Electronic and Magnetic Structure of Transition-Metal Dicyanamide Molecule-based Magnets

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Molecular magnets: $Me[N(CN)_2]_2$ Me = Mn, Fe, Co, Ni, Cu

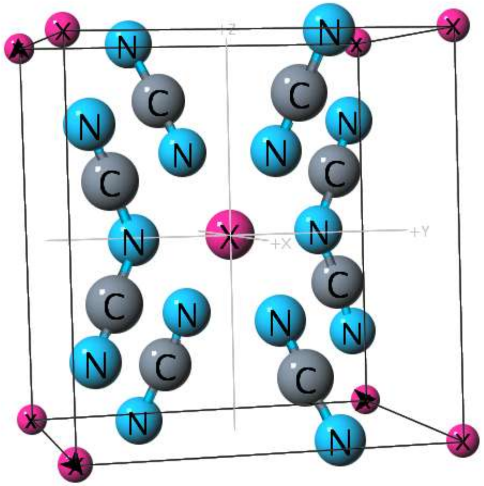
Potential applications, like data storage and processing

$Ni[N(CN)_2]_2$ and $Fe[N(CN)_2]_2$ have largest coercive fields among metal-organic magnets - 7975 Oe and 17800 Oe

Fundamental questions about the origin of magnetic ordering

Similar structures, different magnetic ordering

Compounds with 6 or fewer *3d* e^- order as canted AFM, those with 7 or more *3d* e^- order as FM



Experiment:

Me=Mn & Fe canted AFM
Me=Co & Ni FM
Me=Cu FM below 1.8 K

Structure

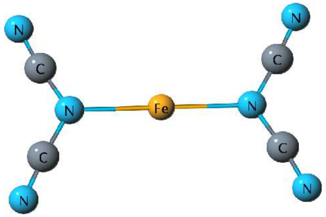
Molecular unit is a TM atom connected with two $N(CN)_2$ groups

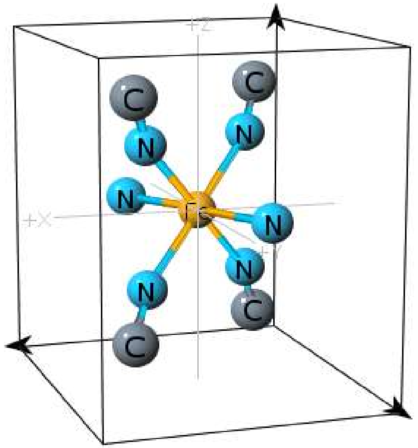
TM atom is octahedrally coordinated by N atoms in solid

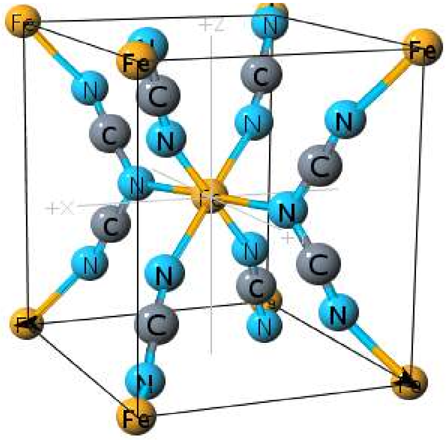
Tetragonal local symmetry around a TM atom

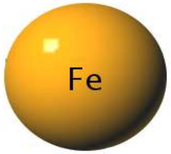
Primitive cell contains two formula units, forming an orthorhombic cell

TM ions are sources of magnetic moment, organic species provide superexchange pathways between the magnetic centers









Fe

C

N

Method of calculation

- First Principles Density Functional calculations for FM, AFM, and NM phases, using experimental crystal structures
- Spins were restricted to be collinear
- GGA approximation for electron-electron interactions
- Planewave basis sets and ultrasoft pseudopotentials
- Electronic wavefunctions are expanded in plane waves with kinetic energy of 435 eV
- VASP[*]

[*] G. Kresse and J. Furthmuller, Comput. Mater. Sci. **6**, 15 (1996); Phys. Rev. B **54**, 11169 (1996).

Magnetic ordering

Total energies

Δ E (eV) / Compound	NM-AF	AF-FM	Calculations	Experiment
$Mn[N(CN)_2]_2$	2.490	-0.018	AFM	Canted AFM
$Fe[N(CN)_2]_2$	0.862	0.025	FM	Canted AFM
$Co[N(CN)_2]_2$	0.735	0.023	FM	FM
$Ni[N(CN)_2]_2$	0.939	0.015	FM	FM
$Cu[N(CN)_2]_2$	0.287	0.000	inconclusive	FM below 1.8K

- Calculations yield metallic state for AF $Fe[N(CN)_2]_2$

Experimental data: C. R. Kmety et al., PRB **60**, 60 (1999); PRB **62**, 5576 (2000); Magn. Magn. Mater. **248**, 52 (2002).

Magnetic properties

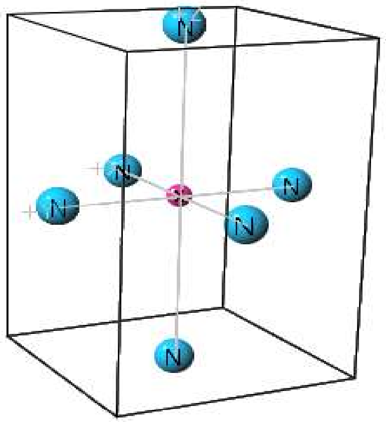
Magnetic moments

Measured magnetic moments include both spin and orbital contribution --> the mm are severely underestimated by DFT for Me=Fe and Ni

For octahedrally (with tetragonal distortion) coordinated TM ion, ideally L is quenched for Mn, Ni, and Cu, and unquenched for Fe and Co

No mechanism for unquenching the orbital moment in calculations

Example $Fe[N(CN)_2]_2$: spins are not collinear ~25 degrees, spin-orbit coupling is ignored



$\mu[\mu_B]$ Atom	Calc.	Expt.
Mn	4.50	4.61
Fe	3.59	4.53
Co	2.54	2.67
Ni	1.59	2.21
Cu	0.65	1.05

Superexchange pathways

Influence of the SXC angle

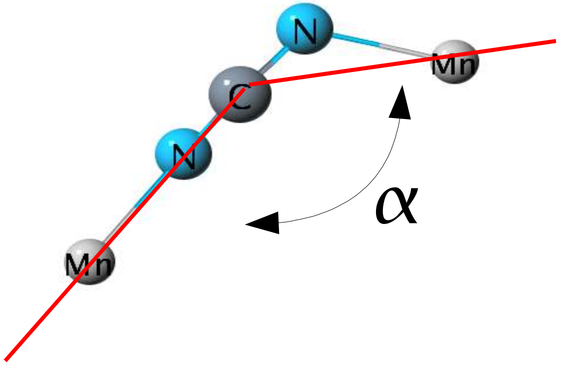
Magnetic ordering is determined by the interplay between the occupation of the d shell and SXC pathway between magnetic centers

Me-[N-C-N]-Me angle increases monotonically going from $Mn[N(CN)_2]_2$ to $Ni[N(CN)_2]_2$ by ~2.6 degrees

Is the angle passing through some critical value, so the change in pathway is the cause of different magnetic ordering?

Replacing the Mn- lattice with Ni- lattice does NOT change energy order for different phases

Occupation of the 3d orbitals is the dominant factor

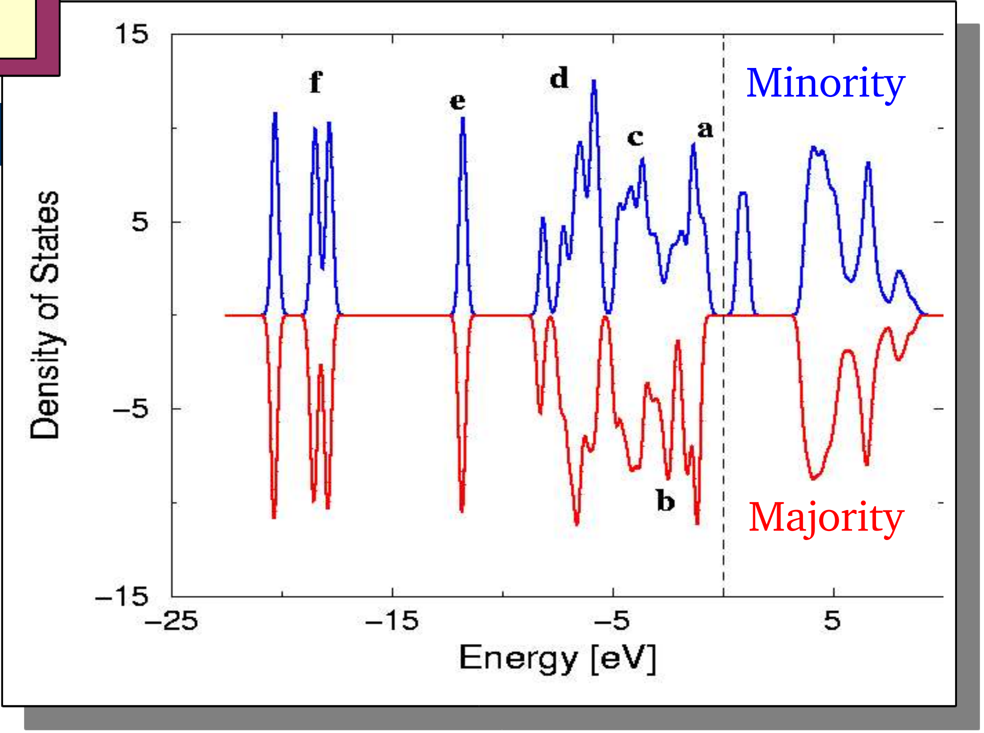


$Mn[N(CN)_2]_2$

Electronic structure

DOS across the spectrum

$Ni[N(CN)_2]_2$



(a),(b) - Ni 3*d* states and some hyb. with C &N 2*p* states

(c),(d) - C & N 2*p* states and some hyb. with Ni 3*d* states

(e) - C 2*p* and 2*s* states

(f) - C & N 2*s* and 2*p* states

general features consistent with experimental XES and XPS data

direct comparison is difficult

DOS similar for the series, except top of the valence band hybridization between N 2p and Me 3d states increases with TM atomic number.

Electronic structure

d states deepening

Calculations: ~1.5 eV shift of main maxima of occupied d bands in Cu [N(CN)$_2$]$_2$ compared to Ni[N(CN)$_2$]

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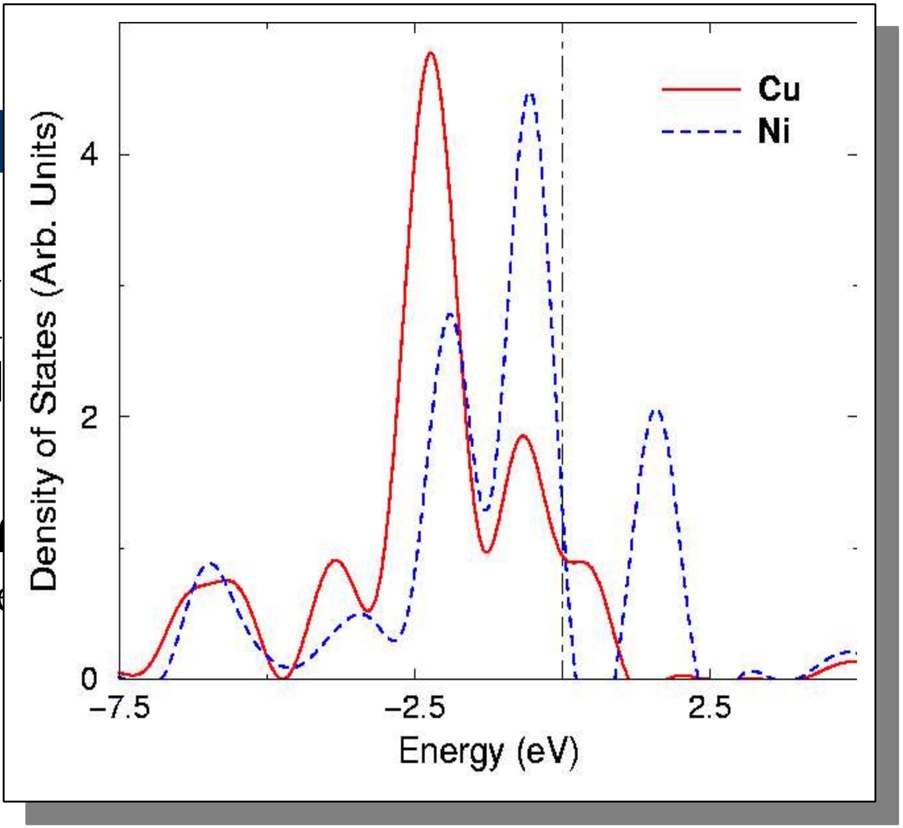
Deepening of 3*d* states is a result of localization of the d electrons at the end of the 3*d* series

Decreasing exchange splitting is a contributing factor

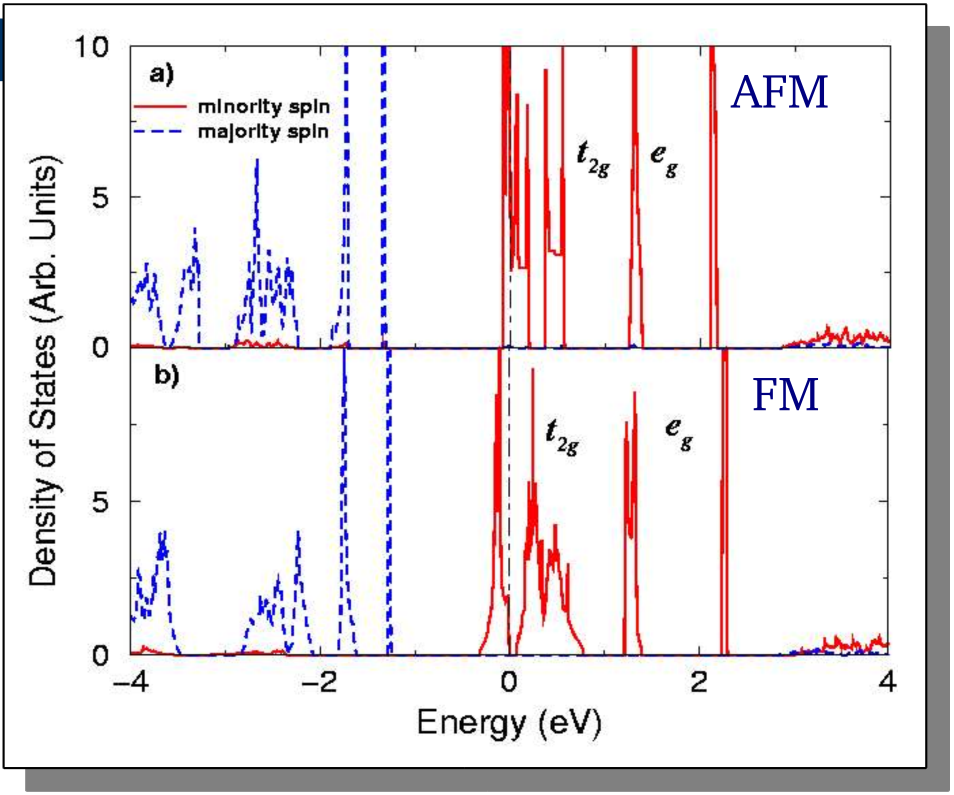


Experiment:
In XPS spectra maximum of the 3d band shifts by ~1.3 eV towards higher binding energy in Cu[N(CN)$_2$]$_2$ compared to in Ni[N(CN)$_2$]$_2$

Electronic structure

Top of the valence band and bandgaps

$Fe[N(CN)_2]_2$ *d*-states



Crystal field splits 3*d* band into t_{2g} and e_g subbands by ~1.5 eV

Tetragonal distortion splits t_{2g} bands into $d_{xz,yz}$ and d_{xy} and e_g into $d_{x^2-y^2}$ and $d_{3z^2-r^2}$

AF – *d*-*d* interactions are suppressed t_{2g} bands are narrow

In $Fe[N(CN)_2]_2$ the ordering of the t_{2g} band reverses in FM phase, thus (one minority e^-) it is a metal in AFM and insulator in FM phases

Electronic structure

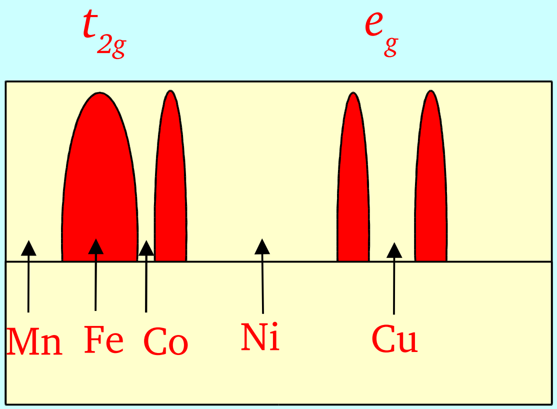
Top of the valence band and bandgaps

FM $Co[N(CN)_2]_2$ - two minority e^- - $d_{xz,yz}$ occupied --> insulator

FM $Ni[N(CN)_2]_2$ - t_{2g} completely occupied --> insulator

FM $Cu[N(CN)_2]_2$ – Jahn-Teller effect enhances tetragonal distortion, increases splitting between e_g

Better agreement for materials with completely empty or occupied t_{2g}



Minority spin *d* band

E_g (eV)	Mn	Fe	Co	Ni	Cu
Calc	2.12	0.00	0.24	1.36	0.52
Expt	2.07	1.46	2.40	1.97	1.91

Conclusions

First principles calculations of the properties of $Me[N(CN)_2]_2$ (Me=Mn,Fe,Co,Ni,Cu) molecular magnets

Band structures are similar, differences: localization of 3*d* bands wrt E_F, and degree of hybridization between Me 3*d* and N 2*p* states

Small differences in structure do not account for magnetic states, occupation of 3*d* band is more important

For most materials GGA underestimates bandgaps and magnetic moments, plus narrow *d*-bands

For these materials, better description requires more accurate (than GGA) treatment of $e^- - e^-$ interactions