

# More Surprises in f-electron Magnetism

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EVROPSKÁ UNIE  
Evropské strukturální a investiční fondy  
Operační program Výzkum, vývoj a vzdělávání



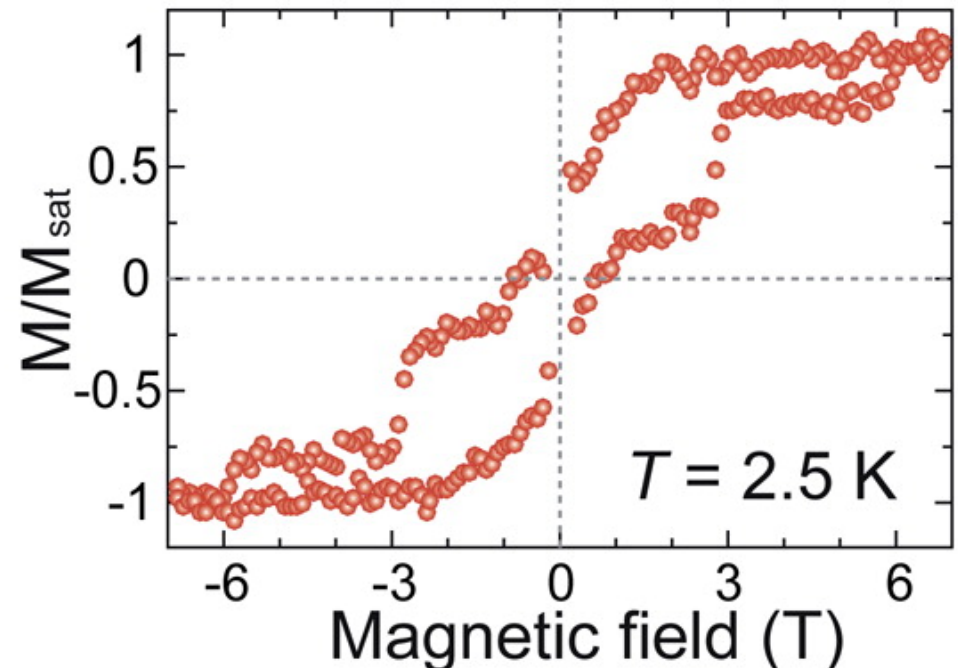
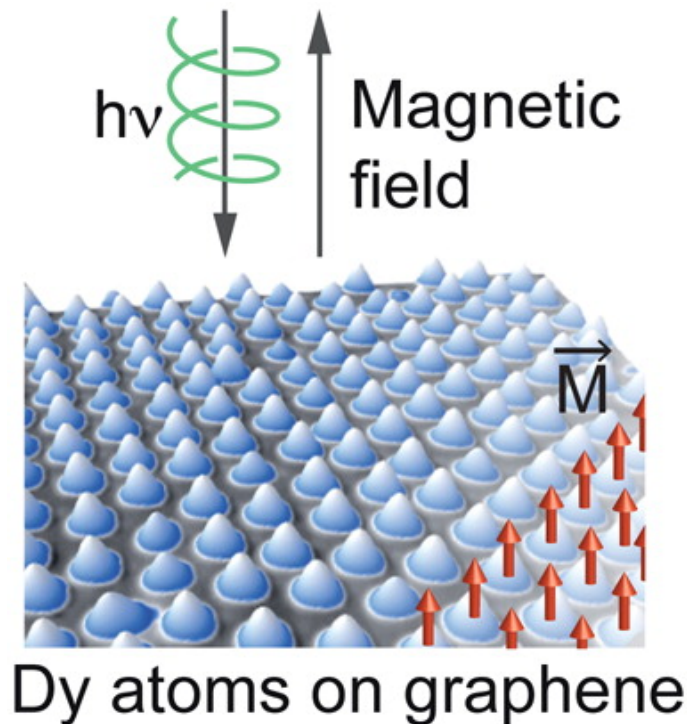
MINISTERSTVO ŠKOLSTVÍ,  
MLÁDEŽE A TĚLOVÝCHOVY

**Projekt Fyzika pevných látek pro 21. století  
CZ.02.1.01/0.0/0.0/16\_019/0000760 je  
spolufinancován Evropskou unií.**

➤ In 1959, Richard Feynman proposed a \$1K prize for the storage of information on a page of a book at the  $1/25000$  scale in such a way that it could be read by an electron microscope. The ultimate fulfilment of this request, has been realized by storing his own words at the 2016 APS conference [F. Kalff et al., Nature Nanotechnology 11, 926 (2016)].

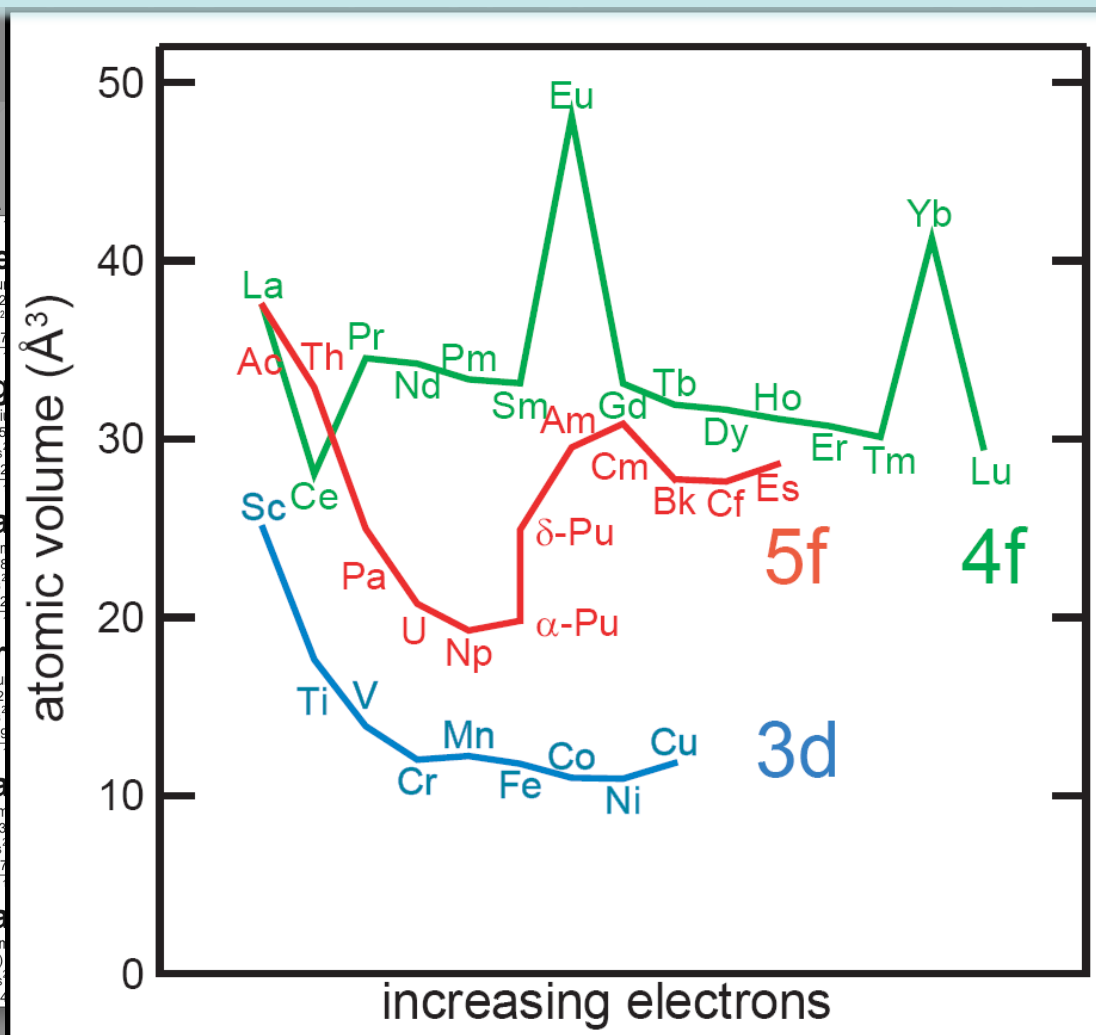
➤ **Quest for ultra-high-density storage media**  
the magnetic storage density above  $100 \text{ Tbit/in}^2$

**R. Baltic et al., Superlattice of Single Atom Magnetis on Graphene, Nano Letters 16 (2016)**



# ◆ Localized nature of 4f-electrons

Group 1 IA	2 IIA
1 <sup>1</sup> S <sub>1/2</sub> <b>H</b> Hydrogen 1.008 1s 13.5984	
2 <sup>2</sup> S <sub>1/2</sub> <b>Li</b> Lithium 6.94 1s <sup>2</sup> 2s 5.3917	3 <sup>2</sup> S <sub>1/2</sub> <b>Be</b> Beryllium 9.0122 1s <sup>2</sup> 2s <sup>2</sup> 9.3227
3 <sup>3</sup> S <sub>1/2</sub> <b>Na</b> Sodium 22.990 [Ne]3s 5.1391	4 <sup>3</sup> S <sub>1/2</sub> <b>Mg</b> Magnesium 24.305 [Ne]3s <sup>2</sup> 7.6462
4 <sup>4</sup> S <sub>1/2</sub> <b>K</b> Potassium 39.098 [Ar]4s 4.3407	5 <sup>4</sup> S <sub>1/2</sub> <b>Ca</b> Calcium 40.078 [Ar]4s 6.1132
5 <sup>5</sup> S <sub>1/2</sub> <b>Rb</b> Rubidium 85.468 [Kr]5s 4.1771	6 <sup>5</sup> S <sub>1/2</sub> <b>Sr</b> Strontium 87.62 [Kr]5s <sup>2</sup> 5.6949
6 <sup>6</sup> S <sub>1/2</sub> <b>Cs</b> Cesium 132.91 [Xe]6s 3.8939	7 <sup>6</sup> S <sub>1/2</sub> <b>Ba</b> Barium 137.33 [Xe]6s 5.2117
7 <sup>7</sup> S <sub>1/2</sub> <b>Fr</b> Francium (223) [Rn]7s 4.0727	8 <sup>7</sup> S <sub>1/2</sub> <b>Ra</b> Radium (226) [Rn]7s 5.2784



National Institute of Standards and Technology  
U.S. Department of Commerce

18  
VIII  
<sup>1</sup>S<sub>0</sub>  
**He**  
Helium  
4.0026  
1s<sup>2</sup>  
24.5874

15  
VA  
<sup>4</sup>S<sub>3/2</sub>  
**N**  
Nitrogen  
14.007  
1s<sup>2</sup>2s<sup>2</sup>2p<sup>3</sup>  
14.5341

16  
VIA  
<sup>3</sup>P<sub>2</sub>  
**O**  
Oxygen  
15.999  
1s<sup>2</sup>2s<sup>2</sup>2p<sup>4</sup>  
13.6181

17  
VIIA  
<sup>2</sup>P<sub>3/2</sub>  
**F**  
Fluorine  
18.998  
1s<sup>2</sup>2s<sup>2</sup>2p<sup>5</sup>  
17.4228

18  
VIII  
<sup>1</sup>S<sub>0</sub>  
**Ne**  
Neon  
20.180  
1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup>  
21.5645

15  
<sup>4</sup>S<sub>3/2</sub>  
**P**  
Phosphorus  
30.974  
[Ne]3s<sup>2</sup>3p<sup>3</sup>  
10.4867

16  
<sup>3</sup>P<sub>2</sub>  
**S**  
Sulfur  
32.06  
[Ne]3s<sup>2</sup>3p<sup>4</sup>  
10.3600

17  
<sup>2</sup>P<sub>3/2</sub>  
**Cl**  
Chlorine  
35.45  
[Ne]3s<sup>2</sup>3p<sup>5</sup>  
12.9676

18  
<sup>1</sup>S<sub>0</sub>  
**Ar**  
Argon  
39.948  
[Ne]3s<sup>2</sup>3p<sup>6</sup>  
15.7596

33  
<sup>4</sup>S<sub>3/2</sub>  
**As**  
Arsenic  
74.922  
[Ar]3d<sup>10</sup>4s<sup>2</sup>4p<sup>3</sup>  
9.7886

34  
<sup>3</sup>P<sub>2</sub>  
**Se**  
Selenium  
78.971  
[Ar]3d<sup>10</sup>4s<sup>2</sup>4p<sup>4</sup>  
9.7524

35  
<sup>2</sup>P<sub>3/2</sub>  
**Br**  
Bromine  
79.904  
[Ar]3d<sup>10</sup>4s<sup>2</sup>4p<sup>5</sup>  
11.8138

36  
<sup>1</sup>S<sub>0</sub>  
**Kr**  
Krypton  
83.798  
[Ar]3d<sup>10</sup>4s<sup>2</sup>4p<sup>6</sup>  
13.9996

51  
<sup>4</sup>S<sub>3/2</sub>  
**Sb**  
Antimony  
121.76  
[Kr]4d<sup>10</sup>5s<sup>2</sup>5p<sup>3</sup>  
8.6084

52  
<sup>3</sup>P<sub>2</sub>  
**Te**  
Tellurium  
127.60  
[Kr]4d<sup>10</sup>5s<sup>2</sup>5p<sup>4</sup>  
9.0097

53  
<sup>2</sup>P<sub>3/2</sub>  
**I**  
Iodine  
126.90  
[Kr]4d<sup>10</sup>5s<sup>2</sup>5p<sup>5</sup>  
10.4513

54  
<sup>1</sup>S<sub>0</sub>  
**Xe**  
Xenon  
131.29  
[Kr]4d<sup>10</sup>5s<sup>2</sup>5p<sup>6</sup>  
12.1298

83  
<sup>4</sup>S<sub>3/2</sub>  
**Bi**  
Bismuth  
208.98  
[Hg]6p<sup>3</sup>  
7.2855

84  
<sup>3</sup>P<sub>2</sub>  
**Po**  
Polonium  
(209)  
[Hg]6p<sup>4</sup>  
8.414

85  
<sup>2</sup>P<sub>3/2</sub>  
**At**  
Astatine  
(210)  
[Hg]6p<sup>5</sup>  
9.3175

86  
<sup>1</sup>S<sub>0</sub>  
**Rn**  
Radon  
(222)  
[Hg]6p<sup>6</sup>  
10.7485

115  
**Mc**  
Moscovium  
(289)

116  
**Lv**  
Livermorium  
(293)

117  
**Ts**  
Tennessine  
(294)

118  
**Og**  
Oganesson  
(294)

Atomic Number	Ground State	57 <sup>4</sup> D <sub>3/2</sub> <b>La</b> Lanthanum 138.91 [Xe]5d6s <sup>2</sup> 5.5789	58 <sup>1</sup> G <sub>4</sub> <b>Ce</b> Cerium 140.116 [Xe]4f5d6s <sup>2</sup> 5.5889	59 <sup>1</sup> G <sub>4</sub> <b>Pr</b> Praseodymium 140.91 [Xe]4f6s <sup>2</sup> 5.4789	60 <sup>1</sup> I <sub>4</sub> <b>Nd</b> Neodymium 144.24 [Xe]4f6s <sup>2</sup> 5.5889	61 <sup>1</sup> H <sub>5/2</sub> <b>Pm</b> Promethium (145) [Xe]4f6s <sup>2</sup> 5.5777	62 <sup>1</sup> F <sub>0</sub> <b>Sm</b> Samarium 150.36 [Xe]4f6s <sup>2</sup> 5.6437	63 <sup>6</sup> S <sub>7/2</sub> <b>Eu</b> Europium 151.96 [Xe]4f7s <sup>2</sup> 5.6764	64 <sup>1</sup> D <sub>2</sub> <b>Gd</b> Gadolinium 157.25 [Xe]4f7d6s <sup>2</sup> 6.4439	65 <sup>1</sup> H <sub>15/2</sub> <b>Tb</b> Terbium 158.93 [Xe]4f7s <sup>2</sup> 5.6889	66 <sup>1</sup> I <sub>8</sub> <b>Dy</b> Dysprosium 162.50 [Xe]4f10s <sup>2</sup> 5.6889	67 <sup>1</sup> T <sub>15/2</sub> <b>Ho</b> Holmium 164.93 [Xe]4f11s <sup>2</sup> 5.6889	68 <sup>3</sup> H <sub>6</sub> <b>Er</b> Erbium 167.26 [Xe]4f12s <sup>2</sup> 5.6777	69 <sup>2</sup> F <sub>7/2</sub> <b>Tm</b> Thulium 168.93 [Xe]4f13s <sup>2</sup> 5.6777	70 <sup>1</sup> S <sub>0</sub> <b>Yb</b> Ytterbium 173.05 [Xe]4f14s <sup>2</sup> 5.6529	71 <sup>2</sup> D <sub>3/2</sub> <b>Lu</b> Lutetium 174.97 [Xe]4f14d6s <sup>2</sup> 5.4589
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## ◆ DFT works poorly for the 4f- and 5f-materials f-electron challenge

<sup>1</sup>Based upon <sup>1</sup>C. ( ) indicates the mass number of the longest-lived isotope.

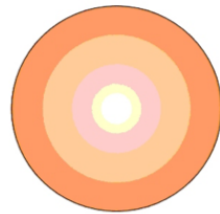
For the most precise values and uncertainties visit [ciaaw.org](http://ciaaw.org) and [pmi.nist.gov/data](http://pmi.nist.gov/data).

◆ **Beyond DFT: combining DFT and Hubbard-I/ED approximation for the Anderson Impurity model**

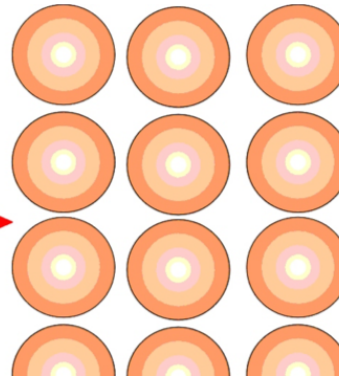
- O. Eriksson group, Elemental rare earth: PRB94 (2016);
  - A. Shick et al., PRB80(2009).

◆ **Interaction between**

**4f-atomic  
multiplets**



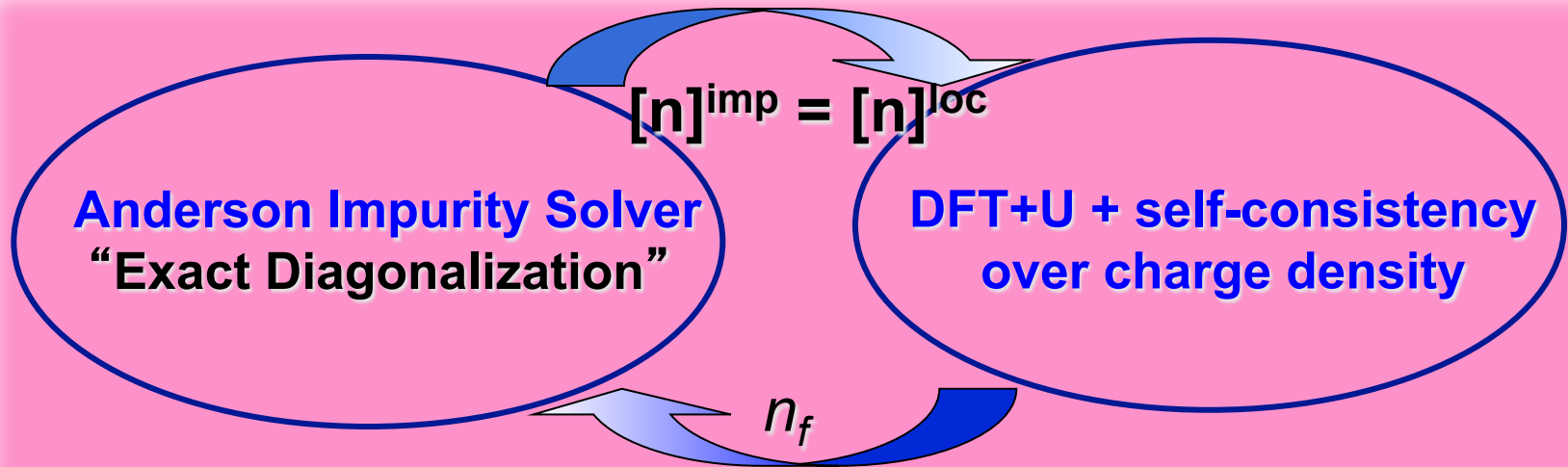
**surface bands**



◆ **Electronic/magnetic character of  
Dy@Ir(111) & Dy@GR/Ir(111)**

- A. B. Shick et. al., Scientific Reports 7, 2751 (2017);
- A. B. Shick and A. I. Lichtenstein, JMMM 454, 61 (2018).
- A. B. Shick and A.Y. Denisov, JMMM 475, 211 (2019).

# DFT + U + Hubbard-I / “Exact Diagonalization”



$$[n] = -\pi^{-1} \text{Im} \int^{E_F} dz \text{Tr} [G(z)]$$

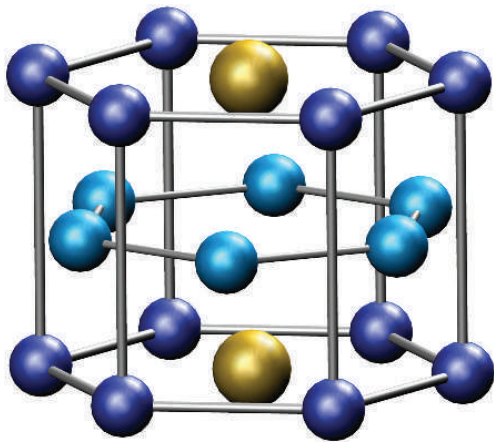
## AIM “Exact Diagonalization”:

- ❖ Spin-orbit coupling + Crystal Field + Exchange splitting
- ❖ Full Coulomb vertex

## DFT + U:

- ❖ Self-consistency over charge density

Full-Potential Linearized Augmented Plane  
Wave (FLAPW) basis


 $\text{Co}_1$ 
 $\text{Co}_2$ 

	Sm	Co <sub>1</sub> (2c)	Co <sub>2</sub> (3g)	
$\mu_S$	-4.22	1.46	1.48	
$\mu_L$	+4.22	0.10	0.09	
$\mu_T$	0	1.56	1.57	7.41

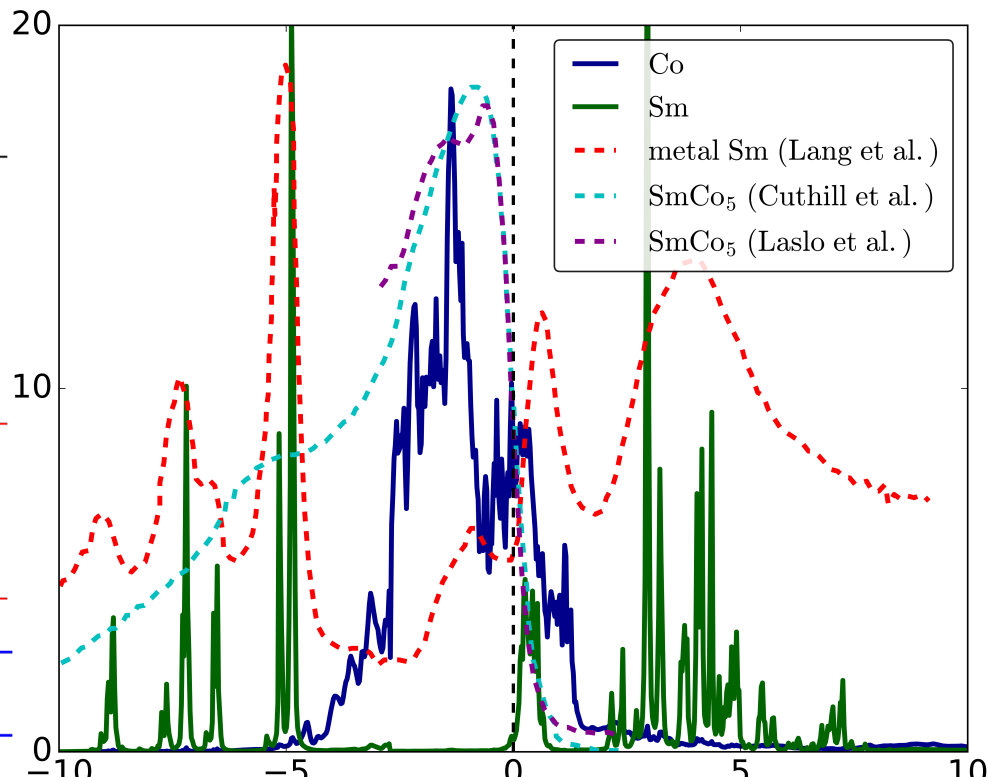
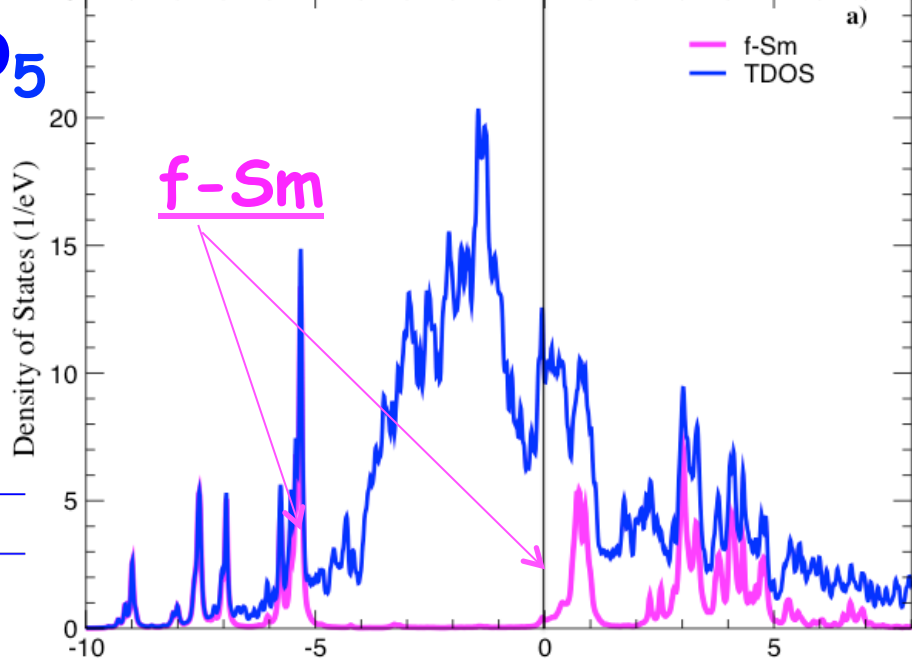
O. Granas *et al.*, DFT+DMFT (2012)

$\mu_S$	-3.47	1.54	1.52	
$\mu_L$	+3.26	0.22	0.18	
$\mu_T$	-0.21	1.76	1.70	8.02

A. Landa *et al.*, DFT+U (2018)

$\mu_S$	-5.34	1.59	1.61	
$\mu_L$	+3.10	0.07	0.12	
$\mu_T$	-2.24	1.66	1.73	5.56

Exp.  $\mu_T$  7.3-8.7



$$\hat{H}_{CEF} = \sum_{kq} A_k^q \langle r^k \rangle \Theta_k(J) \hat{O}_k^q + (g-1)J_z \Delta_{EX}$$

↑ Stevens Operators

Stevens operators.  $X \equiv J(J+1)$  and  $J_{\pm} \equiv J_x \pm iJ_y$ .

$$O_2^0 = 3J_z^2 - X$$

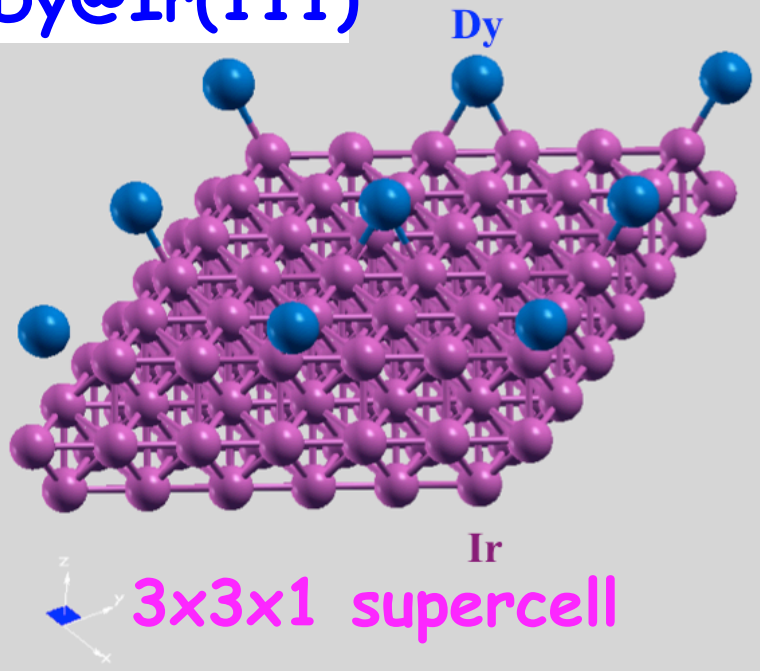
$$O_4^0 = 35J_z^4 - (30X - 25)J_z^2 + 3X^2 - 6X$$

CF (Kelvin)	This Work	Delange		Tils	Zhao Experiment	Givord	Richter Novak	
		↑	↓				CEF-Theory	
$A_2^0 \langle r^2 \rangle$	-190	-313	-262	-326	-330	-200	-755	-160
$A_4^0 \langle r^4 \rangle$	-135	-40	-55	-	-45	0	-37	-33
$A_6^0 \langle r^6 \rangle$	-152	35	25	-	0	50	11	40
$A_6^6 \langle r^6 \rangle$	-763	-731	-593	-	0	0	290	168

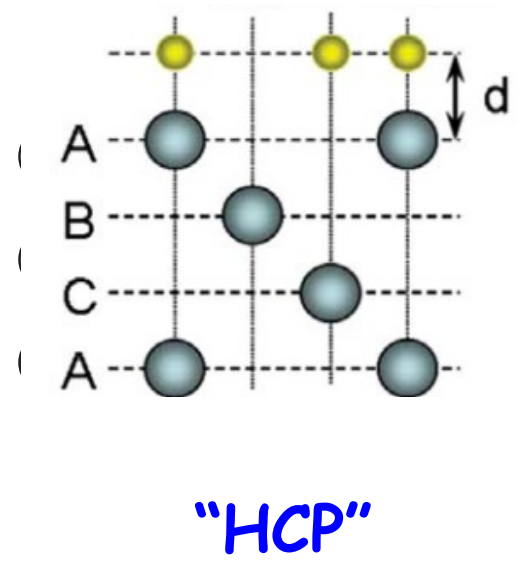
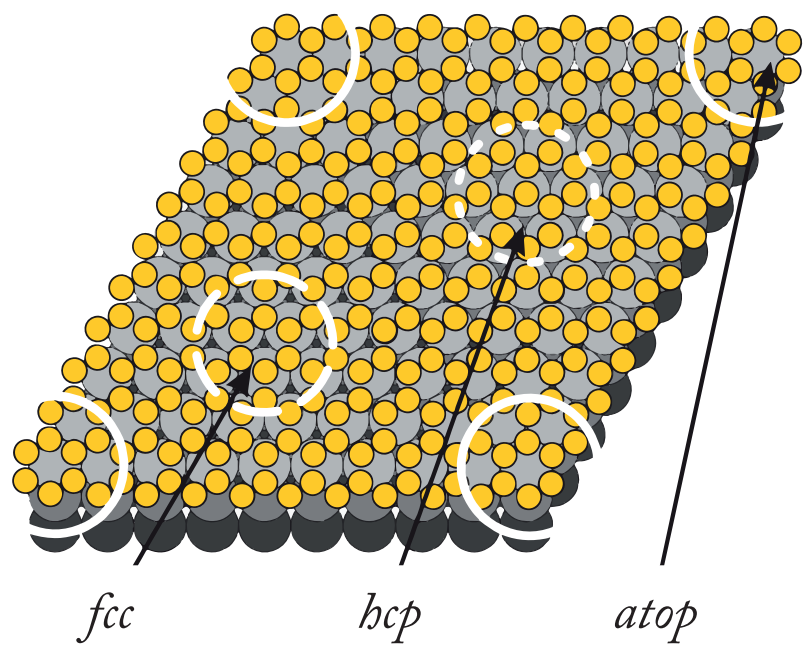
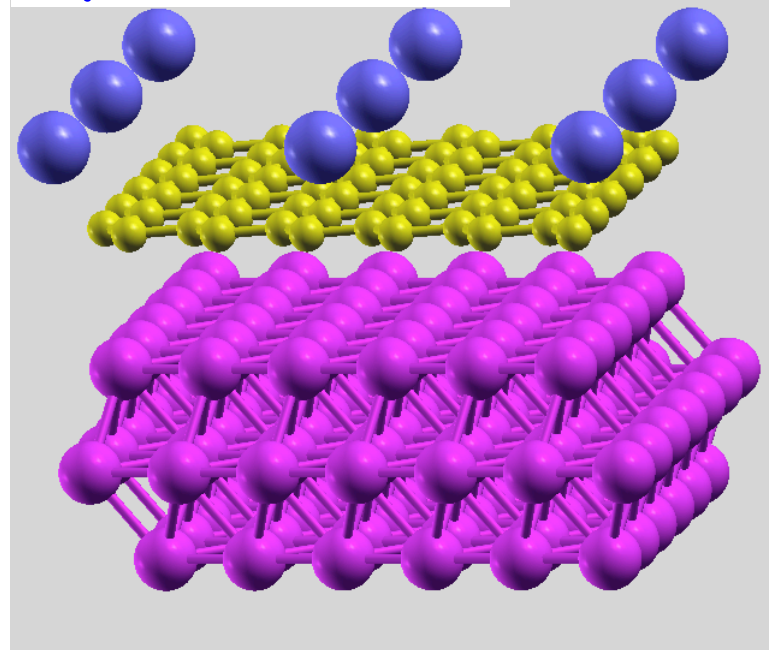
$$E_{MA}(\theta, \phi) = K_1 \sin^2 \theta + K_2 \sin^4 \theta + K_3 \sin^6 \theta + K_4 \sin^6 \theta \cos(6\phi)$$

MAE, meV	$K_1$	$K_2$	$K_3$	$K_4$	MAE
This work	18.6	-7.5	0	0	11.1
DFT+SRM	Soderlind <i>et al.</i> , 2017				10.5
DFT+U	Landa <i>et al.</i> , 2018				-9.9
Experiment					9.2, 13.1

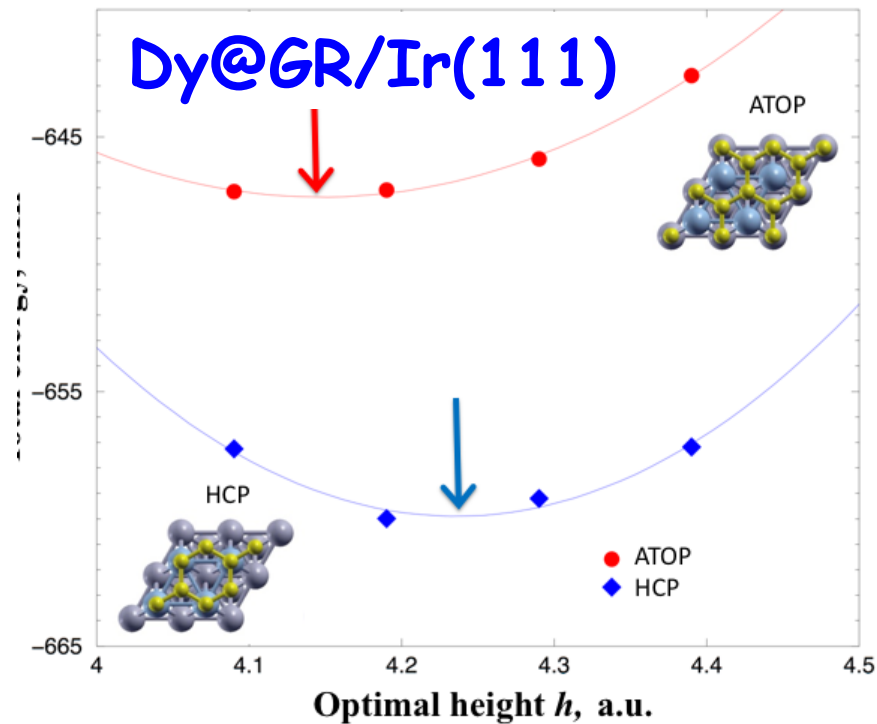
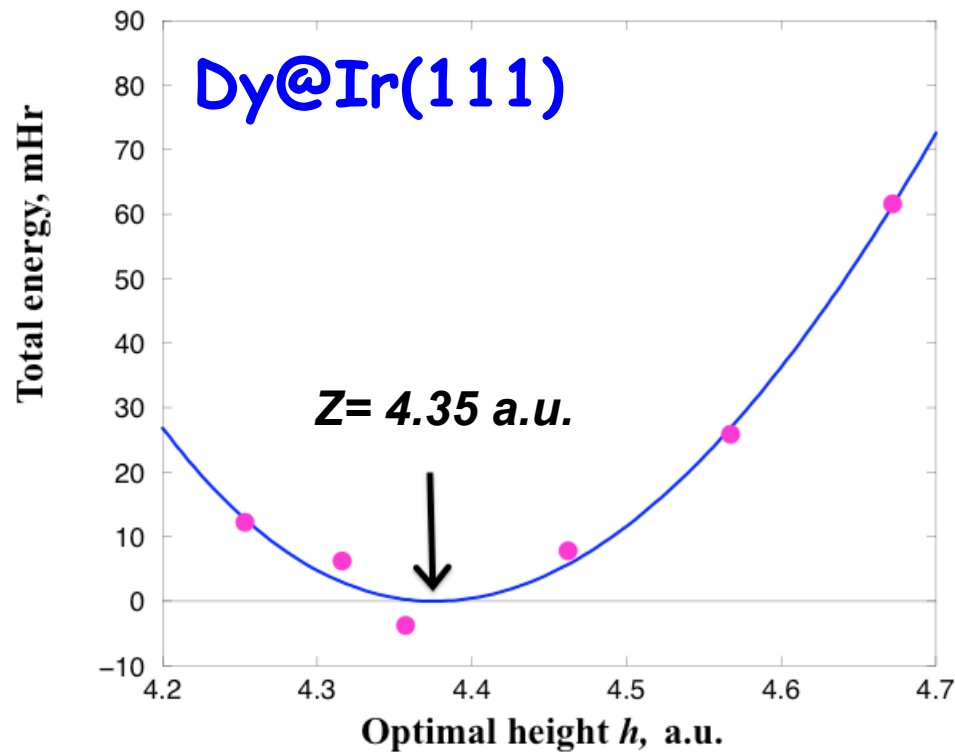
# Dy@Ir(111)



# Dy@GR/Ir(111)





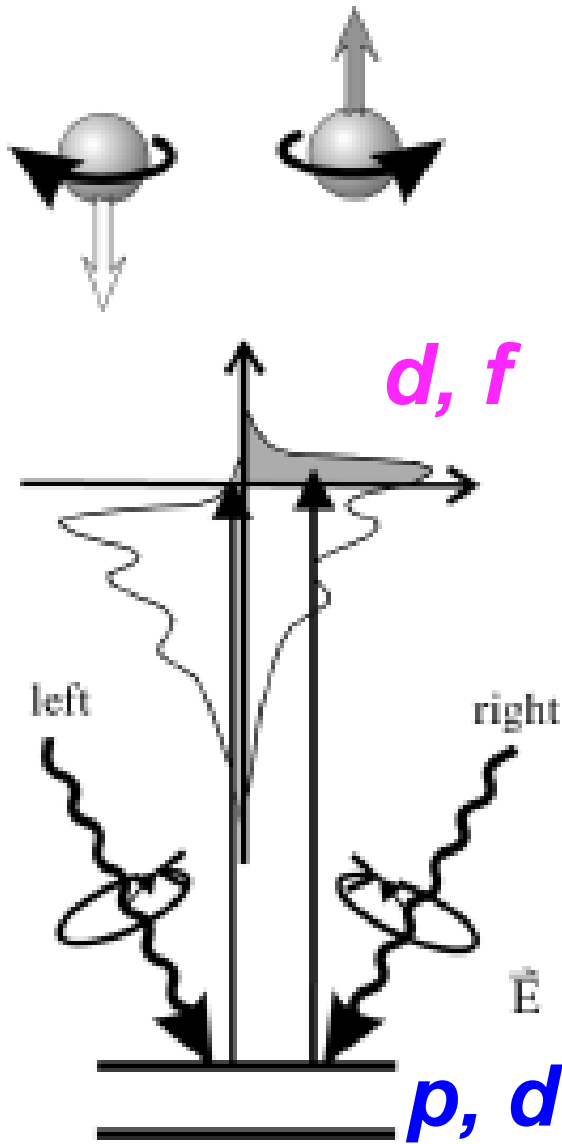


$Z$	$a.u.$
<b>Dy@Ir</b>	4.35
<b>Dy@GR/Ir-HCP</b>	4.235
<b>Dy@GR/Ir-ATOP</b>	4.15

$U=7.0$  eV  $J=0.82$  eV

# XMCD

Probe spin and orbital moments + multiplet structure



Dipole selection rule

$$\Delta j = 0, \pm 1$$

## Sum rules

$$\langle L_z \rangle = \frac{n_h}{I_{M_5} + I_{M_4}} (\Delta I_{M_5} + \Delta I_{M_4})$$

$$\langle S_z \rangle + 3\langle T_z \rangle =$$

$$\frac{n_h}{2(I_{M_5} + I_{M_4})} \left( \Delta I_{M_5} - \frac{3}{2} \Delta I_{M_4} \right)$$

$$\vec{T} = \sum_i [\vec{s}_i - 3(\vec{r}_i \cdot \vec{s}_i)/r_i^2]$$

- magnetic dipole moment

## Comparison with XMCD

	$\langle M_S \rangle$	$\langle M_L \rangle$	$\langle M_S \rangle + \langle M_D \rangle$	$R_{LS}$
Dy@Ir(111)	4.43	4.92	5.78	0.85
XMCD Sum Rules Exp.	-	$2.8 \pm 0.2$	$3.4 \pm 0.2$	0.82
Dy@GR/Ir(111)-HCP	3.78	5.81	4.53	1.28
Dy@GR/Ir(111)-ATOP	3.63	5.72	4.52	1.27
XMCD Sum Rules Exp.	-	$3.9 \pm 0.2$	$3.0 \pm 0.2$	1.30
Multiplet Calculations	3.36	5.32		

✓ **Very good agreement for  $R_{LS}$  ratio  $M_L / [M_S + M_D]$**

**Sum Rules:**

$$\langle L_z \rangle = \frac{3n_h}{I} (\Delta I_{M_5} + \Delta I_{M_4})$$

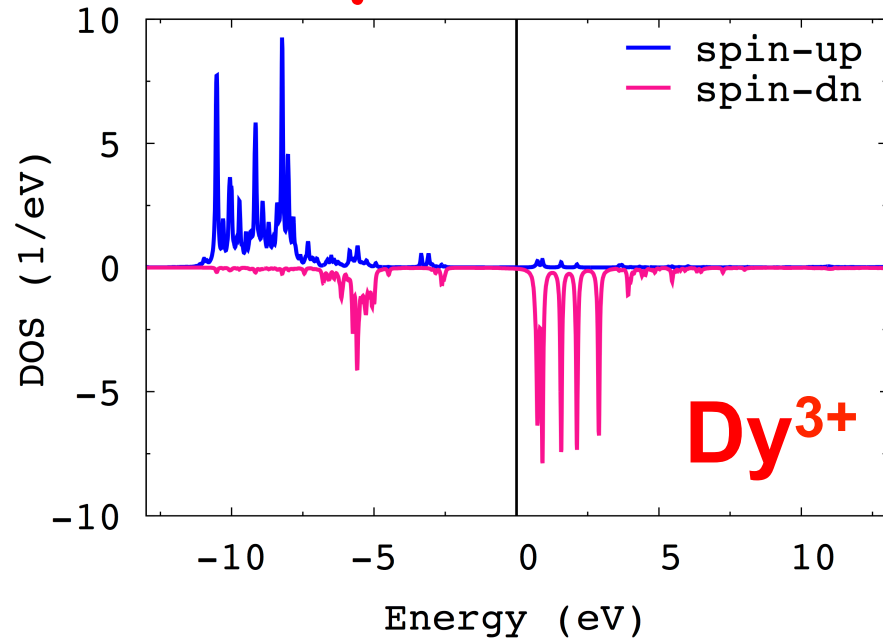
$$[\langle S_z \rangle + 3\langle T_z \rangle] = \frac{3n_h}{I} (2\Delta I_{M_5} - 3\Delta I_{M_4})$$

$$I = \int d\omega (\mu_0(\omega) + \mu_+(\omega) + \mu_-(\omega))$$

➤ **Assumption of isotropic absorption:**

$$\mu_0(\omega) = \frac{1}{2} (\mu_+(\omega) + \mu_-(\omega))$$

# Dy@Ir(111)



$$H_{\text{imp}} \Psi(N) = E_N \Psi(N)$$

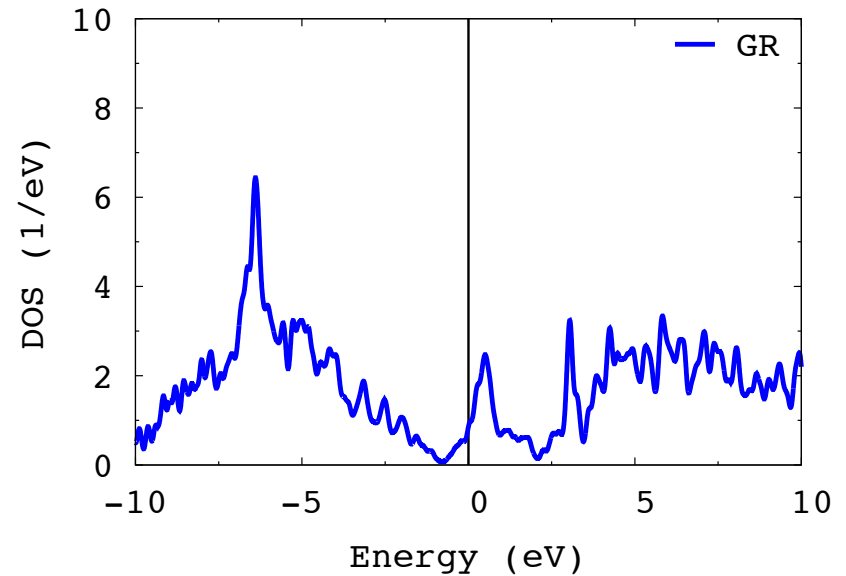
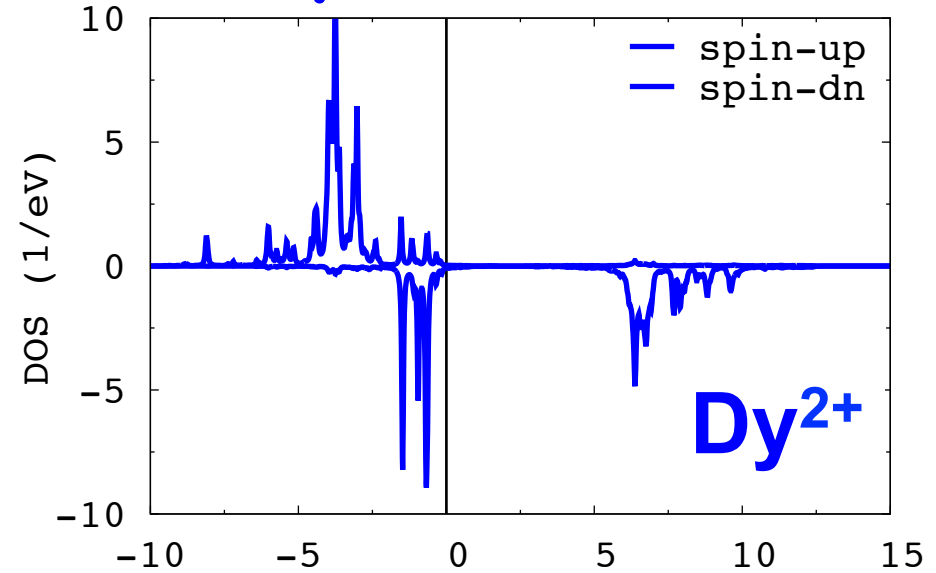
$$|GS\rangle = \Psi(N=9, f^9),$$

$$|J=7.5, J_z=7.5\rangle$$

$$|GS\rangle = \Psi(N=10, f^{10}),$$

$$|J=8, J_z=7.9\rangle$$

# Dy@GR/Ir(111)



✓ Change of Dy valence due to Graphene

# Effective Crystal Field Theory

$$\hat{H}_{CEF} = \sum_{kq} A_k^q \langle r^k \rangle \Theta_k(J) \hat{O}_k^q + (g - 1) J_z \Delta_{EX}$$

	$A_2^0 \langle r^2 \rangle$	$A_4^0 \langle r^4 \rangle$	$A_6^0 \langle r^6 \rangle$	$A_6^6 \langle r^6 \rangle$
Dy@Ir	4.55	1.51	-13.30	37.6
Dy@GR/Ir-HCP	-10.89	6.81	2.79	-7.53
Dy@GR/Ir-ATOP	-9.6	6.8	3.2	-8.1



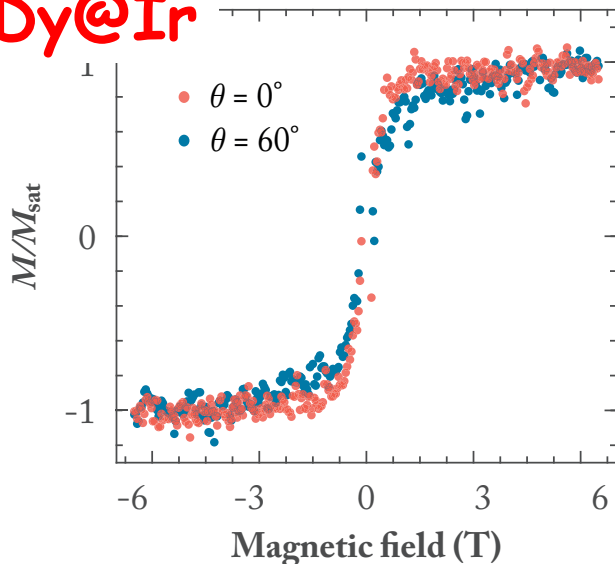
## Magnetic Anisotropy Energy

$$E_{MA}(\theta, \phi) = K_1 \sin^2 \theta + K_2 \sin^4 \theta + K_3 \sin^6 \theta + K_4 \sin^6 \theta \cos(6\phi)$$

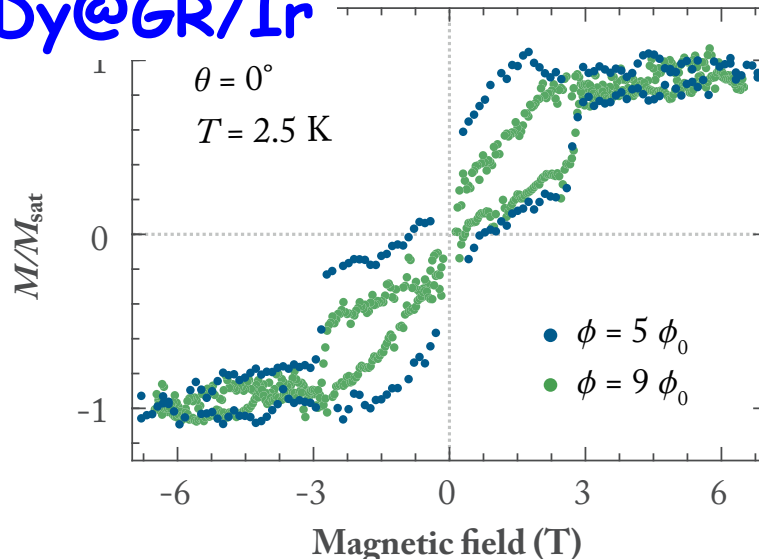
MAE, meV	$K_1$	$K_2$	$K_3$	$K_4$	MAE
Dy@Ir	142.1	-299.4	179.0	2.2	21.7
Dy@GR/Ir-ATOP	83.7	-163.0	86.4	0.9	7.1

# << Magnetic Remanence >>

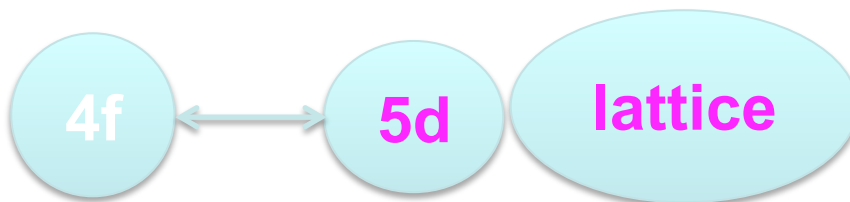
Dy@Ir



Dy@GR/Ir



$$B_2^0 \hat{O}_2^0 + B_4^0 \hat{O}_4^0 + B_6^0 \hat{O}_6^0 + B_6^6 \hat{O}_6^6 + (g - 1) J_z \Delta_{ex} + g J_z B_z$$



$$\Delta_{\text{EX}} = \mathbf{J}_{\text{df}} \mathbf{m}_{5\text{d}} \Rightarrow 0$$

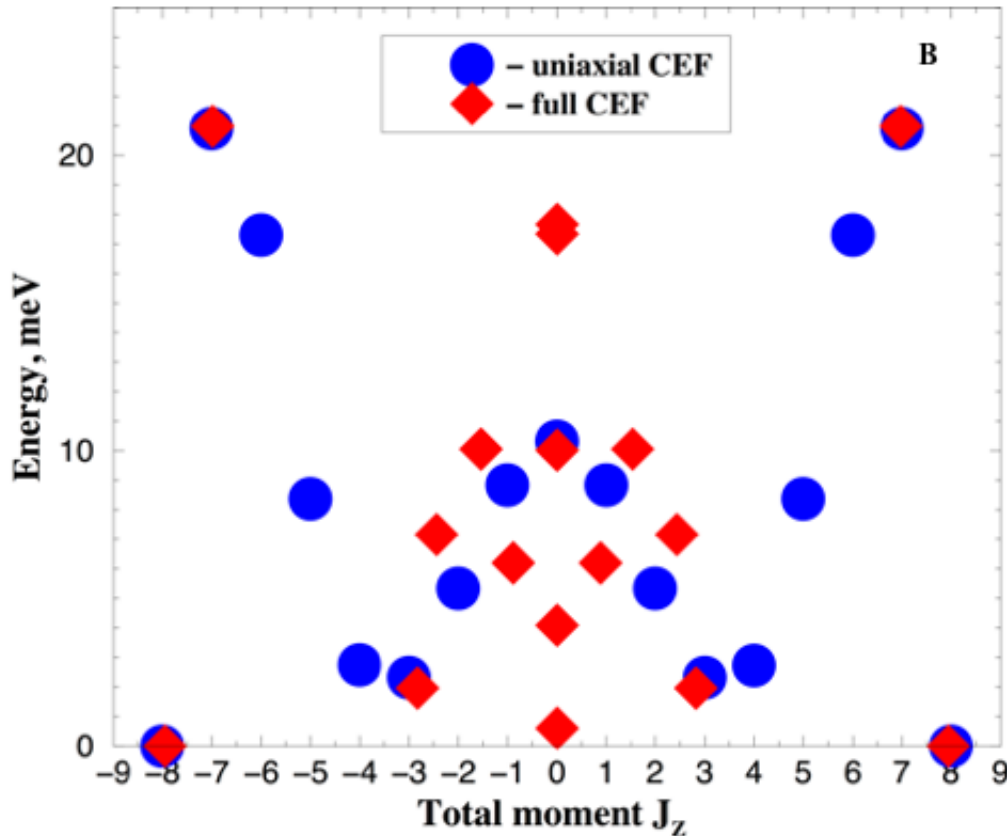
$$|J=7.5, J_z=7.5\rangle \Rightarrow |J=7.5, J_z=2.5\rangle$$

Strong reduction of  $M_z$

$$|J=8, J_z=8\rangle \Rightarrow |J=8, J_z=7.9\rangle$$

No change of  $M_z$

# Role of Quantum Tunneling



$$B_2^0, B_4^0, B_6^0$$

splitting of different  $J_z$  eigenvalues

$$ZFS \approx MAE \sim 10 \text{ meV}$$

$$B_6^6 \hat{O}_6^6$$

couples different  $J_z$  states

$$\langle J_z = m | \hat{O}_6^6 | J_z = n \rangle \neq 0, \\ |m - n| = 6, 12$$

➤ QT leads to strong reduction of the energy barrier

$$\begin{aligned} |J_z=8\rangle &\rightarrow -0.996|J_z=8\rangle + 0.076|J_z=2\rangle - 0.046|J_z=-4\rangle \\ |J_z=0\rangle &\rightarrow 0.707|J_z=3\rangle - 0.707|J_z=-3\rangle \quad (+0.6 \text{ meV}) \\ |J_z=-8\rangle &\rightarrow -0.996|J_z=-8\rangle + 0.076|J_z=-2\rangle - 0.046|J_z=4\rangle \end{aligned}$$

➤ GS remains protected against the moment reversal

# Magnetic stability of Dy@Ir & Dy@Gr/Ir

$$\sum_{kk'} \left[ J_+ c_{k\downarrow}^\dagger c_{k'\uparrow} + J_- c_{k\uparrow}^\dagger c_{k'\downarrow}^\dagger + J_z \left( c_{k\uparrow}^\dagger c_{k'\uparrow} - c_{k\downarrow}^\dagger c_{k'\downarrow} \right) \right]$$

➤ **Kondo exchange:**

$$[J_K N(E_F)] = 2 \frac{\Delta(E_F)}{N_f} \left[ \frac{1}{(\epsilon_f + U - J)} - \frac{1}{\epsilon_f} \right]$$

➤ **Hybridization:**  $\Delta(\epsilon) = \frac{1}{\pi} \Im \text{Tr}[G_{\text{HIA}}^{-1}(\epsilon + i0)]$

	$\epsilon_f, eV$	$\Delta(E_F), eV$	$J_K N(E_F)$
<b>Dy@Ir</b>	<b>-6.16</b>	<b>0.30</b>	<b>2.14</b>
<b>Dy@GR/Ir</b>	<b>-6.15</b>	<b>0.12</b>	<b>0.57</b>

$$\left[ \frac{1}{T_1} \right] \sim [(g_J - 1)J]^2 [J_K N(E_F)]^2 [k_B T]$$

$$\left[ \frac{1}{T_1} \right]_{\text{(Dy@Ir)}} / \left[ \frac{1}{T_1} \right]_{\text{(Dy@GR/Ir)}} = 14$$

✓ Increase of the Dy-moment lifetime due to GR



## Conclusions:

- ◆ DFT+U+HIA/ED calculations are in reasonable agreement with experimental XMCD data for orbital  $M_L$ , effective spin  $M_S+M_D$ , and the ratio  $R_{LS}$ .
- ◆ The role of 5d-4f interorbital exchange polarization is emphasized.
- ◆ Change in valence of Dy adatom due to Graphene:

$Dy^{3+}@Ir(111)$  vs  $Dy^{2+}@GR/Ir(111)$

- ◆ Longer lifetime of  $Dy@GR/Ir$  than of  $Dy@Ir$

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EXTRA SLIDES

# Anderson Impurity Model: "Exact Diagonalization"

$$\begin{aligned}
 H_{\text{imp}} = & \sum_{\substack{kmm' \\ \sigma\sigma'}} [\epsilon^k]_{mm'}^{\sigma\sigma'} b_{km\sigma}^\dagger b_{km'\sigma'} + \sum_{m\sigma} \epsilon_f f_{m\sigma}^\dagger f_{m\sigma} \\
 & \quad \text{"bath"} \quad \text{-chemical potential} \\
 & + \sum_{mm'\sigma\sigma'} \left[ \xi \mathbf{1} \cdot \mathbf{s} + \Delta_{\text{CF}} + \Delta_{\text{ex}} s_z \right]_{mm'}^{\sigma\sigma'} f_{m\sigma}^\dagger f_{m'\sigma'} \\
 & \quad \text{SOC Crystal Field d-f Exchange} \\
 & + \sum_{\substack{kmm' \\ \sigma\sigma'}} \left( [V^k]_{mm'}^{\sigma\sigma'} f_{m\sigma}^\dagger b_{km'\sigma'} + \text{h.c.} \right) \\
 & \quad \text{Hybridization} \\
 & + \frac{1}{2} \sum_{\substack{mm'm''m''' \\ m'''\sigma\sigma'}} U_{mm'm''m'''} f_{m\sigma}^\dagger f_{m'\sigma'}^\dagger f_{m'''\sigma'} f_{m''\sigma} \\
 & \quad \text{Coulomb Interaction} \\
 & \pi \sum_k |V_j^k|^2 \delta(\epsilon_j^k - \epsilon) = \Delta(\epsilon) - \text{Hybridization strength}
 \end{aligned}$$

# Anderson Impurity Model parameters

- ✓ **SOC** -  $\xi$  from **DFT**

$$\xi_l = \int_0^{R^{MT}} dr r \frac{1}{(2Mc)^2} \frac{dV(r)}{dr} u_l(r) u_l(r)$$

- ✓ **Crystal Field matrix**

$$[H]_{\gamma_1 \gamma_2} = \int_{\epsilon_b}^{\epsilon_t} d\epsilon \epsilon [N(\epsilon)]_{\gamma_1 \gamma_2} \quad \Rightarrow \quad \Delta_{CF}$$

removing the interacting DFT+U potential and SOC

- ✓  $\Delta_{EX} = J_{df} m_{5d} \sim 5-10 \text{ meV}$  ( $J_{df} = 0.1 \text{ eV}$ , 5d-4f exchange)
- ✓ **Slater Integrals**  $F_0, F_2, F_4, F_6$   
[S. Lebegue et al., PRB (2006)]

# Charge Self-Consistency

✓ **Self-Energy:** 
$$\left[ \Sigma(z) \right]_{\gamma_1 \gamma_2} = z \delta_{\gamma_1 \gamma_2} - \left[ \xi(\mathbf{l} \cdot \mathbf{s}) + \Delta_{CF} + \left( G^{\text{AIM}}(z) \right)^{-1} \right]_{\gamma_1 \gamma_2}$$

✓ **Dyson Equation and Occupation matrix**

$$\left[ G(z) \right]_{\gamma_1 \gamma_2}^{-1} = \left[ G_0(z) \right]_{\gamma_1 \gamma_2}^{-1} - \Delta \epsilon \delta_{\gamma_1 \gamma_2} + \left[ \Sigma(z) \right]_{\gamma_1 \gamma_2}$$

$$n_{\gamma_1 \gamma_2} = -\pi^{-1} \text{Im} \int^{E_F} dz \left[ G(z) \right]_{\gamma_1 \gamma_2}$$

✓ **Construct DFT+U potential and solve KS equations**

$$\left( -\nabla^2 + V_{LDA}(\mathbf{r}) + V_U + \xi(\mathbf{l} \cdot \mathbf{s}) \right) \Phi_i(\mathbf{r}) = e_i \Phi_i(\mathbf{r}) \quad \rho(\mathbf{r}) = \sum_i^{occ} \Phi_i^\dagger(\mathbf{r}) \Phi_i(\mathbf{r})$$

➤ Non-spherical double counting is removed from DFT part

✓ **Calculate DFT+U Total Energy**

## Projection to LAPW-basis

$$G(z) = \frac{1}{V_{BZ}} \int_{BZ} d\mathbf{k} \sum_b \frac{\langle \phi_m | \Phi^b \rangle \langle \Phi^b | \phi'_m \rangle}{z + \mu - \epsilon^b(\mathbf{k})}$$

$$\Phi_{\mathbf{k}}^b(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k}+\mathbf{G}}^b \phi_{\mathbf{k}+\mathbf{G}}(\mathbf{r})$$

$$\phi_{\mathbf{k}+\mathbf{G}}(\mathbf{r}) = \sum_{l,m} [a_{\mathbf{k}+\mathbf{G}}^{lm} u_l(r_i) + b_{\mathbf{k}+\mathbf{G}}^{lm} \dot{u}_l(r_i)] Y_{lm}(\hat{r}_i)$$

$$\langle \phi_m | \Phi^b \rangle \langle \Phi^b | \phi_{m'} \rangle = \langle u_l Y_{lm} | \Phi^b \rangle \langle \Phi^b | u_l Y_{lm'} \rangle + \frac{1}{\langle \dot{u} | \dot{u} \rangle} \langle \dot{u}_l Y_{lm} | \Phi^b \rangle \langle \Phi^b | \dot{u}_l Y_{lm'} \rangle$$

<b>This work</b>		Sm-f	Sm	Co-1(2c)	Co-2(3g)	Total
	$\mu_S$	-3.95	-4.22	1.46	1.48	
	$\mu_L$	+4.20	+4.22	0.10	0.09	
	$\mu_T$	0.25	0	1.56	1.57	7.41
<b>Granás et al., DMFT (2012)</b>		Sm-f	Sm	Co-1(2c)	Co-2(3g)	Total
	$\mu_S$	-	-3.47	1.54	1.52	
	$\mu_L$	-	+3.26	0.22	0.18	
	$\mu_T$	-	-0.21	1.76	1.70	8.02
<b>Soderlind et al., SRM (2018)</b>		Sm-f	Sm	Co-1(2c)	Co-2(3g)	Total
	$\mu_S$	-	-	1.61	1.60	
	$\mu_L$	-	-	0.22	0.18	
	$\mu_T$	-	-0.30	1.83	1.78	8.27
<b>Partick &amp; Staunton, SIC (2018)</b>		Sm-f	Sm	Co-1(2c)	Co-2(3g)	Total
	$\mu_S$	-	-5.63	-	-	
	$\mu_L$	-	+4.55	-	-	
	$\mu_T$	-	-1.08	-	-	7.13
	Exp. PND	-	0	1.86	1.75	8.97
	Exp.					7.3-8.7