe} by XMCD and V moment m_V obtained as explained in the text. Typical error bars by the VSM and XMCD technique are in the range of 5–10%.

Sample	$m_{tot} \ (\mu_B / \text{atom})$	$m_{Fe} \ (\mu_B / \text{atom})$	$m_V (\mu_B / \text{atom})$
40 nm Fe		2.22	
$(Fe_4/V_2)_{60}$	1.59	2.12	-1.06
$(Fe_4/V_4)_{45}$	1.28	1.70	-0.42
$(Fe_2/V_5)_{50}$	0.67	1.34	-0.27

TABLE I. Calculated magnetic moments from [Fe 5 ML/V n ML] superlattices with perfect interfaces. Magnetic moments are in units of μ_B per atom. The layers labeled "I" are interface layers, while other layers are labeled with their distance from the interface. Thus, Fe I-2 is the atomic layer in the center of the Fe layer. As discussed in more detail in the text, the results indicated with $n=11^*$ refer to a superlattice in which the Fe sublattice, and not the V sublattice, is tetragonally deformed.

n	Fe 1-2	Fe <i>I</i> -1	Fe I	VI	V I-1	V I-2	V I-3	V I-4	V I–5	Fe Avg.	V Avg.
1	2.33	2.46	1.90	-1.05						2.21	-1.05
3	2.31	2.44	1.76	-0.53	-0.08					2.14	-0.38
5	2.29	2.43	1.79	-0.49	-0.02	0.05				2.15	-0.19
7	2.27	2.39	1.83	-0.45	-0.08	0.00	0.00			2.14	-0.15
9	2.28	2.42	1.77	-0.50	-0.05	0.02	0.00	-0.01		2.13	-0.12
11	2.28	2.43	1.80	-0.48	-0.05	0.02	0.01	0.00	-0.01	2.15	-0.09
11*	2,24	2.38	1.75	-0.52	-0.03	-0.01	-0.02	0.01	0.03	2.10	-0.10





Magnetic anisotropy

Anisotropy energy is related to the orbital overlap of the electrons
 The spin interacts with the orbital motion through the spin-orbit coupling

 \Rightarrow Magnetocrystalline anisotropy energy $U_{\rm mc}$.

 $U_{\rm mc}$ is proportional to the anisotropy of the orbital moment $\Delta m_{\rm L}$:

$$U_{mc} = \alpha \frac{\xi}{4\mu_B} \Delta m_L$$



 ξ is the spin-orbit parameter, and the prefactor α contains the bandwith W and the Coulomb integral C.

Since we already know that the band structure changes with size and dimensionality, the magnetic anisotropy can also be manipulated.

Bruno, PRB 39, 8665 (1989)





In bulk cubic crystals, the high symmetry leads to near quenching of the orbital moments: $\Delta m_{\rm L} \approx 10^{-4} \ \mu_{\rm B}/\text{atom}$ ($\approx 0.1 \text{ G}$).

In ultrathin films, multilayers and nanostructures other contributions to the magnetic anisotropy come into play:

Reduced symmetry at surfaces, interfaces or step edges (U_S) Néel, J. Phys. Radium 15, 225 (1954)

Lattice distortions due to strain between the magnetic layers and the substrate or the non-magnetic layers in a superlattice (magnetoelasticity); in pseudomorphic growth, a change of ~10⁻¹ Å in the lattice parameter can increase this contribution by orders of magnitude;

Dipolar forces, responsible for the formation of magnetic domains; importance of shape.





Shape anisotropy: dipolar origin, uniaxial.

The system prefers to have the magnetization oriented along some direction related to its dimensionality, in order to minimize surface charges.

$$U_{sh} = -2\pi M_s^2 \cos^2 \theta$$

Important contribution in systems with reduced dimensions.



Many surface charges \Rightarrow high dipolar fields \Rightarrow energetically unfavorable





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(After O. Fruchart, LLN-Grenoble)

Magnetic anisotropy – interfacial



It appears as a thickness-dependent correction $(0.1 - 1 \text{ erg/cm}^2)$ to the magnetocrystalline anisotropy energy:

$$U_{an} = (U_v^{eff} - 2\pi M_s^2) + U_s/d$$

 U_V^{eff} is an effective volume anisotropy, including all contributions that are not thickness dependent (magnetocrystalline and magnetoelastic).

With this sign criterion, $U_{an} < 0$ implies in-plane magnetization, whereas perpendicular magnetization follows when $U_{an} > 0$.

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Example: Co/Cu(111) and Cu/Co/Cu(111)

Considerable dispersion in theoretical and experimental results:

TABLE I. Comparison of reported values for the different contributions to the magnetic anisotropy in Co/Cu(111) and Cu/Co/Cu(111) systems.

t_{Co} [ML]	t_{Cu} [ML]	$K_S [\mathrm{mJ/m^2}]$	$K_V [MJ/m^3]$	$K_{mc} + K_{me}$ [MJ/m ³]	Ref.
{2-7}	4	(0.32 ± 0.03)	$-(0.74 \pm 0.04)$	(0.53 ± 0.04)	This work
{2-15}	11	0.10	-0.80	0.47	11
	23	0.12	-0.80	0.47	11
{2-20}	5	0.12	-0.86	0.41	12
{2-20}	-	0.18	-0.64	0.63	13
	<u>_</u>	0.13	-0.90	0.37	14
{0-17}	14	0.26	-0.60	121	15
		0.4/0.5	0.0	-	15
5.5	2	-0.51	1.34	2	16
5.5	2	0.37	-0.06	-	16
1	-	0.57	-	-	17

Camarero et al., PRB 64, 125406 (2001)





Experimental determination of the anisotropy energy by means of polar and longitudinal MOKE measurements:



Camarero et al., PRB 64, 125406 (2001)





Magnetic anisotropy – interface



Influence of film roughness:

Pyramidal growth: higher effective thickness, reduced interfacial contribution

Magnetostatic interaction between adjacent islands favours in-plane magnetization



Camarero et al., PRB 64, 125406 (2001)





One dimensional monatomic metal chains



Gambardella et al., Nature 416, 301 (2002)





Magnetic anisotropy – interface

Giant magnetic anisotropy of single Co atoms and nanoparticles



Co/Pt(111)

Gambardella et al., Science 300, 1130 (2003)







- Soft FM film, strongly exchange-coupled to an AFM
- The AFM is not affected by the applied magnetic field
- $T_{\rm C} > T > T_{\rm N}$: field cooling through $T_{\rm N}$
- Increased coercivity
- Shifted hysteresis loops





Exchange-coupled FM-AFM bilayers

1956 "A new type of magnetic anisotropy has been discovered which is best described as an exchange anisotropy. This anisotropy is the result of an interaction between an antiferromagnetic material and a ferromagnetic material" W.H. Meiklejohn and C.P. Bean, Phys Rev B 102 (1956), 413.





Main experimental evidences Unidirectional anisotropy, (i.e. shift in the hysteresis loop)

^{CP} Enhanced coercivity: $H_C(F/AF) > H_C(F)$

Magnetization reversal asymmetry

(borrowed from J. Camarero)





Models of Exchange Bias

(borrowed from J. Camarero)



$$A_{AF} = J_{AF}/a$$
: Exchange stiffness;

 K_{AF} : Uniaxial anisotropy energy

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Magnetization reversal in exchange-biased systems





Different domain nucleation mechanisms

Different domain wall shapes for "positive" and "negative" reversals (competition between easy and hard axes)



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Kirilyuk et al., JAP **91**, 7745 (2002)

Applications for data storage and readout

(from J. Camarero)







Different types of materials:

- Purely organic compounds (very low critical T)
- Sulfur-nitrogen radicals (weak ferromagnets below 35 K)
- Coordination compounds of transition metal ions and organic radicals
- Prussian Blue derivatives

Molecular magnets are exchange-coupled clusters of between 4 and ~30 paramagnetic ions. Typical bridges: O²⁻, OH⁻, OCH³⁻, F⁻, Cl⁻, RCOO⁻

The exchange interaction between the ions is:

- generally isotropic
- very frequently antiferromagnetic

In some cases, this results in ferrimagnetic ground states with large spins.





Prussian blue: $Fe_{4}^{\parallel}[Fe_{4}^{\parallel}(CN)_{6}]_{3}$

Prussian blue analogues: Compounds resulting from the substitution of Fe ions in the original Prussian blue structure by other metallic centers.

fcc network with alternating Fe^{II}, Fe^{III} ions bridged by cyanide ligands.

Orthorrombic symmetry. Excess Fe^{II}.



Interstitial Fe^{II}

Substitution of Fe^{III} by H_2O

The introduction of alcali cations R⁺ allows to control the ratio of metal centers and affects the magnetic behavior.



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All

MIII

C

N

✓ H₂O

R⁺

Ligand Field Theory

Isolated metal atom surrounded by electronic charge representing the environment



Long-range interaction between metal centers separated by the ligand. Proposed by Olivier Kahn, based on Heitler-London two-electron model:

Only unpaired electrons, well-localized;

Small SOC: $\Psi_{\text{total}} = \Psi_{\text{spin}} \times \Psi_{\text{orbital}}$ $\zeta = \langle a(1)|b(1) \rangle \dots 1 e^{-} \text{ overlap} \quad (>0)$ $\beta = \langle a(1)|h(1)|b(1) \rangle \dots 1 e^{-} \text{ resonance} \quad (<0)$ $\kappa = \langle a(1)b(2)|e^{2}/r_{12}^{2}|a(2)b(1) \rangle \dots 2 e^{-} \text{ Coulomb autorepulsion} (>0)$

The singlet – triplet energy difference is:

$$J = 2 \kappa + 4 \beta \zeta = J_{FM} (>0) + J_{AFM} (<0)$$

Ortogonality \rightarrow No overlap ($\zeta = 0$)

Non-Ortogonality \rightarrow Overlap ($\zeta > 0$)

Antiferromagnetism



Ferromagnetism





The superexchange interaction J is directly related to T_{c} (Néel's model):

$$kT_{c} = z|J|\sqrt{C_{A}C_{B}}/N_{A}g^{2}\mu_{B}^{2}$$
 C_{A}, C_{B} : Curie constants

When several electrons are present at each center, the interaction results from the sum over the different "pathways":



Superexchange model

Superexchange model predictions for Cr^{III}–CN–A^{II} pairs:

	V" (<i>t</i> _{2g}) ³	$\mathbf{Cr^{I_l}}$ $(t_{2g})^3(e_g)^1$	Mn " $(t_{2g})^{3}(e_{g})^{2}$	Fe ^{II} $(t_{2g})^4(e_g)^2$	Co ^{II} $(t_{2g})^5(e_g)^2$	Ni " $(t_{2g})^6(e_g)^2$	Cu ^{II} $(t_{2g})^6(e_g)^3$
AFM pathways	9	9	9	6	3	0	0
FM pathways	0	3	6	6	6	6	3
Interaction	AFM	AFM	AFM	afm	afm	FM	FM
T _c (K)	315	240	60	16	23	53	66

- The model correctly predicts the extreme cases
- $_{\rm o}$ Suggests a way to enhance $\rm T_{c}$ by increasing the imbalance of interactions

STRATEGY: Combine the high T_c of **Cr–Cr** compounds with the strong magnetic moments and photosensitivity of **Fe**!





Metastability and Magnetism of PBAs

Electronic delocalization across the cyanide bridge



Sensitivity of the magnetic properties to external stimuli





XAS at room temperature: Sample composition

Model with 3 metal centers:

- Cr^{III}_{ox} at right derives from Cr^{II}
- Central, intrinsic Cr^{III} bonded to both N, C → easy isomerization
- Intervalence charge transfer (IVCT): one electron transferred from Fe^{III} to Cr^{III}_{ox}, resulting in Fe^{III}, Cr^{II}.



Magnetism: neighboring Cr ions can be expected to align AFM: $Cr_{ox}^{III} - Cr_{ox}^{III}$ (similar magnetic moments, compensation)





EXAFS at room temperature – Interatomic distances

Bond lengths and unit cell sizes determined by EXAFS for the different moieties:

Shell	d _N [Å]	d _c [Å]	Unit cell [Å]
Fe [∥] −N≡C−Cr ^Ⅲ	$d_{FeII - N} = 2.12 \pm 0.01$	$d_{CrIII-C} = 2.05 \pm 0.01$	10.72 ± 0.03
Fe [∥] −C≡N−Cr ^Ⅲ	$d_{CrIII-N} = 2.13 \pm 0.03$	$d_{_{FeII}-C} = 2.03 \pm 0.04$	10.65 ± 0.03
Fe ^{III} −N≡C−Cr ^{III}	$d_{FeIII-N} = 2.08 \pm 0.04$	$d_{CrIII-C} = 2.04 \pm 0.01$	10.51 ± 0.01
Cr [⊪] −C≡N−Cr [⊪]	$d_{CrII - N} = 2.11 \pm 0.01$	$d_{CrIII-C} = 2.01 \pm 0.01$	10.55 ± 0.01
Cr ^{III} −C≡N−Cr ^{III}	$d_{CrIII-N} = 2.04 \pm 0.02$	$d_{CrIII-C} = 2.01 \pm 0.02$	10.55 ± 0.02

Importance of misfit strain effects of the Fe sub-lattice within the Cr-Cr matrix!



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EXAFS at room temperature – Interatomic distances

Bond lengths and unit cell sizes determined by EXAFS for the different moieties:



Importance of misfit strain effects of the Fe sub-lattice within the Cr-Cr matrix!



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Onset of ferromagnetic order

XMCD at the Cr L-edge vs T: magnetization onset at $T_c \sim 210$ K.



XAS upon irradiation with light – time dependence



I ≤ 200 min: Fe^{II} LS → Fe^{II} HS, Cr^{III} WCF → Cr^{III}: isomerization reversed
I > 200 min: Fe^{II} → Fe^{III}, Cr^{III} → Cr^{II}: charge transfer



Molecular magnetism

[BEDT-TTF] [MnCr(oxalato)]: hybrid material



honeycomb layers of oxalato (insulating) + stacks of organic radicals (conducting)

(BEDT-TTF forms conducting and superconducting materials)

strong magnetic coupling within the inorganic layers;

weak interactions between the layers

Bulk T_{c} < 5.5 K

Coronado et al., Nature **408**, 447 (2000)

(a) lattice; (b) organic layers;(c) inorganic layers

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Single-molecule magnets

Some molecules show slow relaxation: after being magnetized at low temperature, they remain their magnetization for a long time, in absence of external field



Property of the individual molecules, not depending on long-range interactions





Heisenberg spin Hamiltonian

$$H_{ex} = J \mathbf{S_1} \cdot \mathbf{S_2}$$

Strong exchange approximation: all other terms are neglected

The ground state has 2S+1 microstates (values of M_s in absence of transverse anisotropy)

Zero-field splitting: caused by spin-orbit coupling or dipolar interaction if $S > \frac{1}{2}$:

$$H_{ZFS} = S \cdot D \cdot S = D[S_z^2 - S(S+1)/3] + E(S_x^2 - S_y^2)$$

The D term changes the energies of the M_s states The E term mixes the M_s states and changes their character: they are no more energy eigenstates





Single-molecule magnets

Energy of the eigenstates against M_s or against the angle between the magnetic moment and the quantization axis



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The system oscillates between these two states: the magnetization can tunnel incoherently

Possible mechanisms for magnetization inversion:

- thermal relaxation
- thermally (phonon-) assisted tunneling
- ground-state tunneling







$[Mn_{12}O_{16}(CH_{3}COO)_{16}(H_{2}O)4].4H_{2}O.2CH_{3}COOH = Mn12Ac$

Ring of 8 Mn (III) ions + Tetrahedron of Mn (IV) connected by oxide bridges like in a manganite

Low T: ground S = 10 state ■ 8× (S = 2) Mn (III) ↑ ■ 4× (S = 3/2) Mn (IV) ↓

Acetate ligands can be replaced to tune properties, link to surfaces...

Thomas et al., Nature **383**, 145 (1996) Friedman et al., Phys. Rev. Lett. **76**, 3830 (1996) Gatteschi et al., Angw. Chem. Int. Ed. Engl. **42**, 268 (2003)







$[Mn_4O_3Cl_4(CH_3CH_2COO)_3(py)_3]_2 : (Mn_4)_2$

1× Mn⁴⁺ (S = 3/2) S = 3/2 ↓ 3× Mn³⁺ (S = 2) S = 6 ↑

Total spin: S = 9/2

Mn ions bridged by O^{2^-} , CI^- , proprionate

Pyridine, Cl⁻ bound on the outside

Weak superexchange interaction between the two molecules in the dimer



Wernsdorfer et al., Nature **416**, 406 (2000)

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Single-molecule magnets

Cluster with 76 Mo⁶⁺ and 30 Fe³⁺ ions:



Yellow spheres: Fe(III) ions



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Mo atoms are non-magnetic

AFM interaction between Fe ions, highly frustrated due to the cluster symmetry

Müller et al., ChemPhysChem 2, 517 (2001)

Summary

Magnetism is a collective phenomenon

Many aspects affect multiple magnetic properties:

- Dimensionality
- Shape
- Coordination
- Interfaces

Possibilities to:

- Design and fabricate novel materials with specific properties
- Manipulate the magnetic response by external stimuli



