More Surprises in f-electron Magnetism

Alexander Shick

Institute of Physics ASCR, Prague, CZ

FZU
Fyzikální ústav Akademie
věd České republiky

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

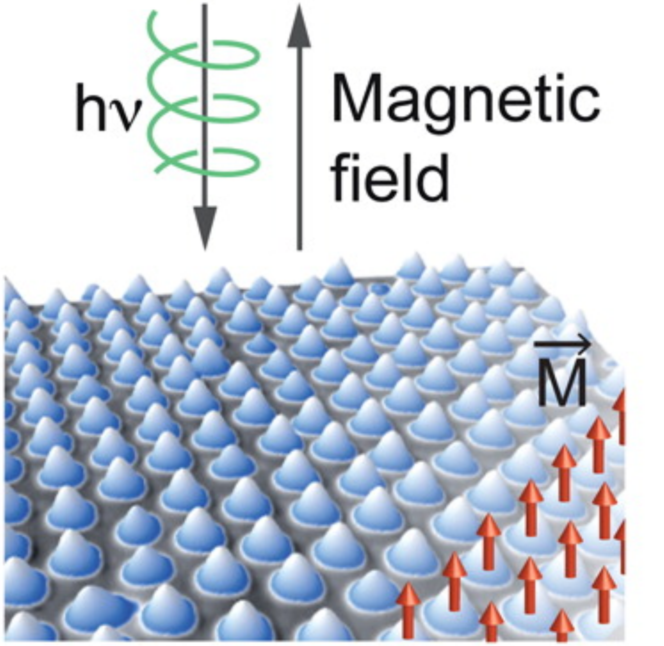
MINISTERSTVO ŠKOLSTVÍ,
MLÁDEŽE A TĚLOVÝCHOVY

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

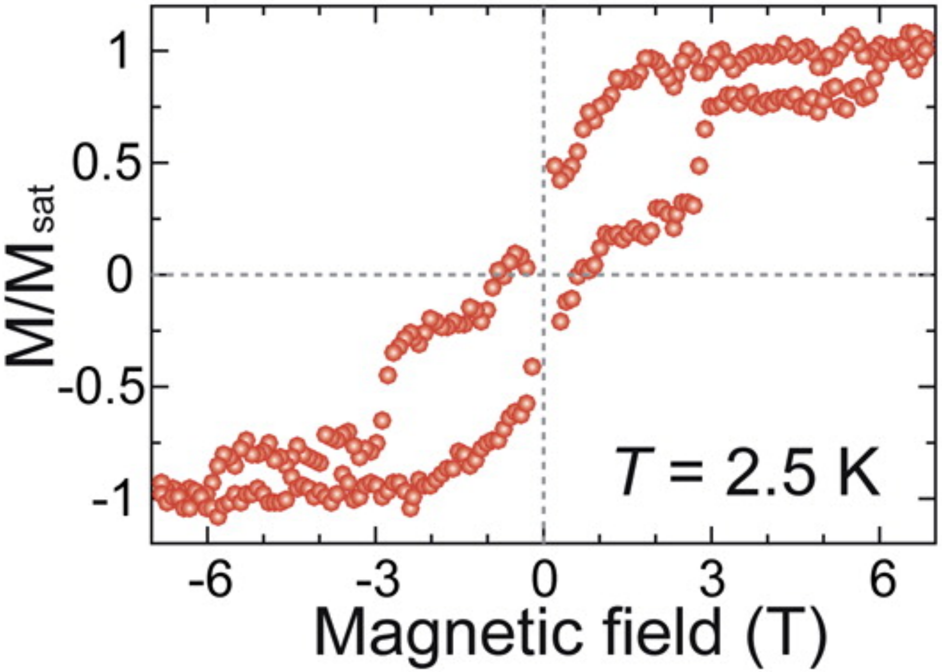
- In 1959, Richard Feynman proposed a $1K prize for the storage of information on a page of a book at the 1/25000 scale in such a way that it could be read by an electron microscope. The ultimate fulfilment of this request, has been realized by storing his own words at the 2016 APS conference [F. Kalff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

- **Quest for ultra-high-density storage media the magnetic storage density above 100 Tbit/in^2**

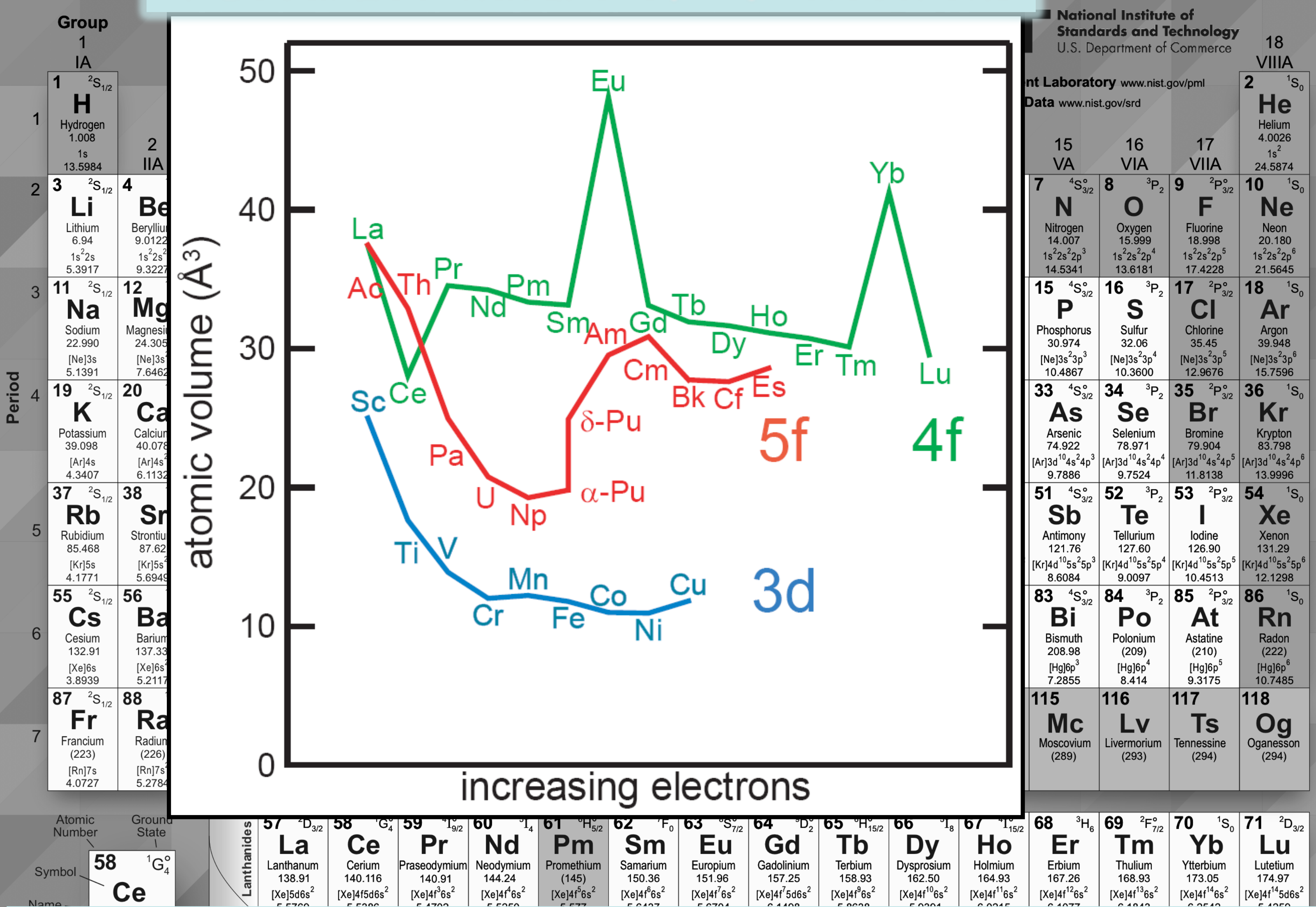
R. Baltic *et al*., Superlattice of Single Atom Magnetis on Graphene, Nano Letters 16 (2016)



Dy atoms on graphene



◆ Localized nature of 4f-electrons



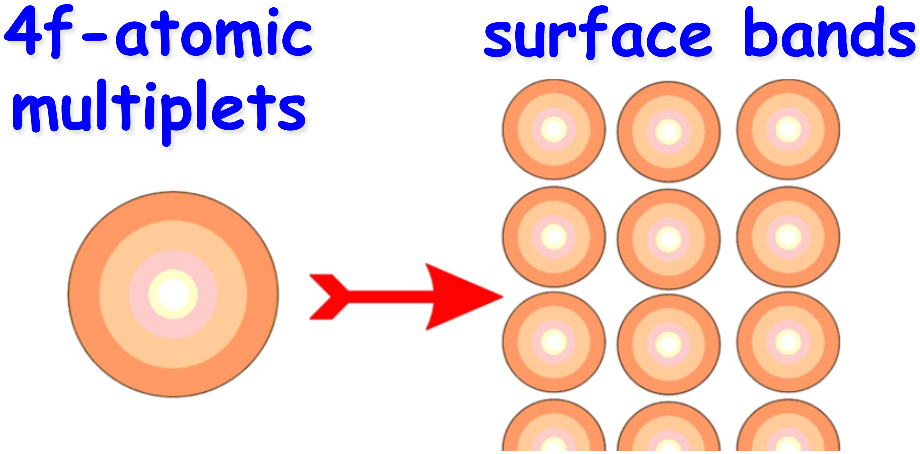
◆ **DFT works poorly for the 4f- and 5f-materials**

***f*-electron challenge**

◆ 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).

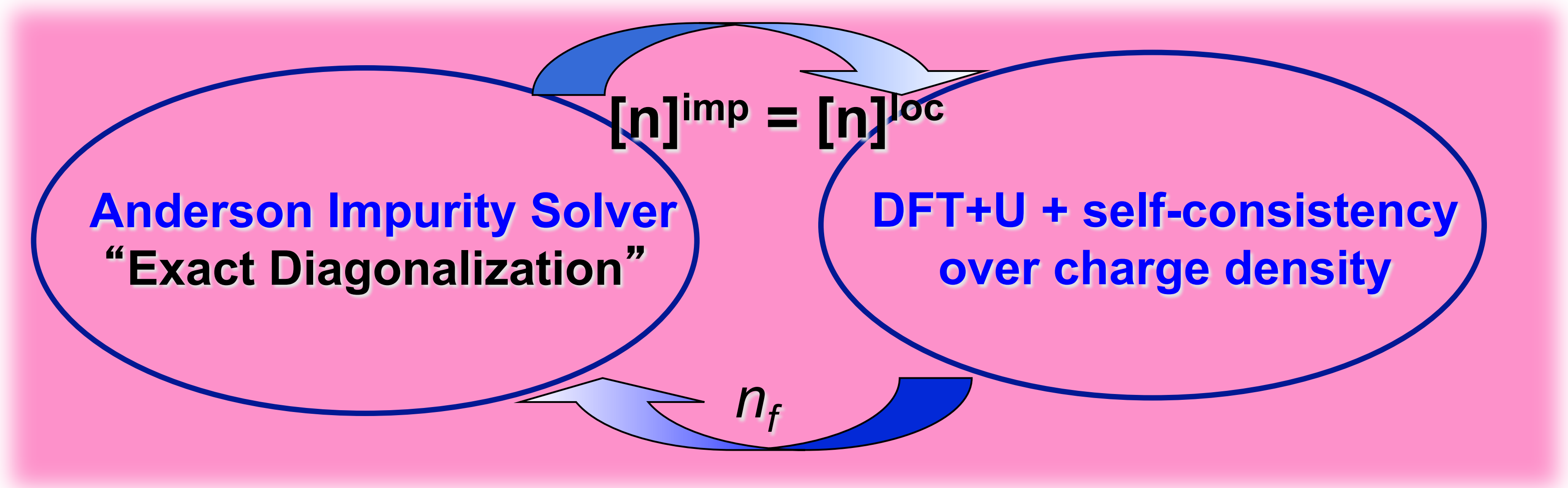
◆ Interaction between



◆ 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"



$[n]^{imp} = [n]^{loc}$

Anderson Impurity Solver
"Exact Diagonalization"

DFT+U + self-consistency
over charge density

n_f

$$[n] = -\pi^{-1}\,\mathrm{Im}\int^{E_F} \mathrm{d}z\ \mathrm{Tr}\left[G(z)\right]$$

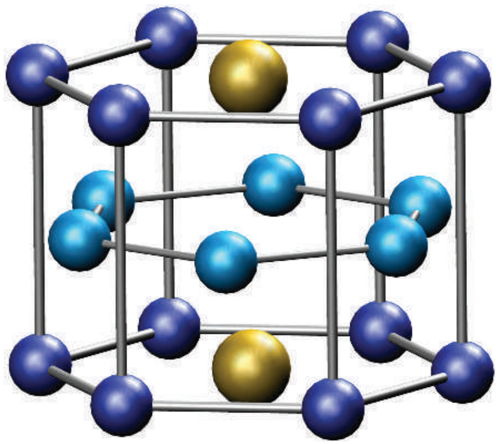
AIM "Exact Diagonalization":

- 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

$SmCo_5$



	Sm	$Co_1(2c)$	$Co_2(3g)$	
μ_S	-4.22	1.46	1.48	
μ_L	+4.22	0.10	0.09	
μ_T	0	1.56	1.57	7.41

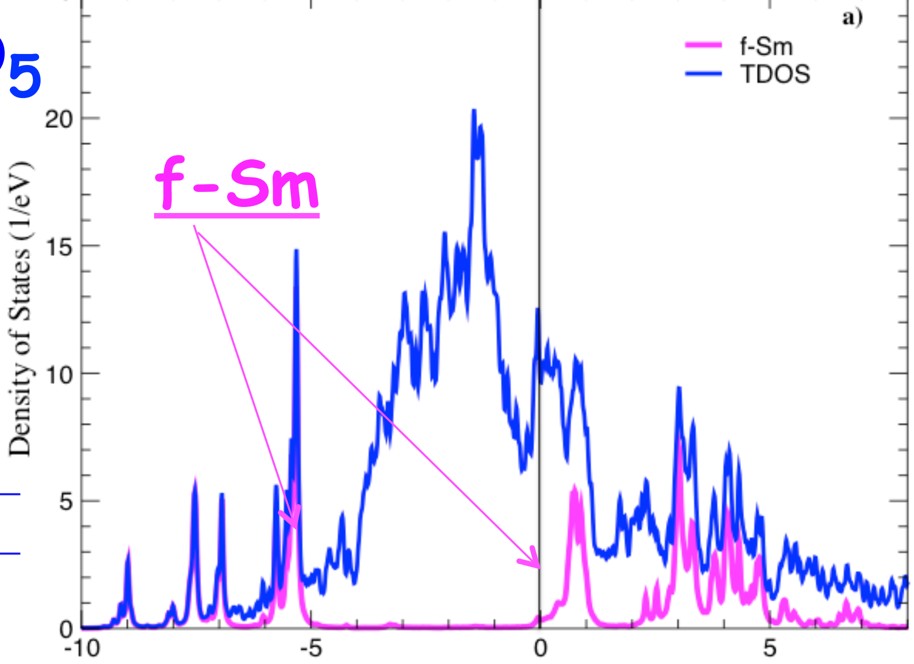
O.Granas *et al.*, DFT+DMFT (2012)

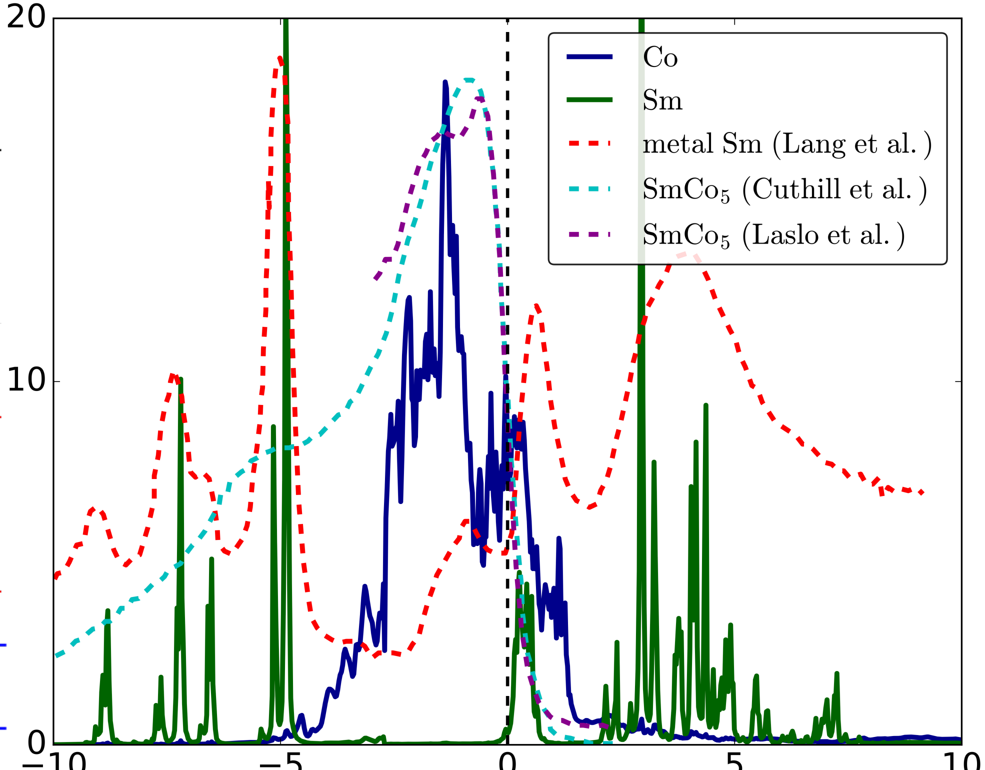
μ_S	-3.47	1.54	1.52	
μ_L	+3.26	0.22	0.18	
μ_T	-0.21	1.76	1.70	8.02

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

μ_S	-5.34	1,59	1.61	
μ_L	+3.10	0.07	0.12	
μ_T	-2.24	1.66	1.73	5.56

Exp. μ_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 $J_\pm \equiv J_x \pm iJ_y$.

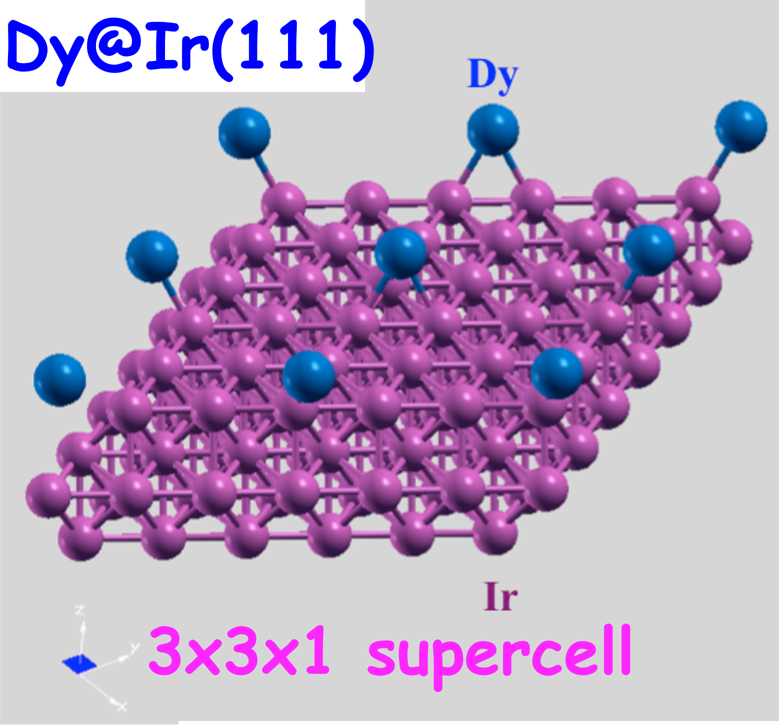
$$O_2^0 = 3J_z^2 - X$$

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

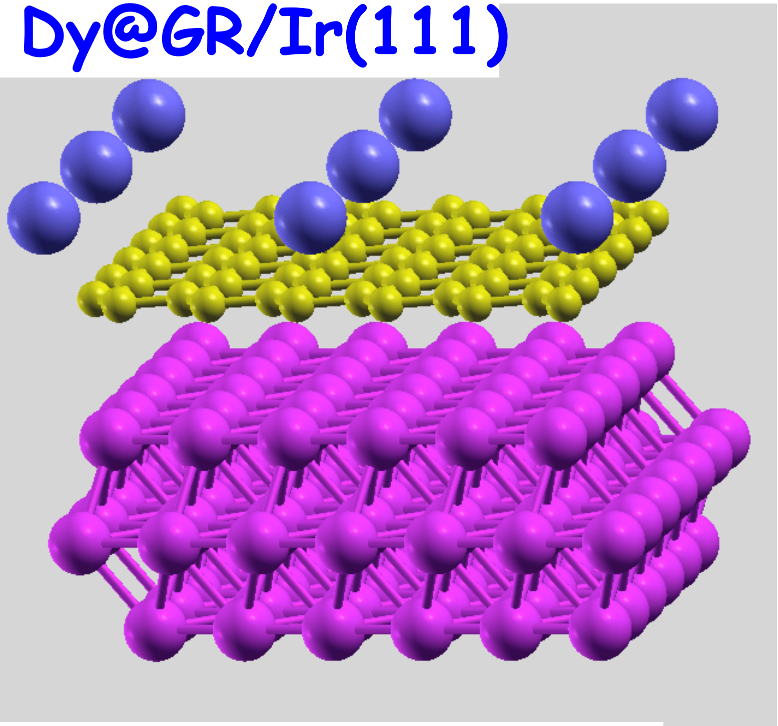
CF	This	Delange		Tils	Zhao	Givord	Richter	Novak
(Kelvin)	Work	↑	↓	Experiment			CEF-Theory	
$A_2^0\langle r^2\rangle$	-190	-313	-262	-326	-330	-200	-755	-160
$A_4^0\langle r^4\rangle$	-135	-40	-55	-	-45	0	-37	-33
$A_6^0\langle r^6\rangle$	-152	35	25	-	0	50	11	40
$A_6^6\langle r^6\rangle$	-763	-731	-593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

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

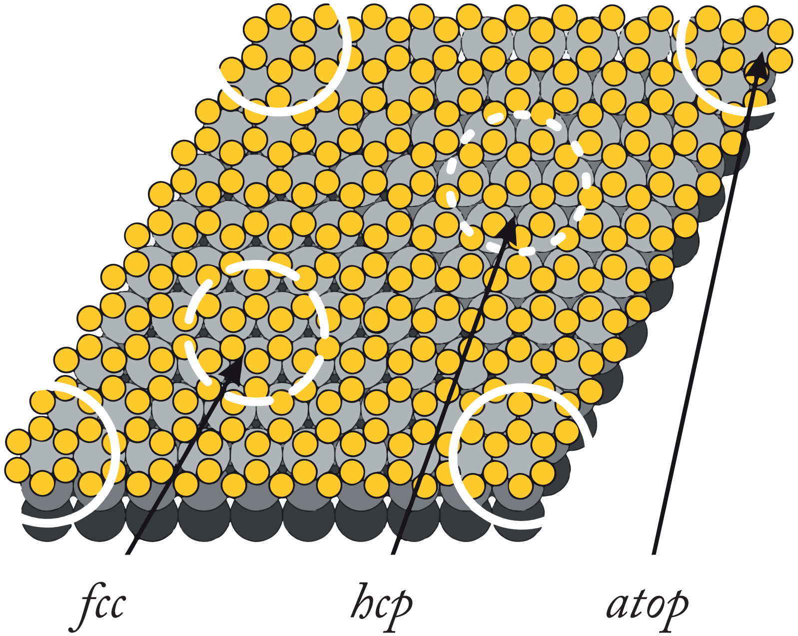
MAE, meV	K_1	K_2	K_3	K_4	MAE
This work	18.6	-7.5	0	0	11.1
DFT+SRM	Soderlind *et al.*, 2017				10.5
DFT+U	Landa *et al.*, 2018				-9.9
Experiment					9.2, 13.1

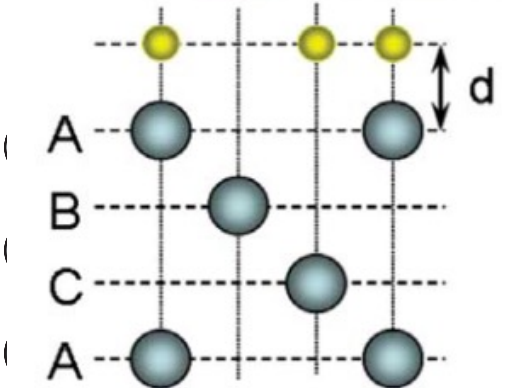


Dy@Ir(111)

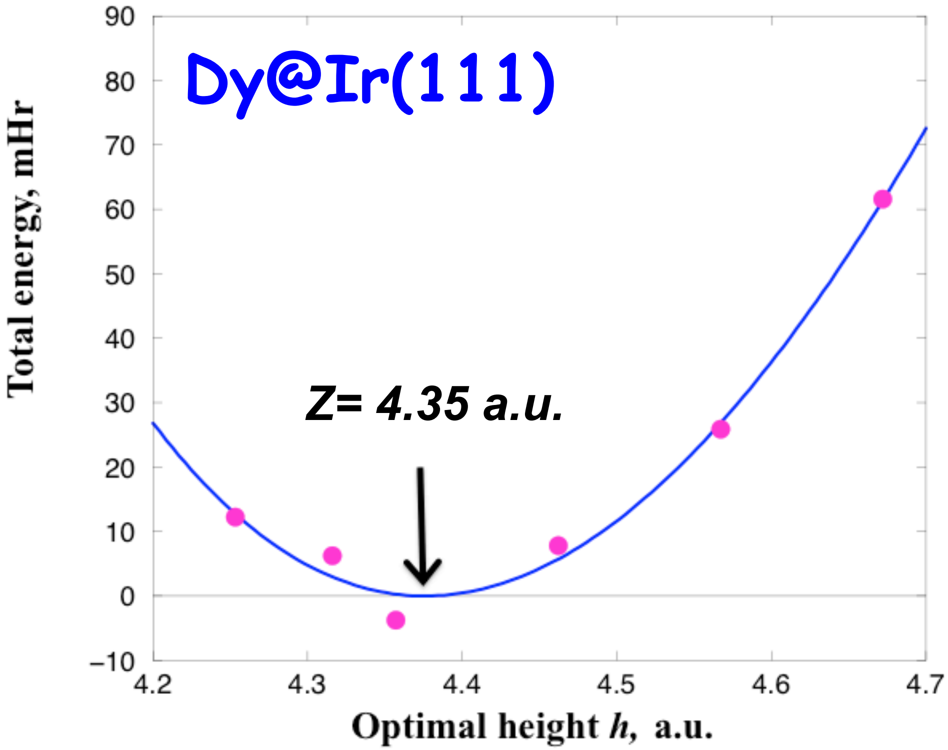


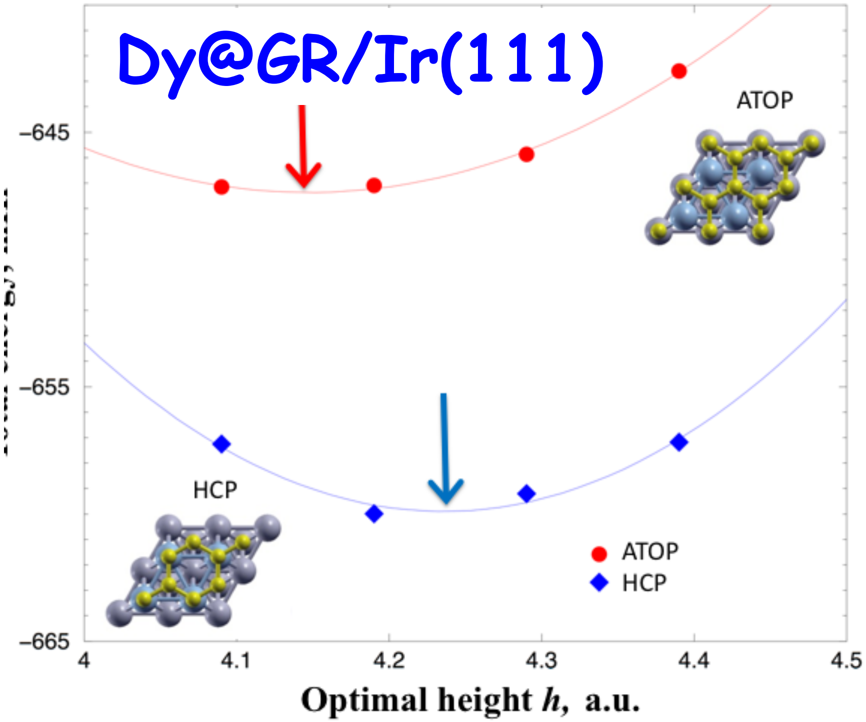
Dy@GR/Ir(111)





"HCP"

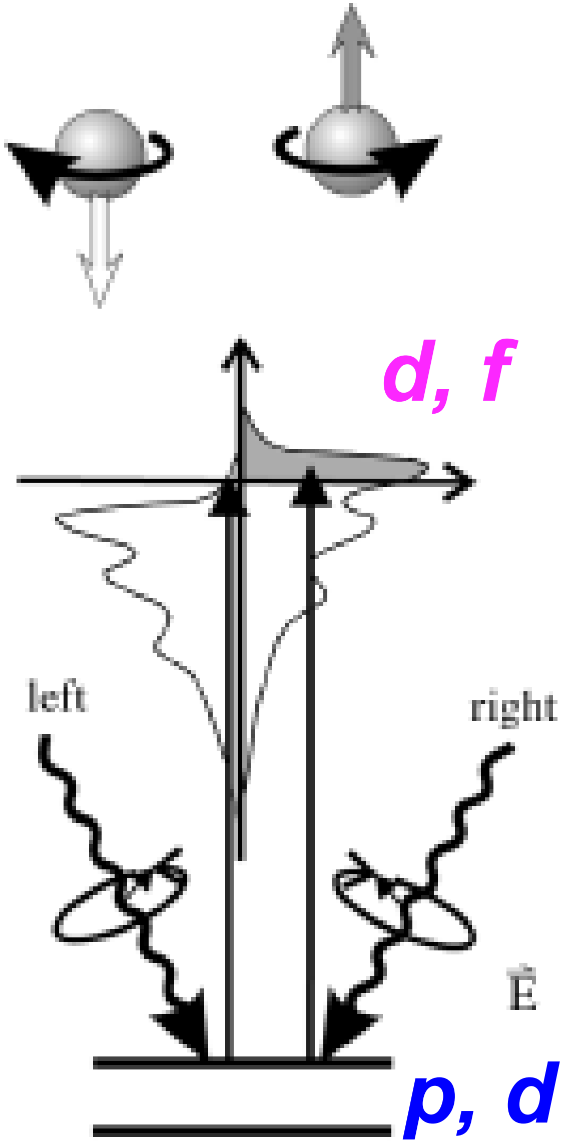




Z	a.u.
Dy@Ir	4.35
Dy@GR/Ir-HCP	4.235
Dy@GR/Ir-ATOP	4.15

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

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

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

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

- 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±0.2	3.4±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±0.2	3.0±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:

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

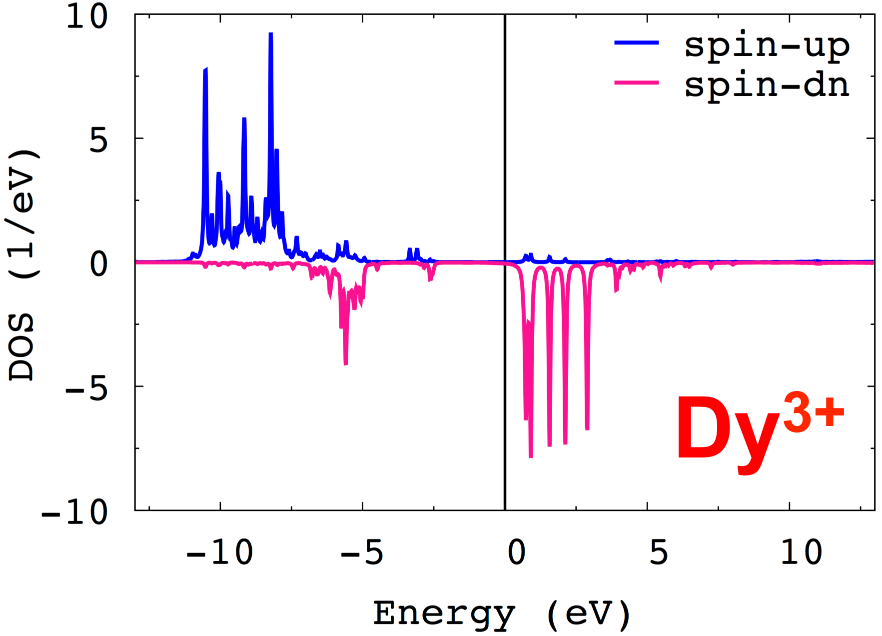
$$[\langle S_z \rangle + 3\langle T_z \rangle] = \frac{3n_h}{I}(2\Delta I_{M_5} - 3\Delta I_{M_4})$$

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

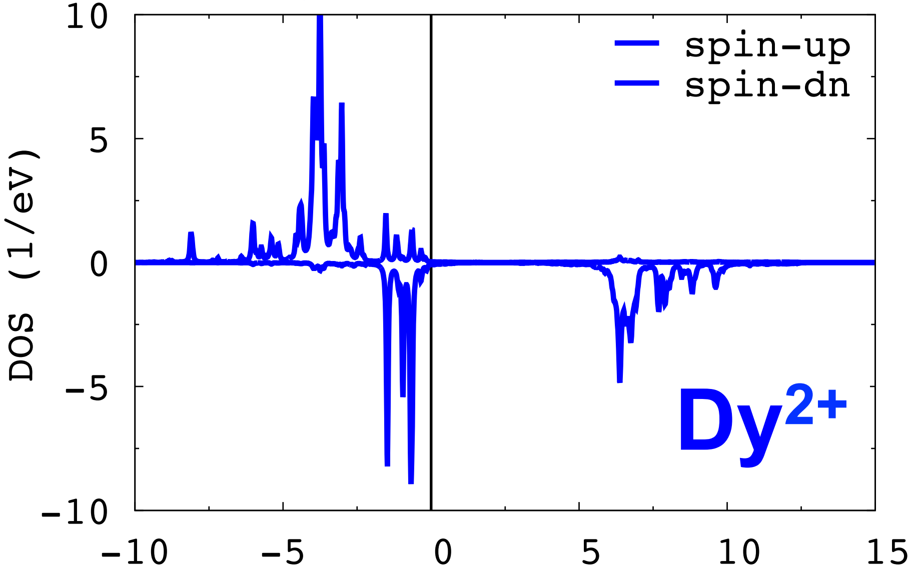
➢ **Assumtion of isotropic absorbtion:**

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

Dy@Ir(111)



Dy@GR/Ir(111)



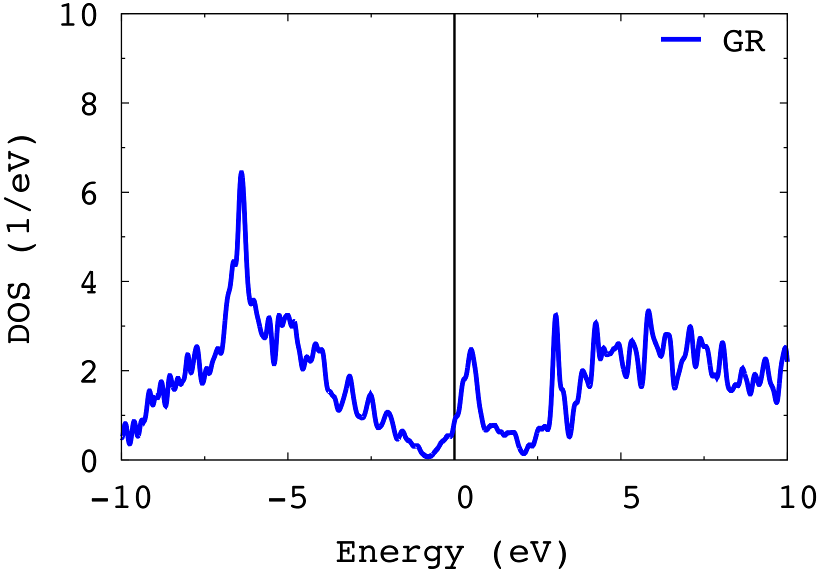
$$H_{imp}\Psi(N)=E_N\Psi(N)$$

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

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

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

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



✓ 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

⇩

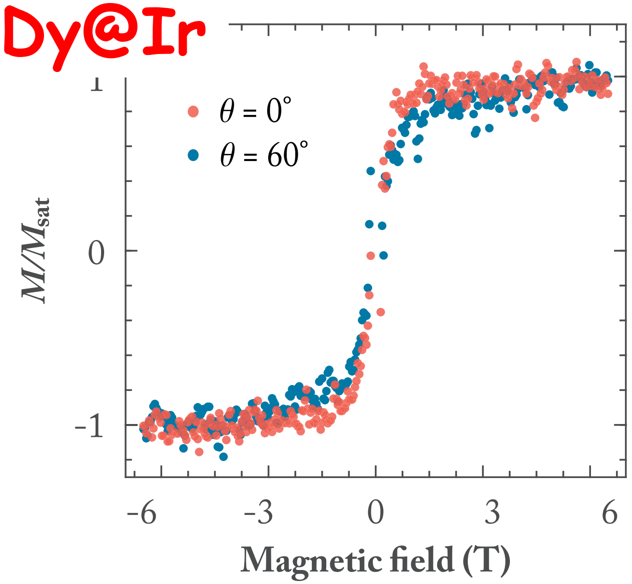
Magnetic Anisotropy Energy

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

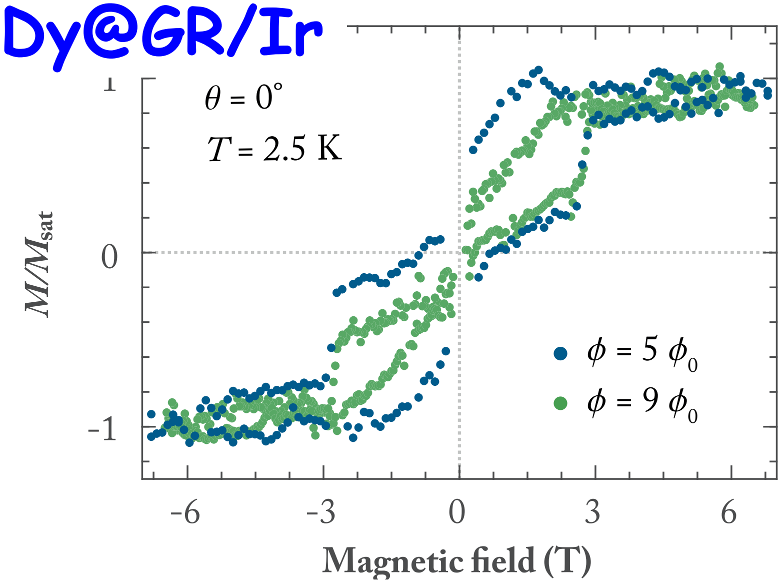
MAE, meV	K_1	K_2	K_3	K_4	MAE
Dy@Ir	142.1	-299.4	179.0	2.2	21.7
Dy@GR/Ir-ATOP	83.7	-163.0	86.4	0.9	7.1

<<Magnetic Remanence>>

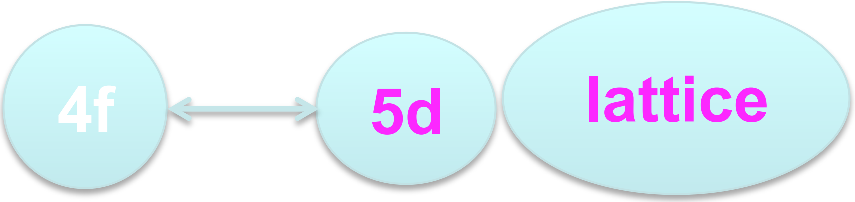
Dy@Ir



Dy@GR/Ir



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

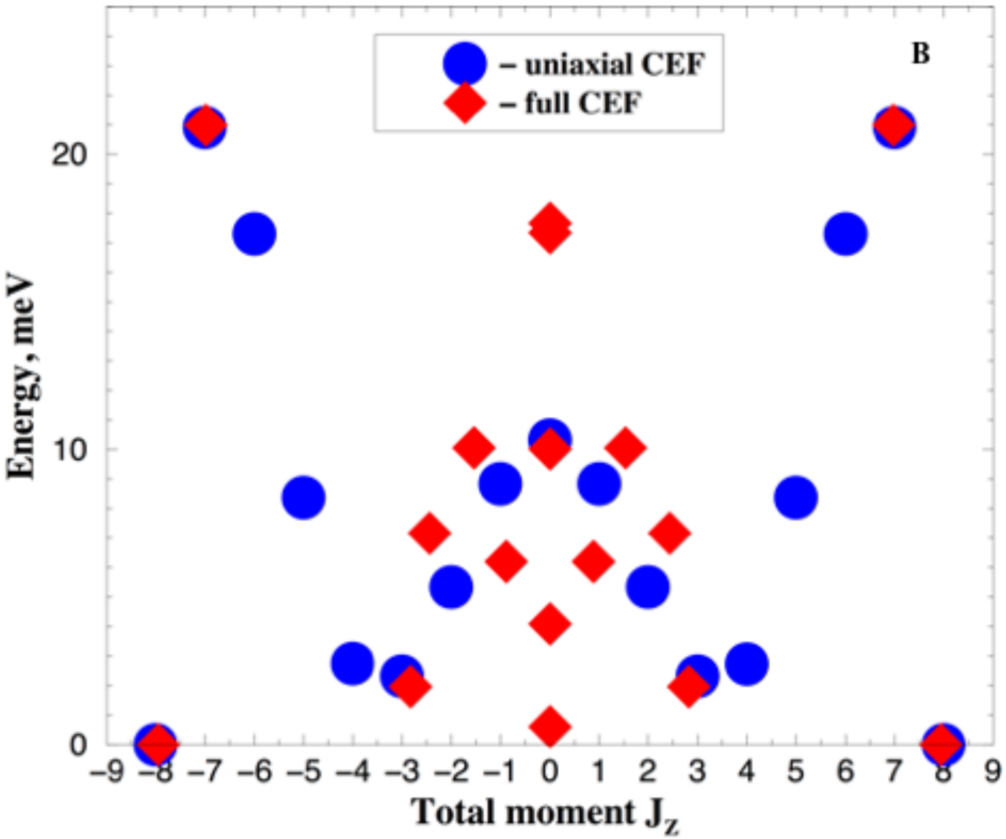


$\Delta_{EX} = J_{df}\ m_{5d}$ ➡ 0

$|J=7.5, J_z=7.5\rangle$ ➡ $|J=7.5, J_z=2.5\rangle$ $|J=8, J_z=8\rangle$ ➡ $|J=8,\ J_z=7.9\rangle$

Strong reduction of M_z **No change of M_z**

Role of Quantum Tunneling



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

splitting of different **J_z** eigenvalues

$$ZFS \approx MAE \sim 10\ meV$$

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

couples different **J_z** states

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

- **QT leads to strong reduction of the energy barrier**

$|J_z=8>$ ➡ $-0.996|J_z=8> +0.076|J_z=2> -0.046|J_z=-4>$

$|J_z=0>$ ➡ $0.707|J_z=3> -0.707|J_z=-3>$ (+0.6 meV)

$|J_z=-8>$ ➡ $-0.996|J_z=-8> +0.076|J_z=-2> -0.046|J_z=4>$

- **GS remains protected against the moment reversal**

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

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

- **Kondo exchange:**

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

- **Hybridization:** $\Delta(\epsilon) = \frac{1}{\pi}\Im\,\mathrm{Tr}[G^{-1}_{\mathrm{HIA}}(\epsilon + i0)]$

	$\epsilon_{\mathrm{f}}, eV$	$\Delta(E_F), eV$	$J_{\mathrm{K}}N(E_{\mathrm{F}})$
Dy@Ir	**-6.16**	**0.30**	**2.14**
Dy@GR/Ir	**-6.15**	**0.12**	**0.57**

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

$\left[\frac{1}{T_1}\right]$**(Dy@Ir)**/$\left[\frac{1}{T_1}\right]$**(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**

✓ Acknowledge collaboration with

J. Kolorenc, FZU ASCR, Prague;

A. Denisov, Ural Federal University, Yekaterinburg;

A. Lichtenstein, University of Hamburg

EXTRA SLIDES

Anderson Impurity Model:"Exact Diagonalization"

$$H_{\text{imp}} = \sum_{\substack{kmm' \\ \sigma\sigma'}} [\epsilon^k]^{\sigma\ \ \sigma'}_{mm'} b^\dagger_{km\sigma} b_{km'\sigma'} + \sum_{m\sigma} \epsilon_f f^\dagger_{m\sigma} f_{m\sigma}$$

"bath" -chemical potential

$$+ \sum_{mm'\sigma\sigma'} \left[\xi \mathbf{l}\cdot\mathbf{s} + \Delta_{\text{CF}} + \Delta_{\text{ex}} s_z\right]^{\sigma\ \ \sigma'}_{mm'} f^\dagger_{m\sigma} f_{m'\sigma'}$$

SOC Crystal Field d-f Exchange

$$+ \sum_{\substack{kmm' \\ \sigma\sigma'}} \left([V^k]^{\sigma\ \ \sigma'}_{mm'} f^\dagger_{m\sigma} b_{km'\sigma'} + \text{h.c.} \right)$$

Hybridization

$$+\frac{1}{2} \sum_{\substack{mm'm'' \\ m'''\sigma\sigma'}} U_{mm'm''m'''} f^\dagger_{m\sigma} f^\dagger_{m'\sigma'} f_{m'''\sigma'} f_{m''\sigma}$$

Coulomb Interaction

$\pi \sum_k |V_j^k|^2 \delta(\epsilon_j^k - \epsilon) = \Delta(\epsilon)$ - Hybridization strength

Anderson Impurity Model parameters

✓ **SOC** - ξ from **DFT**

$$\xi_l = \int_0^{R^{MT}} \mathrm{d}r \, r \frac{1}{(2Mc)^2} \frac{\mathrm{d}V(r)}{\mathrm{d}r} u_l(r) u_l(r)$$

✓ **Crystal Field matrix**

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

removing the interacting DFT+U potential and SOC

✓ **$\Delta_{\mathrm{EX}} = J_{\mathrm{df}}\, m_{\mathrm{5d}} \sim$ 5-10 meV (J_{df}=0.1 eV, 5d-4f exchange)**

✓ **Slater Intergrals F_0, F_2, F_4, F_6**
[S. Lebegue et al., PRB (2006)]

Charge Self-Consistency

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

✓ **Dyson Equation and Occupation matrix**

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

$$n_{\gamma_1\gamma_2} = -\pi^{-1}\,\mathrm{Im}\int^{E_F} \mathrm{d}z\,[G(z)]_{\gamma_1\gamma_2}$$

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

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

➢ Non-spherical double counting is removed from DFT part

✓ **Calculate DFT+U Total Energy**

Projection to LAPW-basis

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

$$\Phi^b_{\mathbf{k}}(\mathbf{r}) \ = \ \sum_{\mathbf{G}} \ c^b_{\mathbf{k}+\mathbf{G}} \phi_{\mathbf{k}+\mathbf{G}}(\mathbf{r})$$

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

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

This work

	Sm-f	Sm	Co-1(2c)	Co-2(3g)	Total
μ_S	-3.95	-4.22	1.46	1.48	
μ_L	+4.20	+4.22	0.10	0.09	
μ_T	0.25	0	1.56	1.57	7.41

Granas et al., DMFT (2012)

	Sm-f	Sm	Co-1(2c)	Co-2(3g)	Total
μ_S	-	-3.47	1.54	1.52	
μ_L	-	+3.26	0.22	0.18	
μ_T	-	-0.21	1.76	1.70	8.02

Soderlind et al., SRM (2018)

	Sm-f	Sm	Co-1(2c)	Co-2(3g)	Total
μ_S	-	-	1.61	1.60	
μ_L	-	-	0.22	0.18	
μ_T	-	-0.30	1.83	1.78	8.27

Partick & Staunton, SIC (2018)

	Sm-f	Sm	Co-1(2c)	Co-2(3g)	Total
μ_S	-	-5.63	-	-	
μ_L	-	+4.55	-	-	
μ_T	-	-1.08	-	-	7.13
Exp. PND	-	0	1.86	1.75	8.97
Exp.					7.3-8.7