Crystal-field effects and temperature dependence of magnetic anisotropy in rare-earth-based hard magnets

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October 10 2023

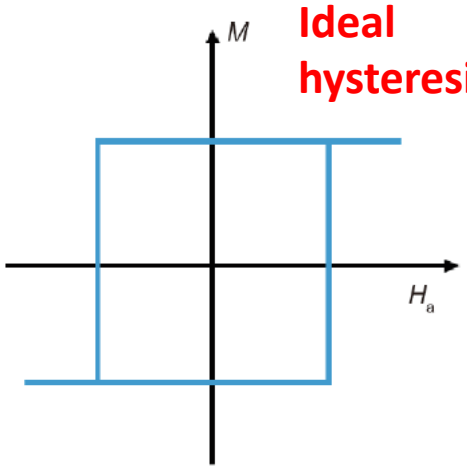
OUTLINE

- Rare-earth (RE) based permanent magnets: performance and cost challenges
- Two-sublattice model of magnetic transition-metal-RE intermetallics
- Brief summary of crystal-field theory
- DFT+DMFT with quasiatomic (Hubbard-I) treatment of RE *4f*
- RE *4f* crystal fields from DFT+Hubbard-I
- High-rank crystal field, magnetization and CF excitations of $NdCo_5$
- Complex 2-14-1 magnets: CF, anisotropy, effect of RE substitutions

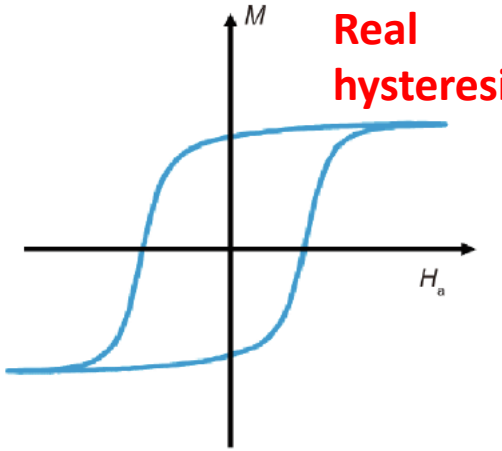
Performance of permanent magnets

Before advent of rare-earth magnets (pre 1950)

Rare-earth permanent magnets (after 1950)



Ideal hysteresis



Real hysteresis

Demagnetizing field

$\boldsymbol{H_d = -NM}$ $(0 \le N \le 1)$

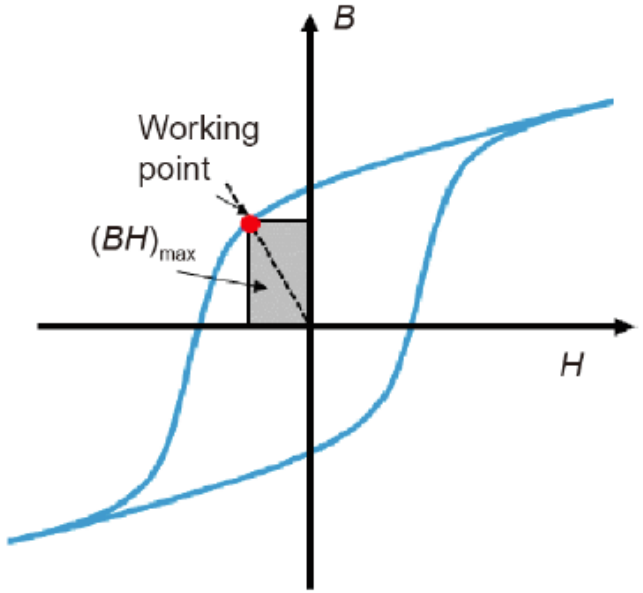
vs coercivity $\boldsymbol{H_c}$

$H_c < H_d$ unless $N \ll 1$

shaped to minimize N

$H_c > H_d$ at any N

shaped to maximize stray field



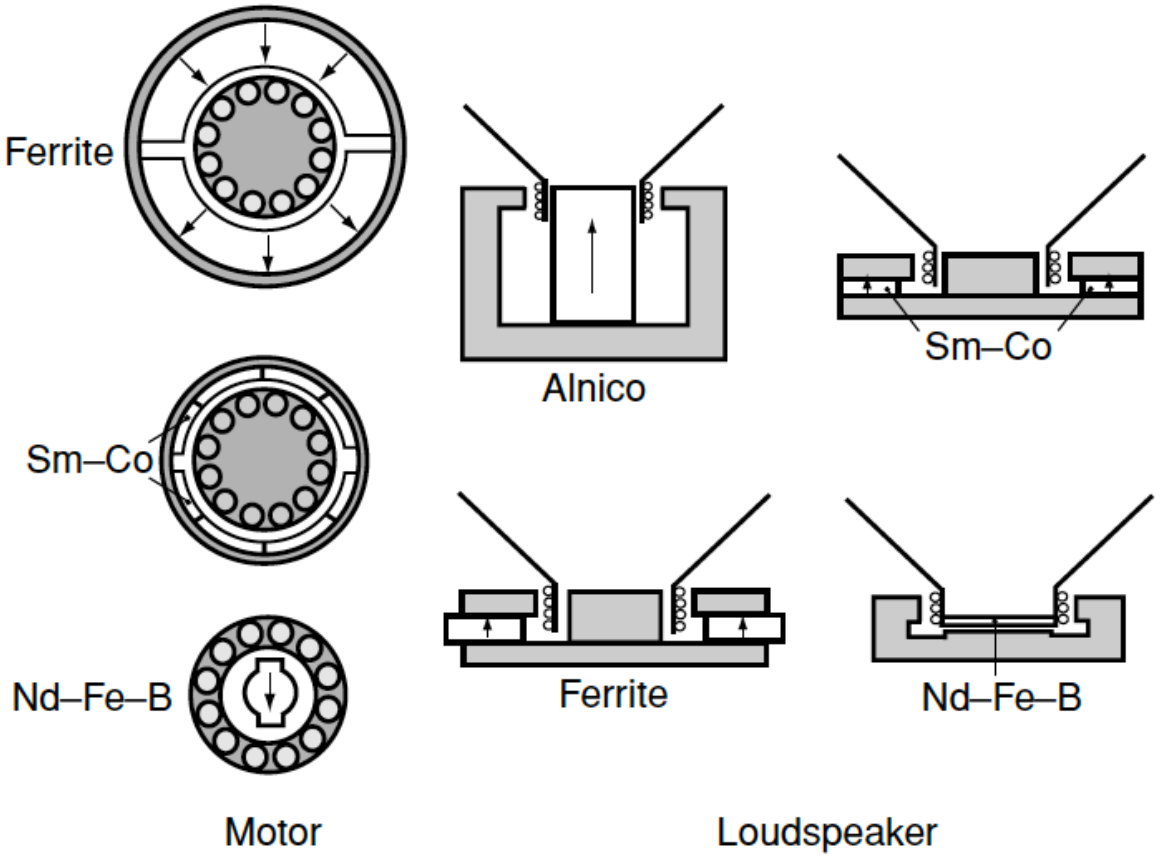
Energy stored in the stray field of ideal magnet

$$BH = \mu_0(H+M)H = \mu_0(1-\mathcal{N})\mathcal{N}M_s^2$$

Ideal magnet $(N = 1/2)$ $|BH|_{MAX} = \mu_0 M_s^2/4$

Coey IEEE Trans. Magn. 47, 4671 (2011), Engineering 6, 119 (2020)

Permanent magnets for applications



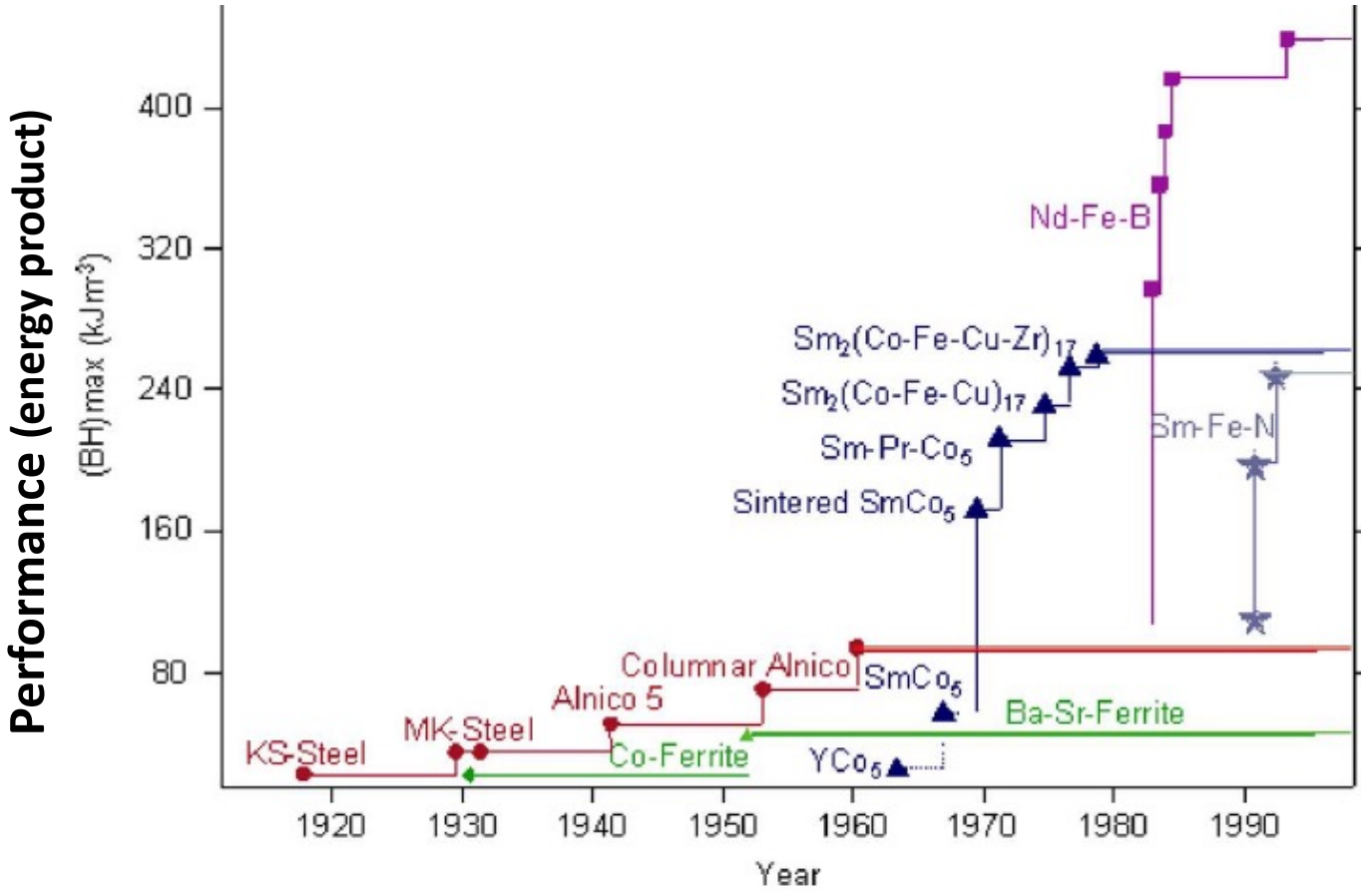
Coey "Magnetism and magnetic materials" (Cambridge 2009)

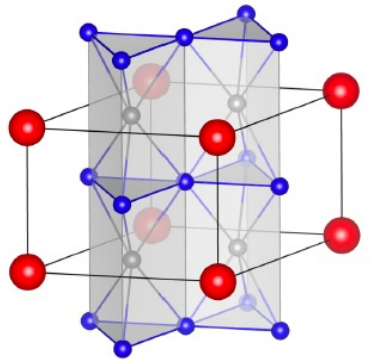
Applications need maximum energy product $|BH|_{MAX}$ at finite T!

- **High magnetic density (M_s)**
  intrinsic property
- **High coercivity (H_c)**
  defined by intrinsic magnetic hardness (anisotropy field H_A) and microstructure.
  Maximum H_c ≈20-30% H_A
- **High Curie temperature (T_c)**
  intrinsic property

Rare-earth-based permanent magnets

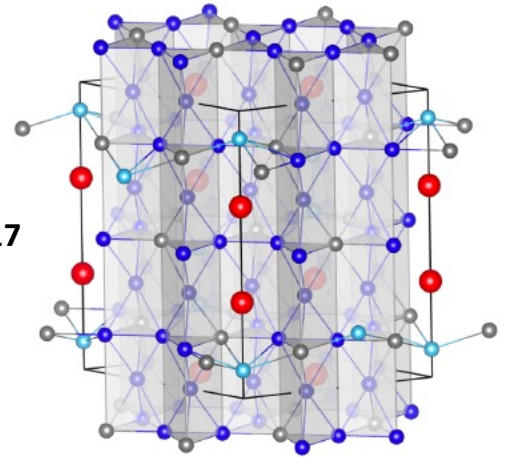
Increasing performance of hard magnets in XX century





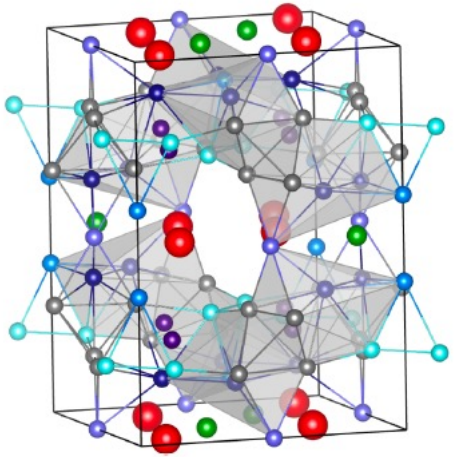
1-5 family (1960s)

$SmCo_5$



2-17 family (1970s)

$Sm_2(Co, Fe, Cu\ Zr)_{17}$



2-14-1 family (1980s)

$Nd_2Fe_{14}B$

$(Nd,Dy)_2Fe_{14}B$

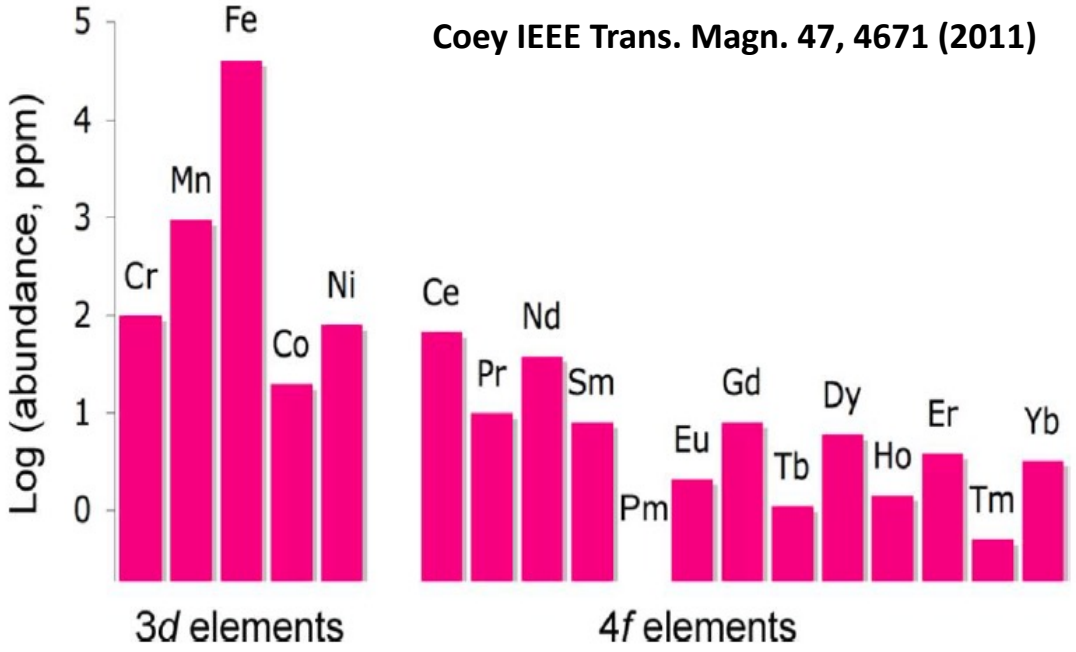
Coey IEEE Trans. Magn. 47, 4671 (2011)

Myake & Akai JPSJ 87, 041009 (2018)

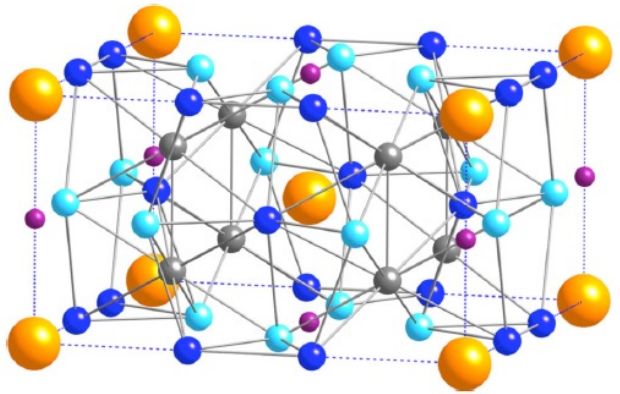
Rare-earth-base permanent magnets: current challenges

Abundance of elements in Earth crust

Coey IEEE Trans. Magn. 47, 4671 (2011)



"1-12" family:



$RFe_{11}X$

(i) low concentration of RE; (ii) good intrinsic properties, but (iii) poor thermodynamic stability and microstructure challenges

- **Heavy REs are rare and expensive**
- **Light RE (Ce) do not provide sufficient magnetic hardness**
- **No new industry relevant RE-based permanent magnets family discovered since 1980s**

Goals: predict intrinsic hardness (magnetocrysalline anisotropy)

in perspective TM-RE systems to search for new RE permanent magnets

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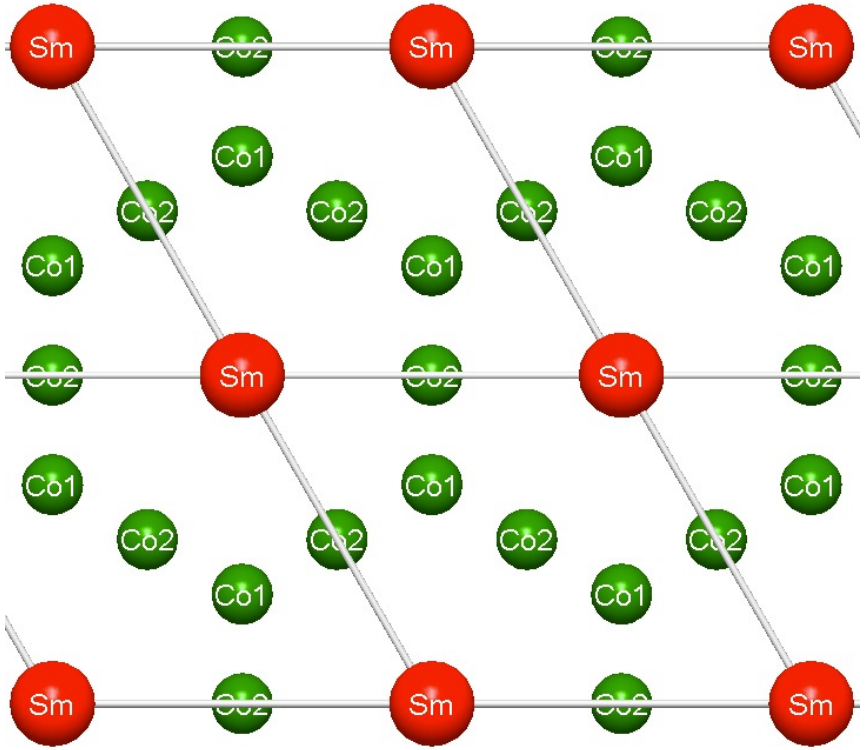
Hard-magnetic intermetallics: a two-sublattice picture

$SmCo_5$: view along hex *c* axis



- **Dense TM lattice (Fe, Co):**
  - **high magnetization density**
  - **high Curie temperature**
- **Rare-earth sublattice:**
  - **large spin-orbit → high single-ion anisotropy**

Hierarchy of intersite interactions:

$$(3d\text{-}3d) \gg (3d\text{-}4f) \gg (4f\text{-}4f)$$

- **TM: strong spin-polarization, no dynamical correlations** → **magnetic GS in DFT**
- **RE: atomic 4*f* multiplets perturbed by environment (crystal and exchange fields)** → **beyond standard DFT**

TM magnetism and TM-RE exchange coupling

Total TM moments (μ_B) per site

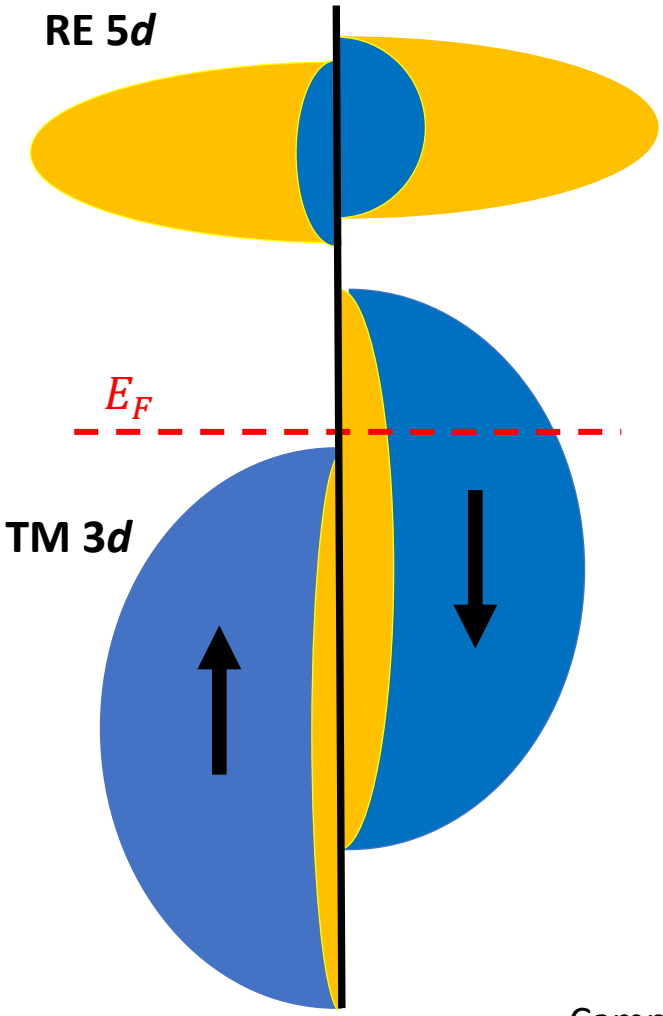
$Nd_2Fe_{14}B$	bcc-Fe	$SmCo_5$	hcp-Co
2.2	2.22	1.79	1.72

similar to elemental itinerant 3d ferromagnets

Curie temperature (K)

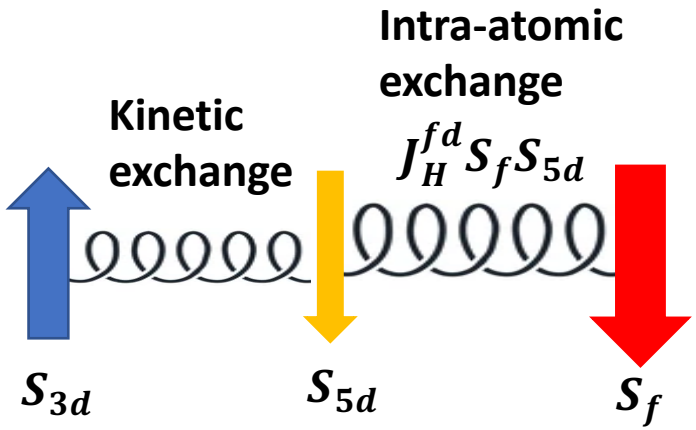
$Nd_2Fe_{14}B$	bcc-Fe	$SmCo_5$	hcp-Co
585	1044	997	1360

lower than in elemental 3d ferromagnets



$$M_S(3d) > 0$$

Hybridization-admixed 5d below E_F $M_S(5d) < 0$



Coey "Magnetism and magnetic materials" (Cambridge 2009)
Herbst, Rev. Mod. Phys. 1991
Givord et al. J. Appl. Phys. 1979

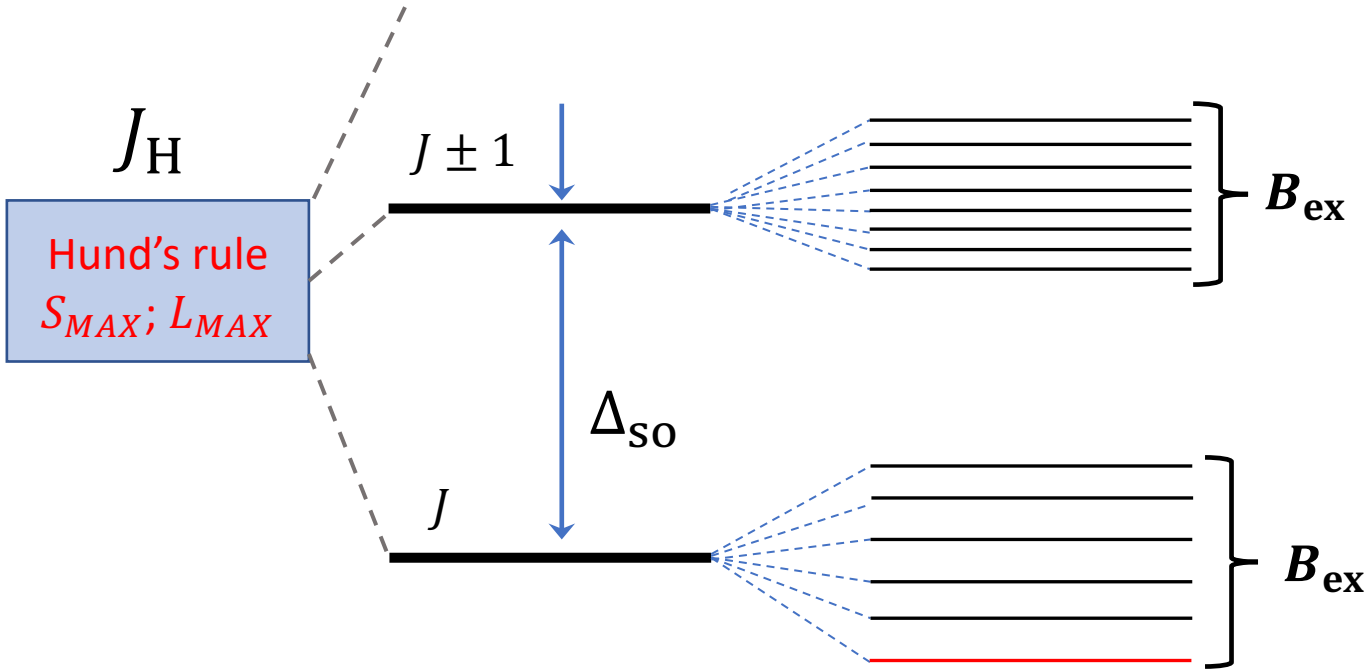
Campbell J. Phys. F: Met. Phys. 1972
Brooks et al. J. Phys.: Cond. Mat. 1989

Rare-earth single ion anisotropy: the origin

Hierarchy of interaction on the 4f shells in RE permanent magnets

$$U \gg J_{\mathrm{H}} \gg \Delta_{\mathrm{so}} \gg B_{\mathrm{ex}} > \Delta_{\mathrm{cf}}$$

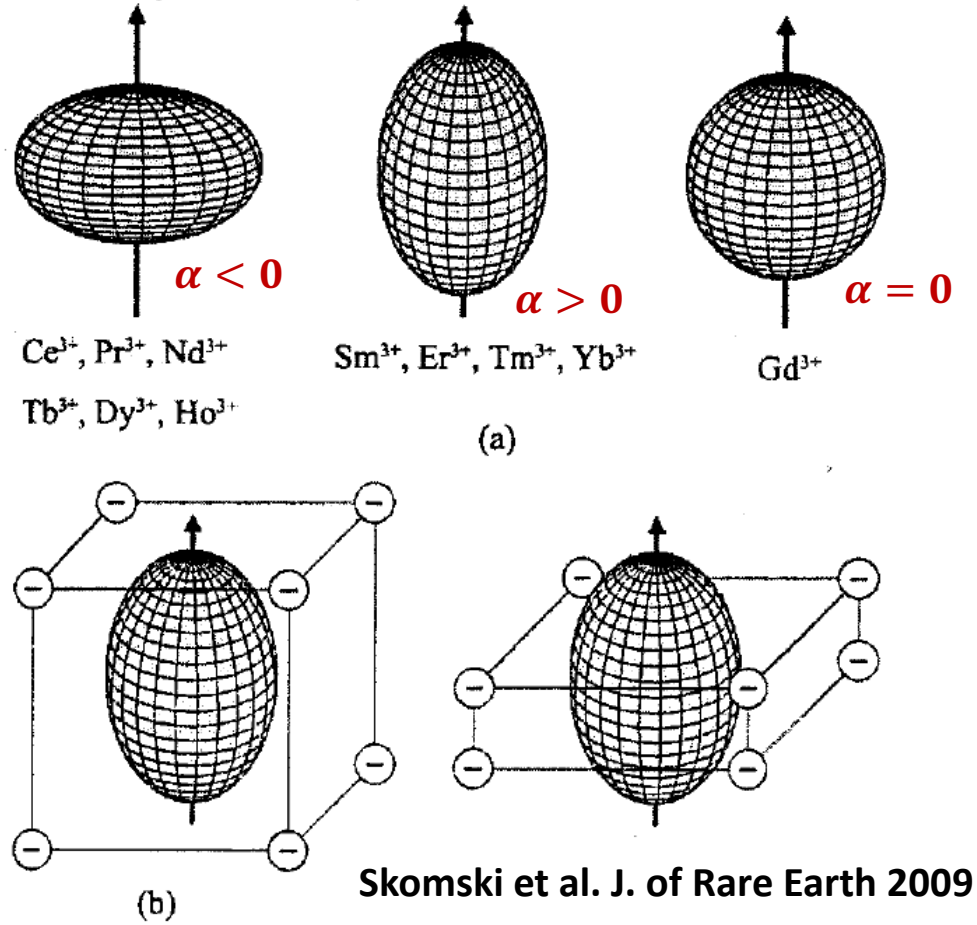
Coulomb — Hund's rule — Spin-orbit — Exchange field — Crystal field



Ground state: $J_z = J;\ S_z = (g-1)J$

4*f* charge density coupled to spin by SO

Charge density clouds for RE 3+ ions



Skomski et al. J. of Rare Earth 2009

Point-charge model: intuitive, but not quantitative!

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Crystal-field formalism

e.g. Kuz'min & Tishin, in Handbook of Magnetic Materials, Vol. 17 (2007)

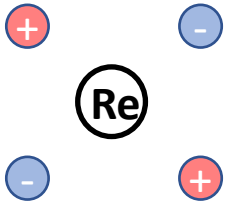
4f shell Hamiltonian: $H_{4f} = E_0 + H_U + H_{\mathrm{so}} + 2\mu_B \boldsymbol{B}_{\mathrm{ex}} \hat{\boldsymbol{S}}_f + H_{\mathrm{cf}}$

Crystal field within 4*f* shell $\langle \varphi^f_m \sigma | H_{\mathrm{cf}} | \varphi^f_{m'} \sigma' \rangle = \delta_{\sigma\sigma'} \langle \varphi^f_m | V_{\mathrm{ns}}(\boldsymbol{r}) | \varphi^f_{m'} \rangle$

Non-spherical 1-electron potential expanded in real spherical tensors $V_{\mathrm{ns}}(\mathbf{r}) = \sum_{k=1}^{\infty} \sum_{q=0}^{k} A_k^q(r) T_k^q(\hat{r})$

$$T_k^q(\hat{r}) = \begin{matrix} Y_k^0(\hat{r})/N_k & q = 0 \\ [Y_k^q(\hat{r}) + Y_k^{-q}(\hat{r})]/N_k & q > 0 \end{matrix}$$

[in point-charge model $\langle \varphi^f | A_k^q(r) | \varphi^f \rangle = \langle \varphi^f | A_k^q r^k | \varphi^f \rangle = A_k^q \langle r^k \rangle$ → popular CFP notation]



CF is a one-electron operator: $H_{\mathrm{cf}} = \sum_{kq} A_k^q \langle r^k \rangle \hat{T}_k^q \; ; \quad \hat{T}_k^q = \sum_{mm'\sigma} \langle Y_3^m | T_k^q | Y_3^{m'} \rangle f^\dagger_{m\sigma} f_{m'\sigma}$

Only even $k = 2, \ldots, 2l (= 2, 4, 6$ for *f*-electrons$)$ contribute ⇒ max. 15 crystal-field parameters (CFP) in total

$0 \le q \le k$ in a system with inversion

$[3\, A_2^q + 5\, A_4^q + 7\, A_6^q]$

Reduced by point-group symmetry: **only 2 independent CFP in cubic symmetry** A_4^0 and A_6^0

4 CFPs in hexagonal case A_2^0, A_4^0, A_6^0 and A_6^6

Full two-sublattice model at finite temperature: our approach

$$F = F_{3d} + F_{4f} + F_Z$$

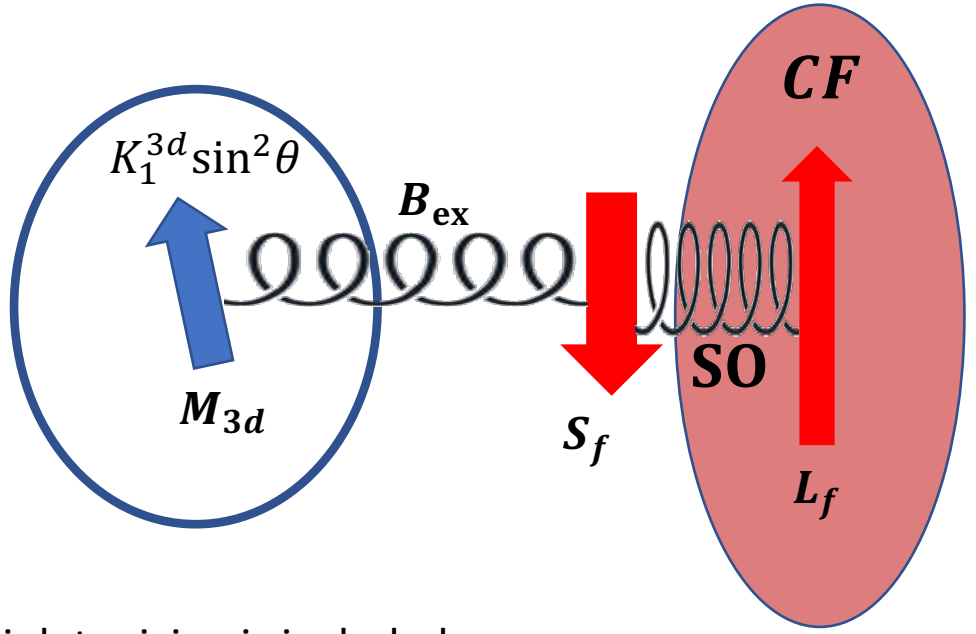
$F_{3d} = K_1^{3d}(T)\sin^2\theta$ **TM anisotropy**

$F_{4f} = -T \ln \mathrm{Tr}[\exp(-H_{4f}/T)]$ **RE ions in quasiatiomic picture**

$$H_{4f} = H_{\mathrm{SO}} + H_{\mathrm{ex}} + H_{\mathrm{cf}}$$

$$= \lambda_{\mathrm{SO}} \boldsymbol{S}_f \boldsymbol{L}_f + 2\mu_B B_{\mathrm{ex}}(T) \boldsymbol{n}_S^{3d} \boldsymbol{S}_f + \sum_{kq} A_k^q \langle r^k \rangle \hat{T}_k^q$$ multiplet mixing is included

$F_Z = -H_{\mathrm{ext}}[M_{4f}(T) + M_{3d}(T)]$ **external field**



- F_{4f} ⇒ all parameters are from ab initio: CFPs $A_k^q\langle r^k\rangle$, exchange field B_{ex}, spin-orbit λ_{SO}
- F_{3d} ⇒ zero-temperature ab initio (M_{3d}, K_1^{3d}), semi-empirical temperature dependence

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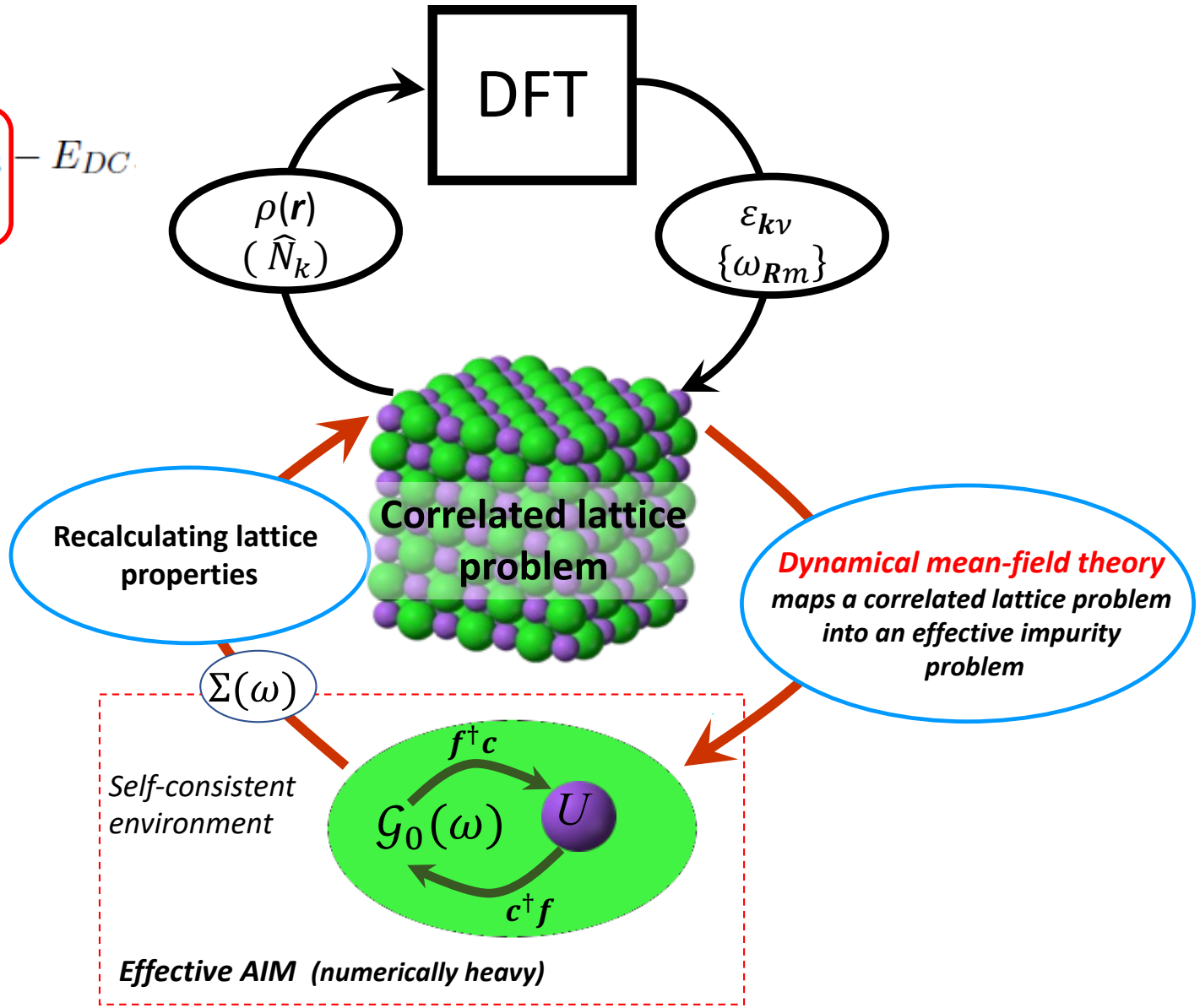
Ab initio approach to correlated states: DFT+DMFT

Correlated lattice problem:

$$\hat{H}_{DFT+U} = \sum_{k\nu} \varepsilon_{k\nu} c^{\dagger}_{k\nu} c_{k\nu} + \sum_{\substack{i, \\ 1,2,3,4}} \langle 12|U|34\rangle f^{\dagger}_{i1} f^{\dagger}_{i2} f_{i4} f_{i3} - E_{DC}$$

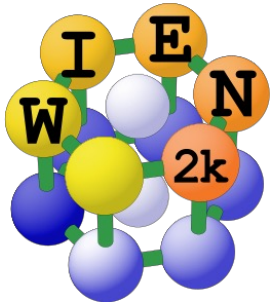
Metzner & Vollhardt PRL 1989
Georges & Kotliar PRB 1992
Anisimov et al. J. Phys. Cond.Mat. 1997
Lichtenstein & Katsnelson PRB 1998

some reviews:
Georges et al. Rev. Mod. Phys. 1996
Kotliar et al. Rev. Mod. Phys. 2006
Georges AIP Conf. Proc. 2004
arXiv:0403123



DFT+DMFT: details of implementation and calculations

- **Wien2k electronic structure code**
  http://susi.theochem.tuwien.ac.at/



- **"TRIQS" implementation of DMFT and its interface with Wien2k**
  https://triqs.github.io/

TRIQS

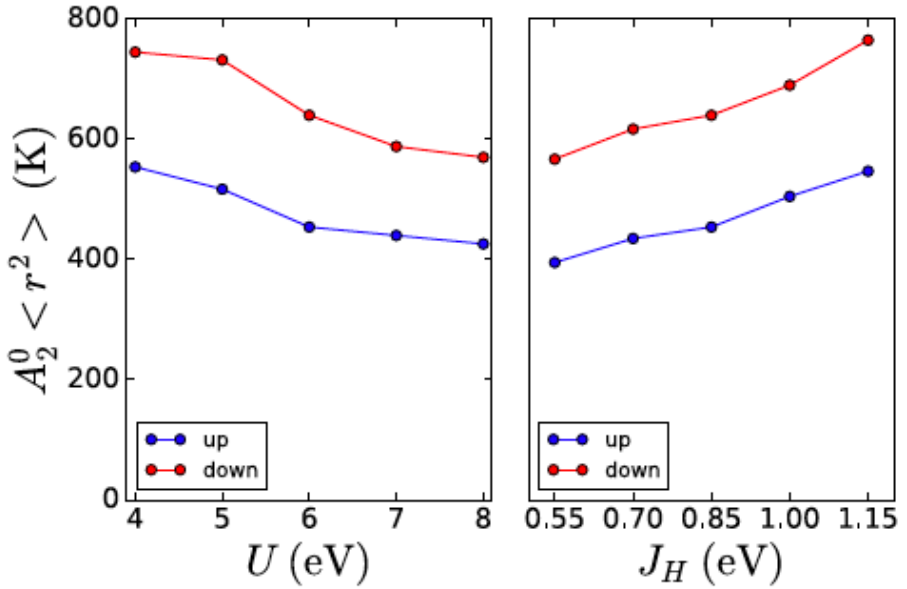
M. Aichhorn et al. Computer Physics Communications 204, 200 (2016)

- ***U* and J_H : have little impact on results as long as they are sufficiently large**

U=6 to 8 eV

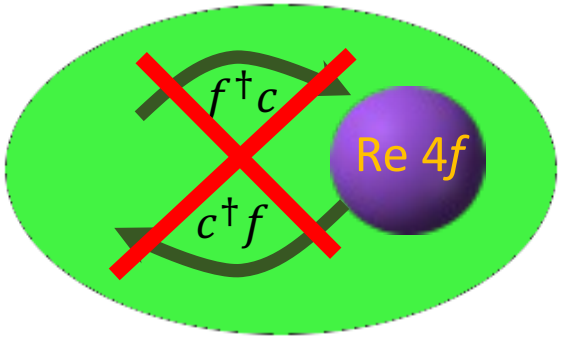
J_H [independent from crystalline environment for RE]
from optical measurements on RF_3
Carnall et al. J. Chem. Phys. 90, 3443 (1989)

CFP in $NdFe_{11}N$ vs U and J_H
Delange et al. PRB 96, 155132

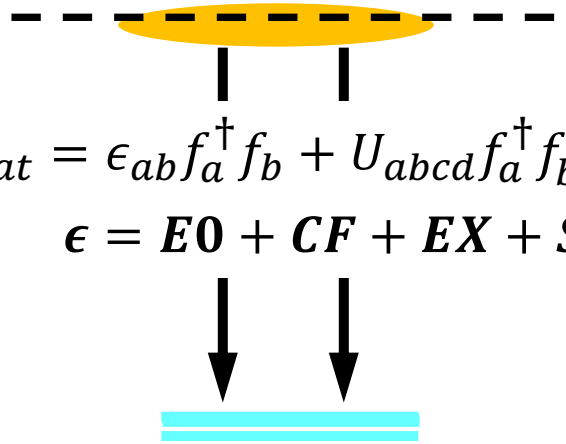


Quasi-atomic (Hubbard-I) approximation

J. Hubbard, Proc. R. Soc. A 1963



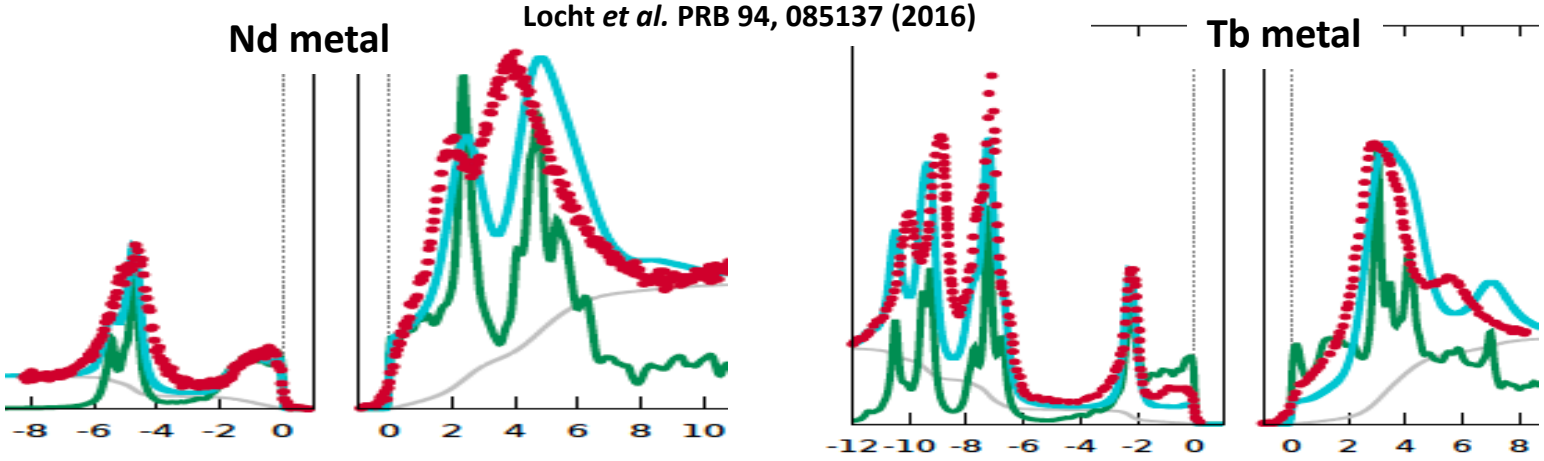
DFT 4*f* levels E_F



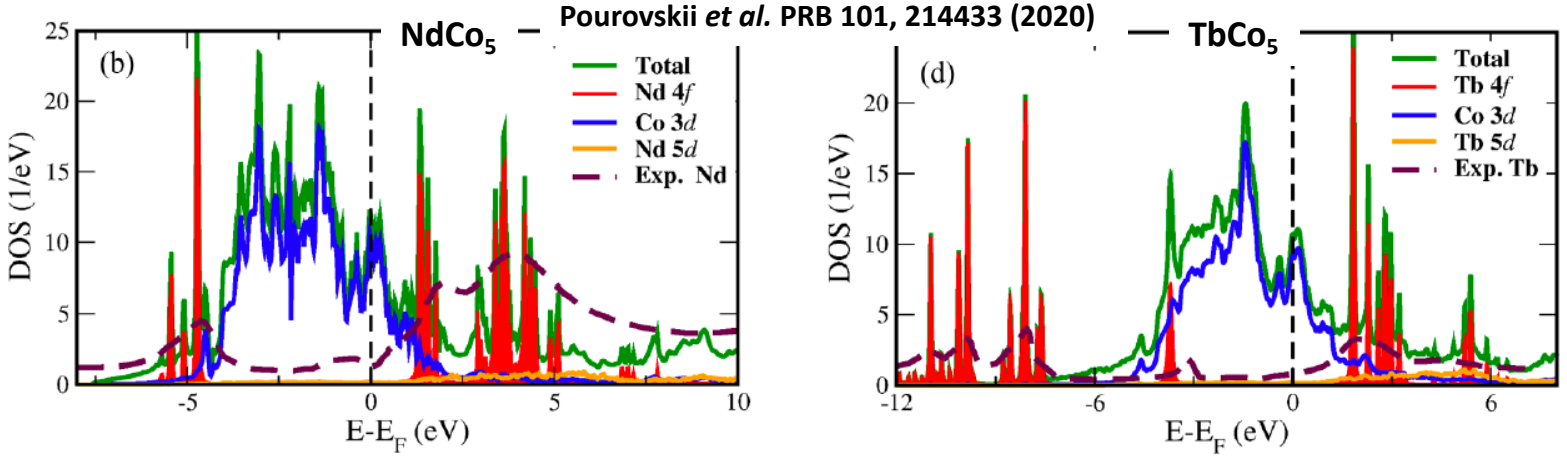
$$H_{at} = \epsilon_{ab} f_a^\dagger f_b + U_{abcd} f_a^\dagger f_b^\dagger f_d f_c$$

$$\epsilon = \boldsymbol{E0} + \boldsymbol{CF} + \boldsymbol{EX} + \boldsymbol{SO}$$

Locht *et al.* PRB 94, 085137 (2016)



Pourovskii *et al.* PRB 101, 214433 (2020)



DFT+Hubl **cannot** describe

- **Kondo/intermediate valence effects**

BUT can be very useful to describe:

- **quasi-atomic electronic structure 4*f***
- **crystal field (CF)and the resulting RE single-ion magnetic anisotropy**

- RE *4f* crystal fields from DFT+Hubbard-I

PHYSICAL REVIEW B **96**, 155132 (2017)

Crystal-field splittings in rare-earth-based hard magnets: An *ab initio* approach

Pascal Delange,[1] Silke Biermann,[1,2] Takashi Miyake,[3] and Leonid Pourovskii[1,2,4]

Crystal-field from DFT+Hubbard-I: a straightforward naive approach

1. **Obtain one-electron levels for RE 4f shell by self-consistent DFT+Hubbard-I:**

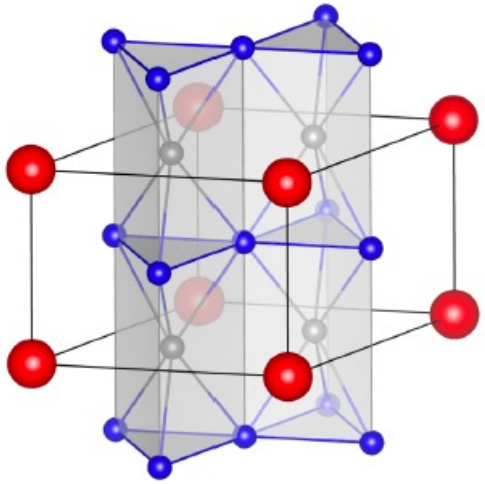
$$\epsilon = -I\mu + \sum_{\mathbf{k}} P_{\mathbf{k}} H^{\mathbf{k}}_{\mathrm{KS}} P^{\dagger}_{\mathbf{k}} - \Sigma_{\mathrm{dc}}$$

2. **Fit them to the expected form** $H_{4f} = E_0 + 2\mu_B \boldsymbol{B}_{\mathrm{ex}} \hat{S}_z + H_{\mathrm{so}} + H_{\mathrm{cf}} + H_U$

$$\epsilon^{\sigma\sigma'}_{mm'} = \langle \varphi^f_m \sigma | H_{4f} | \varphi^f_{m'} \sigma' \rangle = (E_0 + \mu_B B_{\mathrm{ex}}) \delta_{mm'} \delta_{\sigma\sigma'} + \langle \varphi^f_m \sigma | \lambda_{\mathrm{SO}} \textstyle\sum_i \boldsymbol{l}_i \boldsymbol{s}_i | \varphi^f_{m'} \sigma' \rangle + \textstyle\sum_{kq} A^q_k \langle r^k \rangle \hat{T}^q_k$$

by a least-square ⇒ SO coupling λ_{SO}, CF parameters $A^q_k\langle r^k\rangle$ and exchange field B_{ex}

Test: $SmCo_5$



$A^0_2\langle r^2\rangle$ (K)	$A^0_4\langle r^4\rangle$ (K)	$A^0_6\langle r^6\rangle$ (K)	$A^6_6\langle r^6\rangle$ (K)	B_{ex} (Tesla)
305	**34**	**32**	**875**	**235**

Estimating anisotropy = $K_1 \sin^2\theta$:

$$K_1 = -3J\left(J - \tfrac{1}{2}\right) \alpha A^0_2 \langle r^2 \rangle$$

Sm^{3+}: J=5/2 $\alpha > 0$

$A^0_2\langle r^2\rangle > 0 \Rightarrow K_1 < 0$

easy-plane anisotropy

Wrong!!

Crystal field from DFT+Hubbard-I: correcting self-interaction

Exact XC: $\langle \varphi_m^f \sigma | H_H + H_{\mathrm{XC}} | \varphi_m^f \sigma \rangle = 0$ but

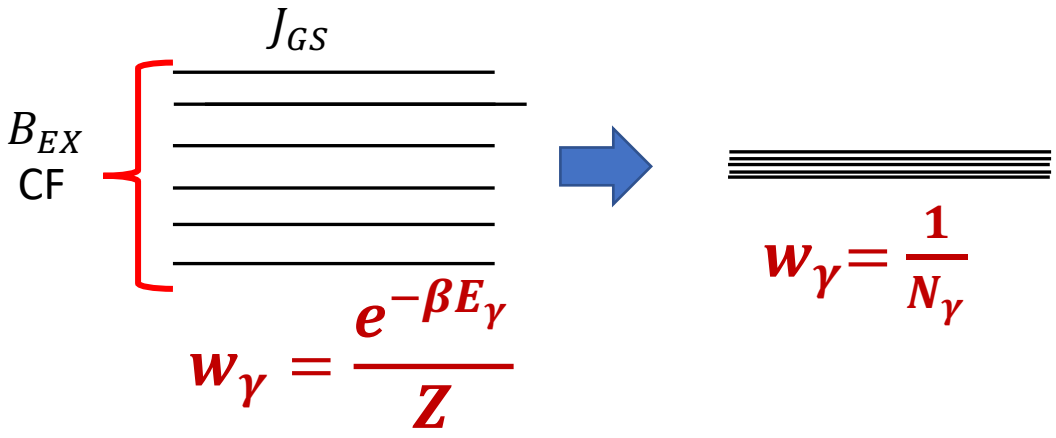
with approximate XC functionals (LDA, GGA...) $\langle \varphi_m^f \sigma | H_H + H_{\mathrm{XC}} | \varphi_m^f \sigma \rangle \neq 0$ ⇒ self-interaction!

LDA self-interaction error impacts CF splitting [Brooks *et al.*, PRL 79, 2546 (1997)] **:**

Non-uniform occupancy of 4f orbitals in DFT → Orbitally-dependent self-interaction error in $\epsilon_{mm'}^{\sigma\sigma'}$ → **wrong CF!**

Solution:

spherically averaging the ground state multiplet in self-consistent DFT+Hub-I



equal occupancy of one-electron orbitals

orbitally-independent self-interaction error (simple shift)

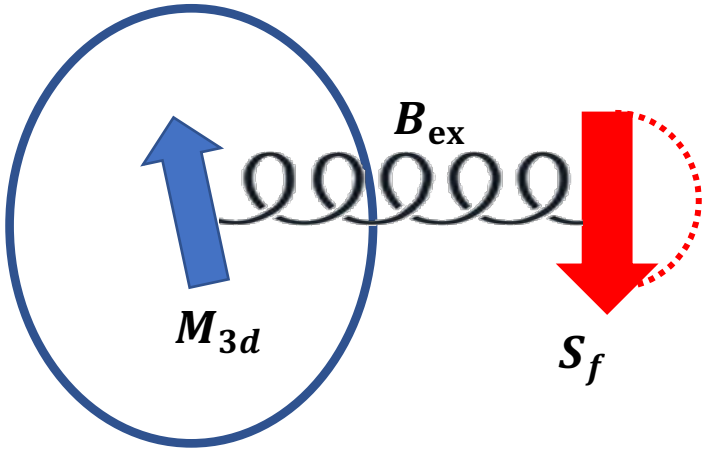
Delange et al. PRB 96, 155132 (2017)

Exchange field from DFT+Hubbard-I: suppressing spurious intra-4*f* contribution

TM magnetization ⇒ Exchange field $\boldsymbol{B}_{\mathrm{ex}}$ ⇒ 4*f* spin polarization $\langle \boldsymbol{S}_f \rangle$

but $\langle \boldsymbol{S}_f \rangle$ ⇒ DFT XC potential ⇒ 4*f* own exchange field (B_{ex}^{ff})

4*f* Hund's rule included in $\hat{H}_U$ ⇒ B_{ex}^{ff} is double counting (DC)



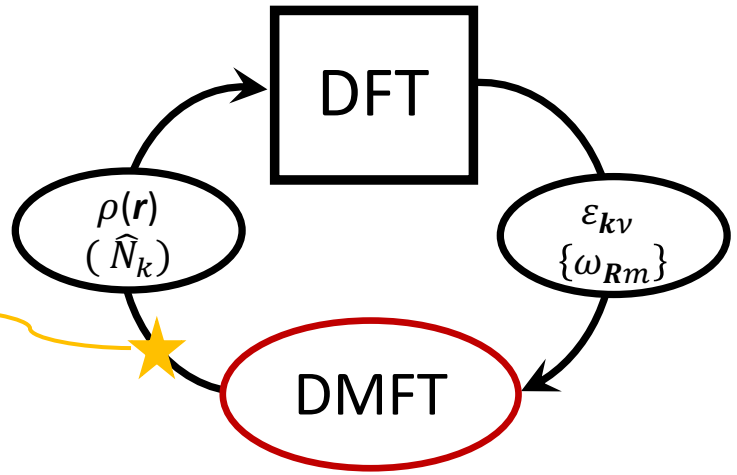
removing it by a DC correction is hard : $\dfrac{\boldsymbol{B}_{\mathrm{ex}}}{\boldsymbol{B}_{\mathrm{ex}}^{ff}} \sim \dfrac{\boldsymbol{\mu_B}\ \boldsymbol{B}_{\mathrm{ex}}}{\langle \boldsymbol{S}_f \rangle \boldsymbol{J_H}} \sim \dfrac{100 \text{ to } 300 \text{ K}}{1 \text{ to } 3 \text{ eV}}$ **< 1% !**

Solution: removing 4f spin polarization from output DMFT density

Delange et al. PRB 96, 155132 (2017)

$$\tilde{N}^{\mathbf{k}} = N^{\mathbf{k}} + \tfrac{1}{2} P^{\dagger}(\mathbf{k})[T n^{ff}(\mathbf{k}) T^{\dagger} - n^{ff}(\mathbf{k})] P(\mathbf{k})$$

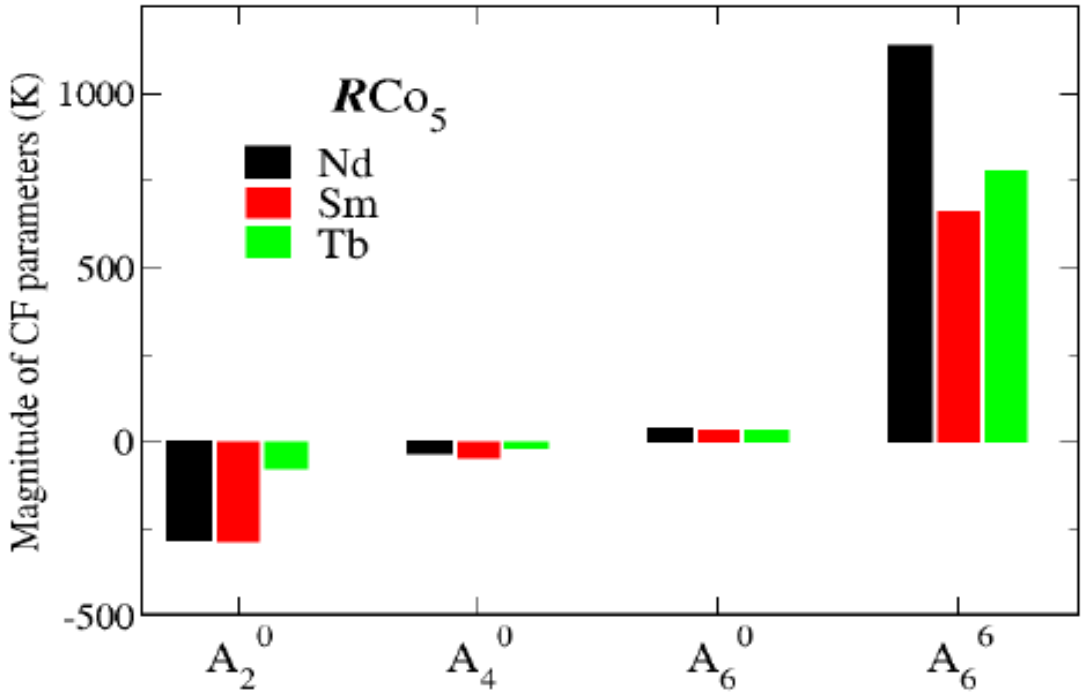
where T is the time-reversal operator



Benchmarking on RCo$_5$: CF parameters and states in SmCo$_5$

Calculated crystal-field parameters ($A_k^q\langle r^k\rangle$) in K

Delange et al. PRB 96, 155132 ; Pourovskii et al. PRB 101, 214433



$\boldsymbol{K_1} = -3J(J-\frac{1}{2})\,\alpha A_2^0\langle r^2\rangle$. **Sm^{3+}:** J=5/2 α> 0

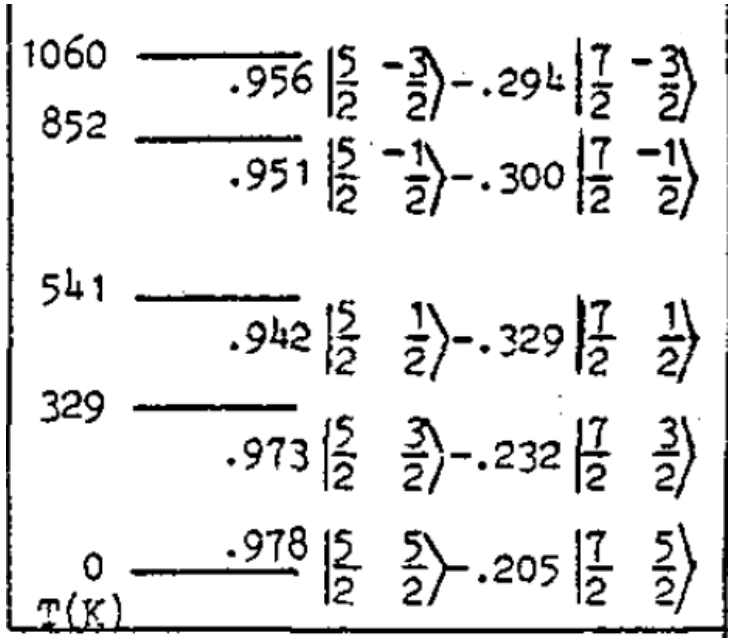
Calculated $A_2^0\langle r^2\rangle = 290$ K <0 ⇒ K_1>0 ! easy-axis anisotropy

Experimental estimates for $A_2^0\langle r^2\rangle$ in SmCo$_5$: from 180 to 330 K

Sm CF states in SmCo$_5$: theory

1097	$+0.989\|5/2;+5/2\rangle - 0.122\|7/2;+5/2\rangle$
1000	$+0.977\|5/2;+3/2\rangle - 0.211\|7/2;+3/2\rangle$
826	$+0.977\|5/2;+1/2\rangle - 0.209\|7/2;+1/2\rangle$
606	$+0.973\|5/2;-1/2\rangle - 0.225\|7/2;-1/2\rangle$
380	$+0.983\|5/2;-3/2\rangle - 0.181\|7/2;-3/2\rangle$
0	$+0.984\|5/2;-5/2\rangle - 0.171\|7/2;-5/2\rangle$

Exp. (magnetic form-factor) Givord et al. JAP 1979



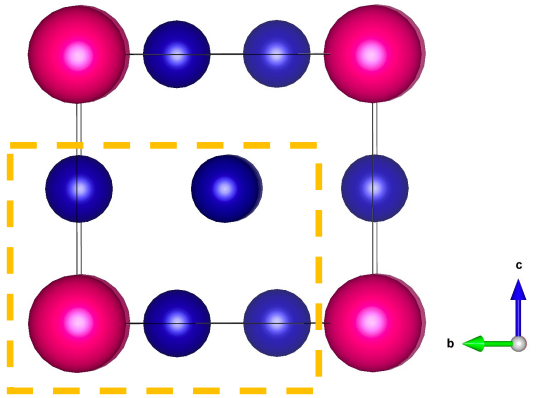
- High-rank crystal field, magnetization and CF excitations in $NdCo_5$

PHYSICAL REVIEW B **101**, 214433 (2020)

Higher-order crystal field and rare-earth magnetism in rare-earth–Co_5 intermetallics

L. V. Pourovskii,[1,2] J. Boust,[1] R. Ballou,[3] G. Gomez Eslava,[3] and D. Givord[3,*]

$NdCo_5$: the puzzle of unsaturated moment



- **Isostructural to $SmCo_5$**
- **Spin-reorientation transition at T_{SR}~280 K**
- **T<T_{SR} Nd anisotropy forces M_{tot}||[100]**

4*f* ground state from magn. form-factor exp.:

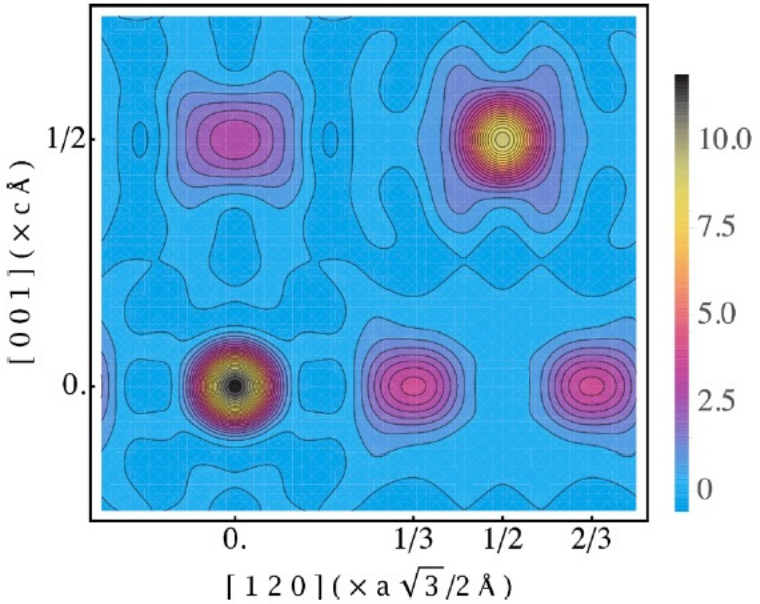
$$|\Psi_G> = .830\,|9/2, -9/2> - .558\,|9/2, -5/2>$$

Alameda *et al.* J. de Physique Colloque 43(C7), 133 (1981)

GS $M_{Nd} = 2.82\mu_B < M_{Nd}^{Sat} = 3.27\ \mu_B$

puzzling unsaturated Nd moment under large exchange field ~300 Tesla

Projected magnetic density from measured magnetic structure factors



Pourovskii et al. PRB 101, 214433 (2020)

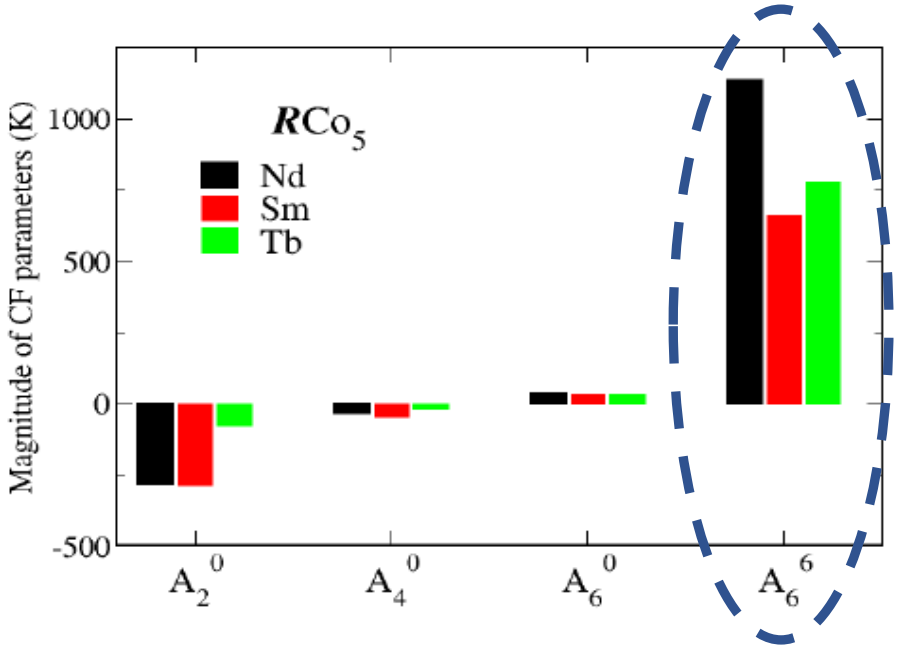
Theoretical Nd 4*f* GS

(1st exited ~220 K above)

$$0.83|9/2; -9/2> -0.54|9/2; -5/2>$$

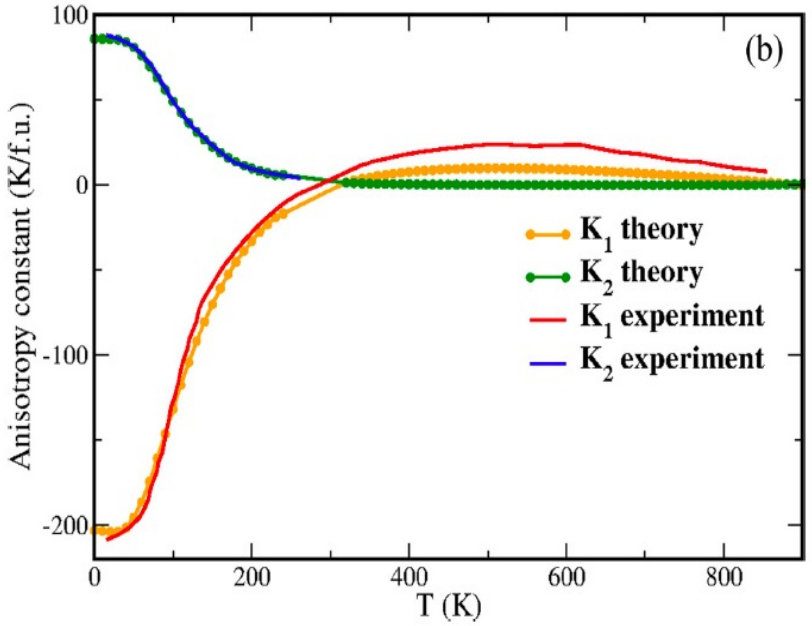
with mag. mom=2.67 μ_B

with $A_6^6\langle r^6\rangle$ set to 0 → Nd 4*f* GS =| $9/2;\ -9/2\rangle$

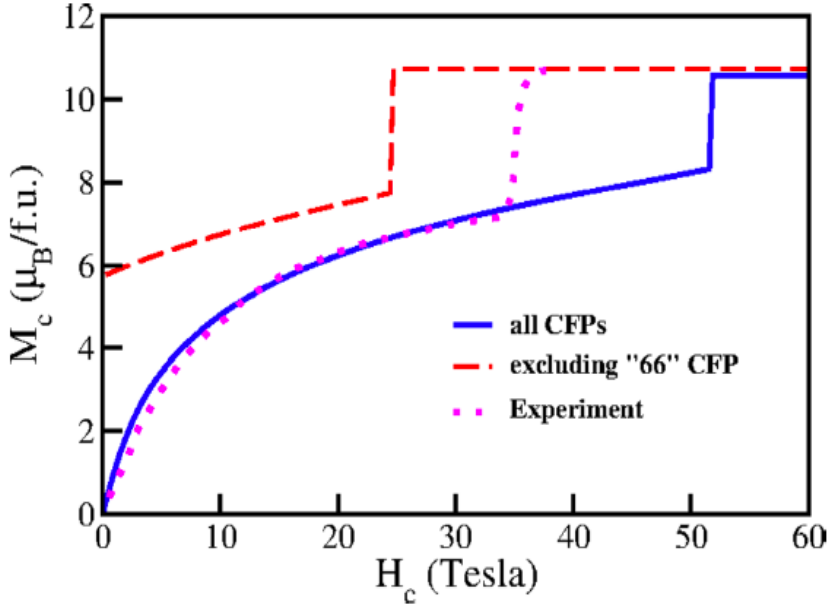


$NdCo_5$: theory vs experiment

Anisotropy constants K_1, K_2

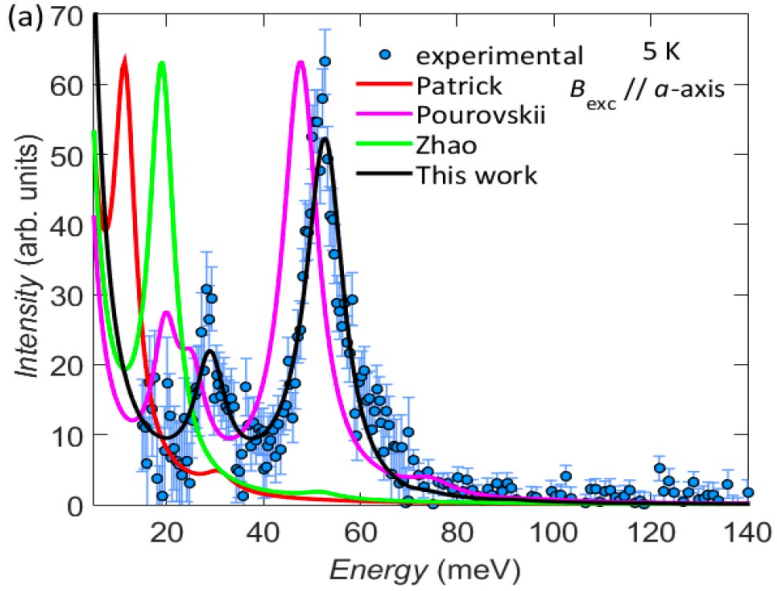


Magnetization curves along hard [001] direction



Inelastic neutron scattering

de Almeida Passos et al. arXiv:2306.00821



- **$K_1(T)$ of YCo_5 is used for Co sublattice**
- **Anisotropy constants extracted from theoretical magnetization curves** [Suscksmith-Thompson(ST) method]

Ab initio theories and magnetization curves fits vs INS

	$A_2^0\langle r^2\rangle$ (K)	$A_6^6\langle r^6\rangle$ (K)	B_{exc} (T)
custom python code	-300	900	535
SPECTRE	-460±170	1026±60	506±5
PyCrystalField	-240±100	1150±60	470±30
Patrick and Staunton PRMat (2019)	-415	146	252
Pourovskii *et al.* [3]	-285	1134	292
Zhao *et al.* PRB 43, 8593 (1991)	-510	143	558

Origin of large "66" crystal field in RCo_5

Pourovskii et al. PRB 101, 214433 (2020)

Projective construction of Wannier basis

Amadon et al. PRB 2008
Aichhorn et al. PRB 2009

$$|\chi^{\mathbf{k}}_{m\sigma}\rangle = \sum_{\nu\in\mathcal{W}} |\psi_{\mathbf{k}\nu}\rangle\langle\psi_{\mathbf{k}\nu}|\chi_{m\sigma}\rangle$$

↓ orthonormalization ↓

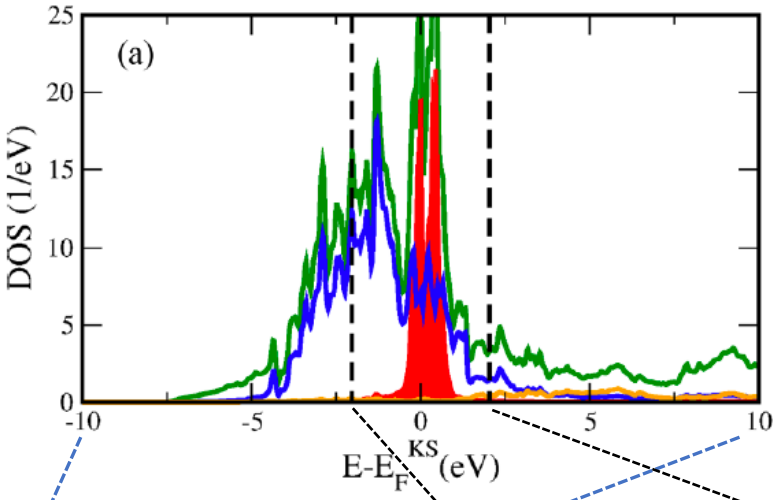
Wannier set $\{\omega^{\mathbf{k}}_{m\sigma}\}$

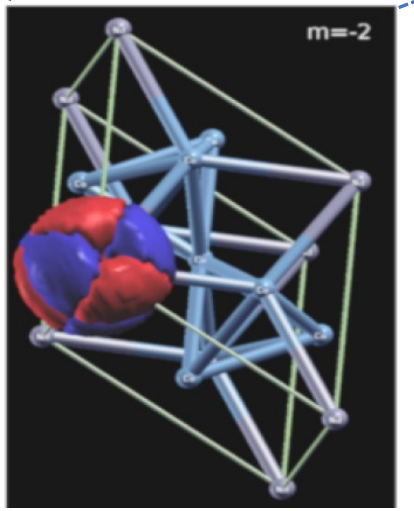
larger $\mathcal{W}$

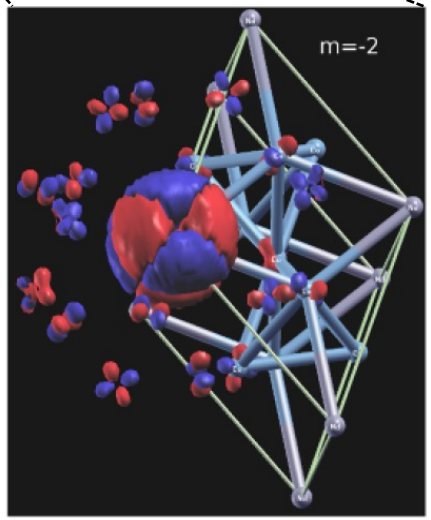
↓

more localized orbitals $\omega^{\mathbf{k}}_{m\sigma}$

$NdCo_5$ Kohn-Sham DOS

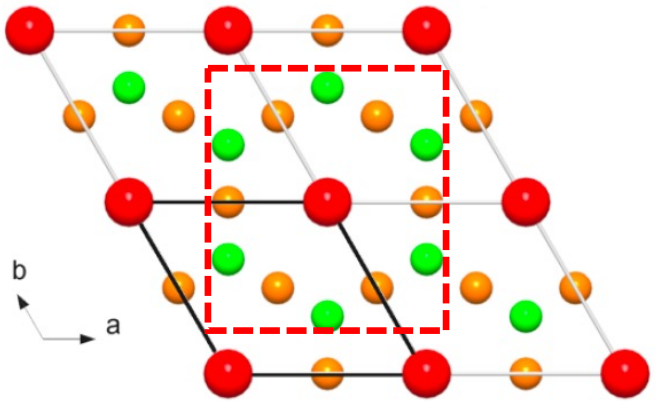






CFP & B_{ex} vs energy window

Energy window (eV)	$A_2^0\langle r^2\rangle$	$A_6^6\langle r^6\rangle$	B_{ex}
$[-10:10]$, $(\mathcal{W}_l)$	−198	45	326
$[-2:2]$, $(\mathcal{W}_s)$	−285	1134	292



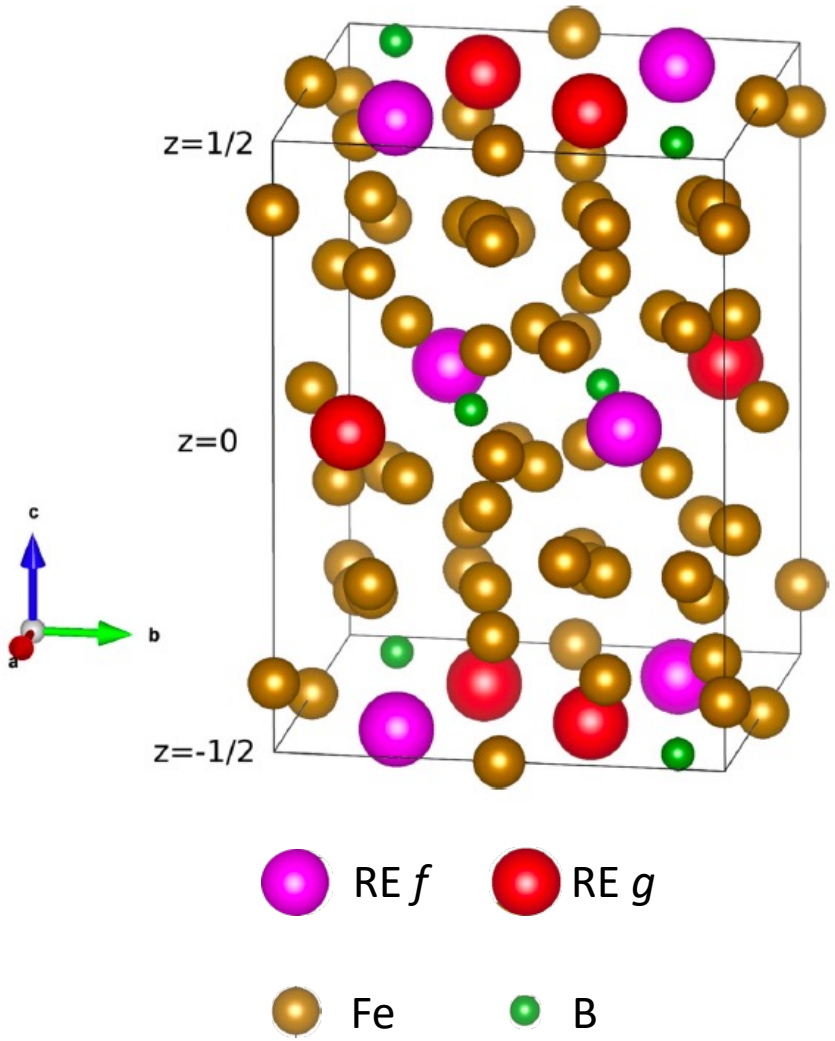
- Complex 2-14-1 magnets: crystal-field, anisotropy, effect of RE substitutions

PHYSICAL REVIEW MATERIALS **6**, 084410 (2022)

Ce and Dy substitutions in $Nd_2Fe_{14}B$: Site-specific magnetic anisotropy from first principles

James Boust,[1] Alex Aubert,[2] Bahar Fayyazi,[2] Konstantin P. Skokov,[2] Yurii Skourski,[3] Oliver Gutfleisch,[2] and Leonid V. Pourovskii[1,4]

$Nd_2Fe_{14}B$: crystal structure, composition and RE substitutions



- **Complex structure, 68 atoms/cell, 2 inequivalent RE sites**
- **Low-symmetry of RE sites → many CF parameters:**

$$H_{\mathrm{cf}} = \sum_{kq} A_k^q \langle r^k \rangle \hat{T}_k^q$$

$$A_k^q \neq 0 \text{ for } kq = 20, 2\bar{2}, 40, 4\bar{2}, 44, 60, 6\bar{2}, 64, 6\bar{6}$$

and different on the two RE sites

for review on "2-14-1" magnets see Herbst Rev. Mod. Phys. 63, 819 (1991)

- **RE substitution: Nd→ cheaper and abundant Ce, La or**

  Nd → expensive heavy RE (Dy)

  - impact on intrinsic properties?

  - effect of substitution site preference?

Generalized two-sublatice model: treatment of multiple RE sites and TM anisotropy

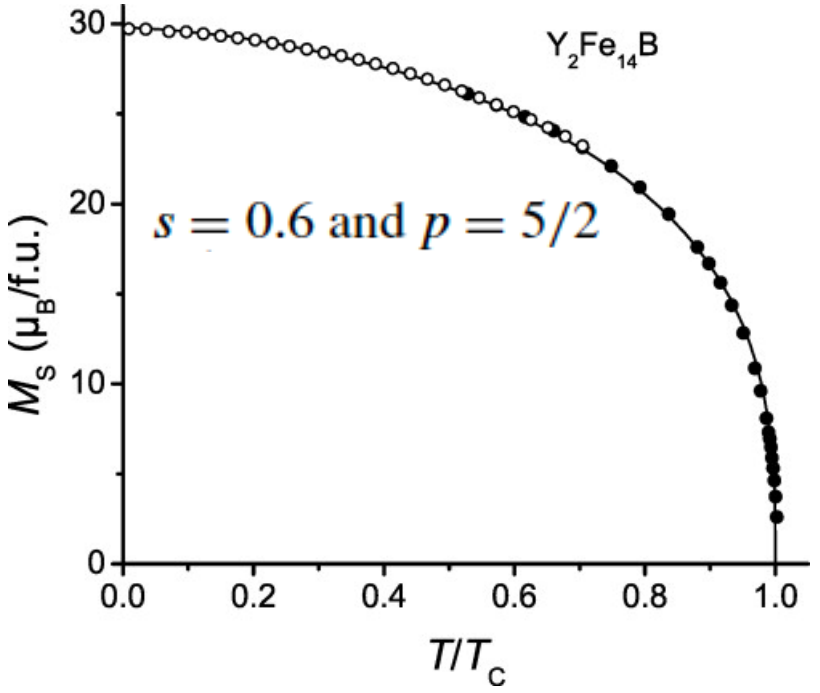
$$F(T) = \sum_{i\alpha} \omega_{i\alpha} F_{4f}^{(i\alpha)}(T) + F_{3d}(T)$$

$\omega_{i\alpha}$: **concentration of magnetic RE element α on site i**

Semi-empirical $F_{3d}(T)$ using ab initio M_{3d} ,experimental T_c and the empirical Kuz'min formula:

$$M_{3d}(T) = M_{3d}\alpha(T), \quad B_{ex}(T) = B_{ex}\alpha(T),$$

$$\alpha(T) = \left[1 - s\left(\frac{T}{T_C}\right)^{\frac{3}{2}} - (1-s)\left(\frac{T}{T_c}\right)^{p}\right]^{\frac{1}{3}}$$



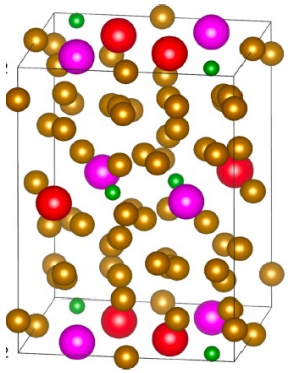
Zener formula for *T*-dependence of $K_1^{3d}(T)$:

$$K_1^{3d}(T) = K_1^{3d}(M_{3d}(T)/M_{3d})^3 = K_1^{3d}\alpha(T)^3$$

K_1^{3d} estimated from ab initio spin-orbital energy of Fe 3*d* in $La_2Fe_{14}B$ [**Liu et al. PRB 102, 205119 (2020)**]

Kuz'min Phys. Rev. Lett. 94, 107204 (2005)
Kuz'min et al. J. Appl. Phys. 107, 113924 (2010)

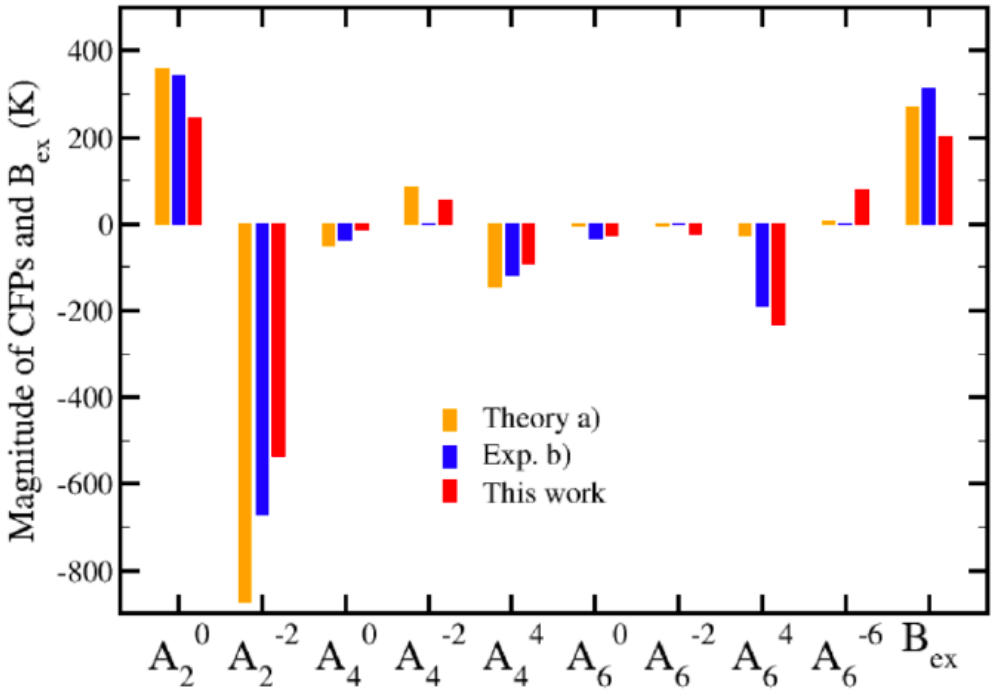
$R_2Fe_{14}B$: Nd crystal-field parameters



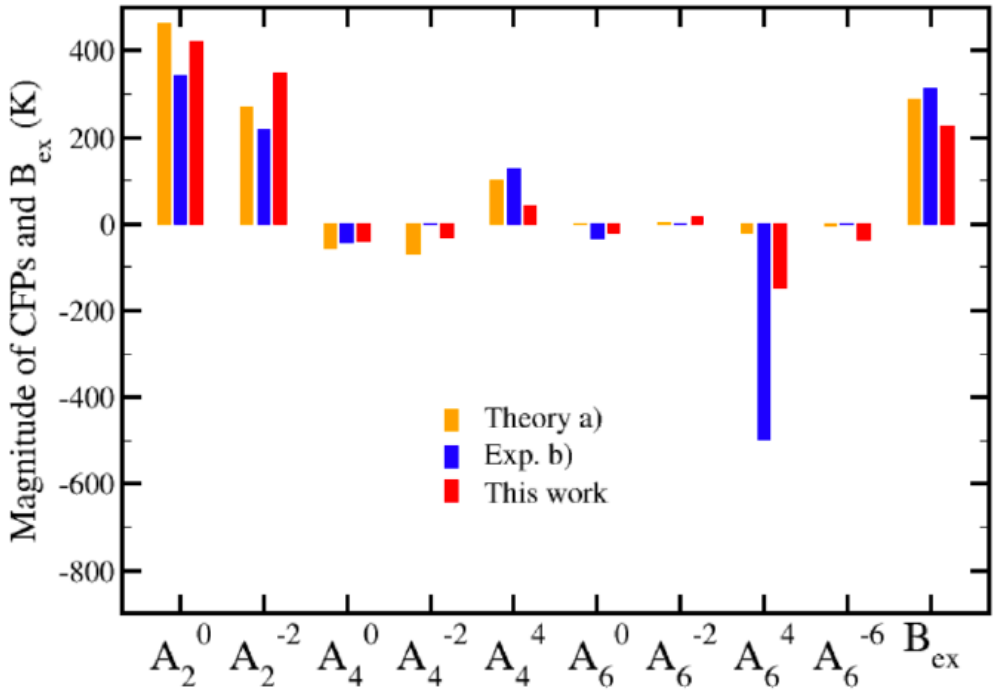
Nd *f*

Nd *g*

site *f*



site *g*

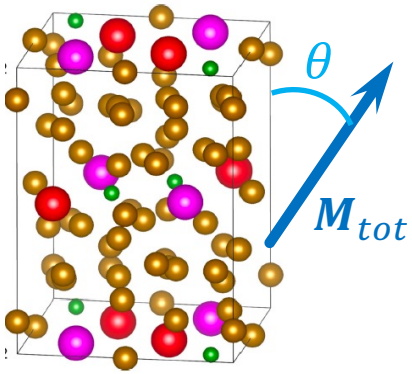


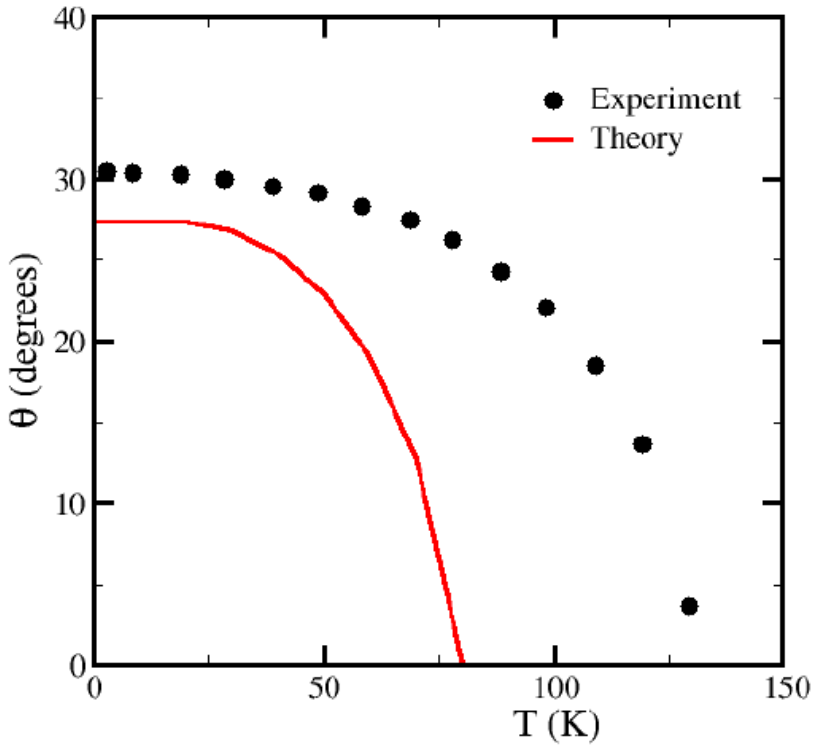
a) Sato et al. AIP Adv. 11, 025224 (2021). **b) Cadogan et al. J. Phys.F: Met. Phys. 18, 779 (1988); Gavigan et al. JMMM 72, L241 (1988)**

- Site *g*: 70% larger "20" CFP → gives the leading contribution to anisotropy
- Effect of the large "22" CFP is canceled between RE planes having opposite signs of A_2^{-2}
- Mixed systems $R_2Fe_{14}B$ → substitution on one RE site does not affect CFPs on the second one

$Nd_2Fe_{14}B$: spin-reorientation transition (SRT) and magnetic anisotropy

Azimuthal angle θ of magnetization vs *T*

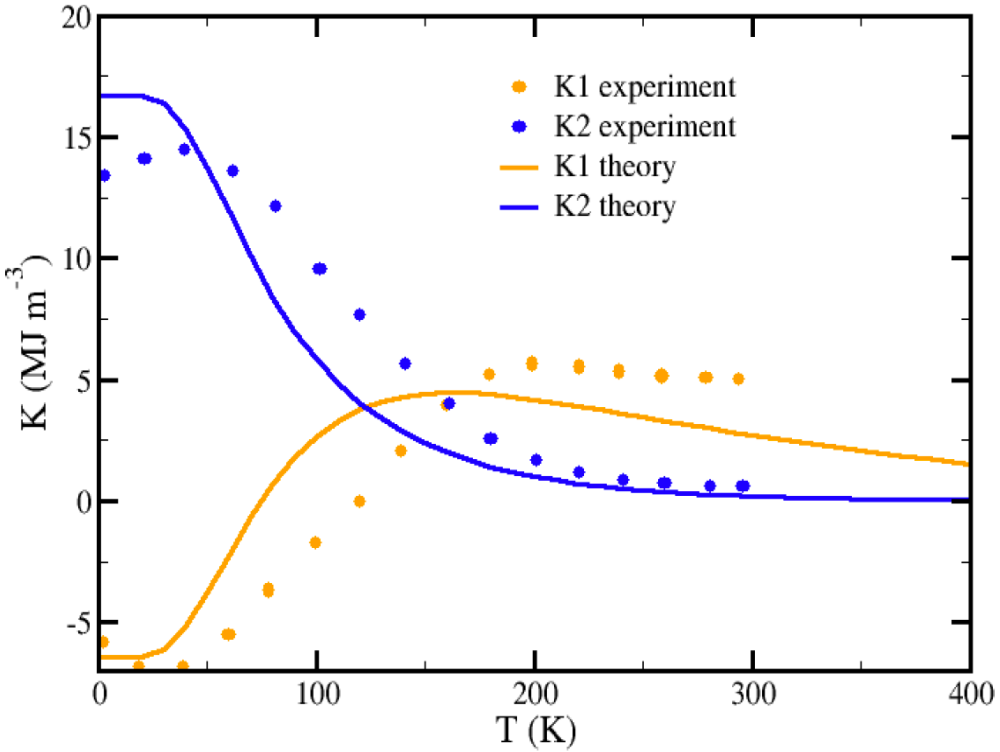




- SRT conical → uniaxial is reproduced (T_{SRT} underestimated)
- Zero-*T* conical angle θ is well reproduced

Exp.: Cadogan et al. J. Phys.F: Met. Phys. 18, 779 (1988)

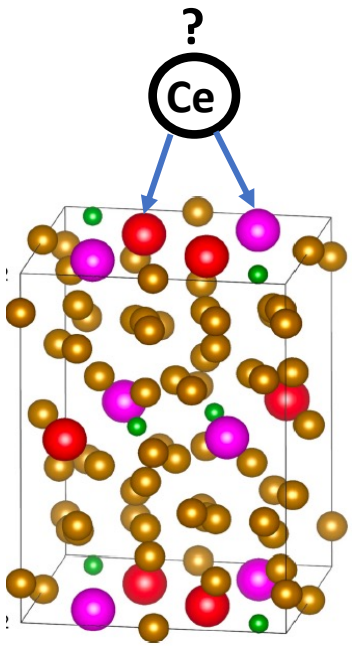
Anisotropy constants vs *T*



- Change of K_1 sign → SRT
- Good agreement, though some underestimation of K_1 at high-*T*

Exp.: Andreev et al. JETP 63, 608 (1986)

Ce substitution: impact of preferential occupancy

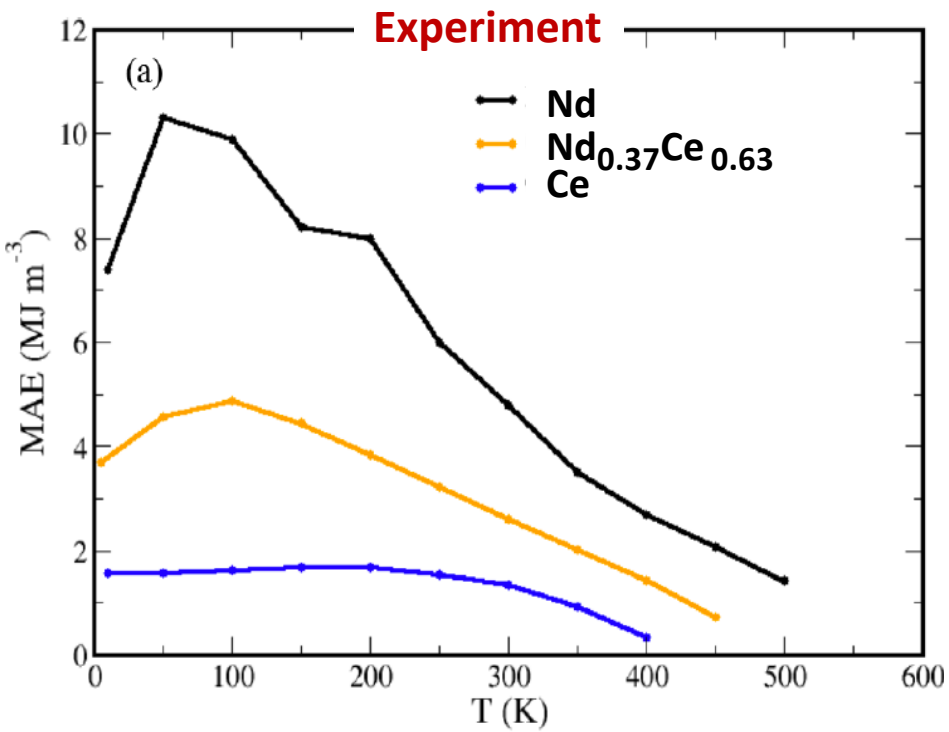


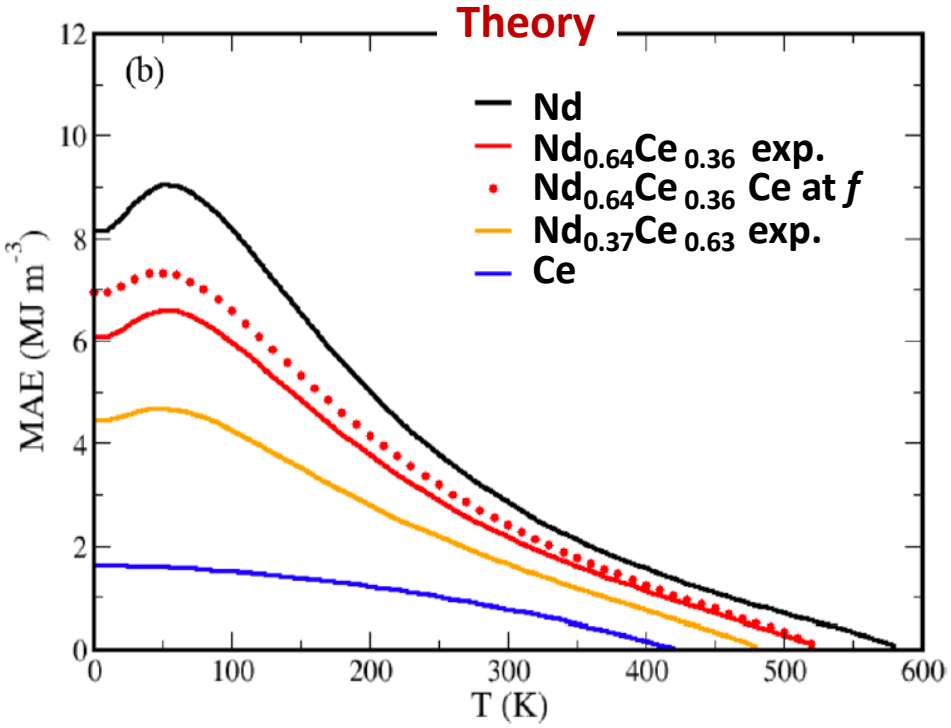
***r*(Ce 4+) < r(Nd 3+)**

Ce likely to occupy smaller ***f*** site

[exp: neutron diffraction
Colin et al. APL 108, 242415 (2016)]

Magnetocrystalline energy (MAE)

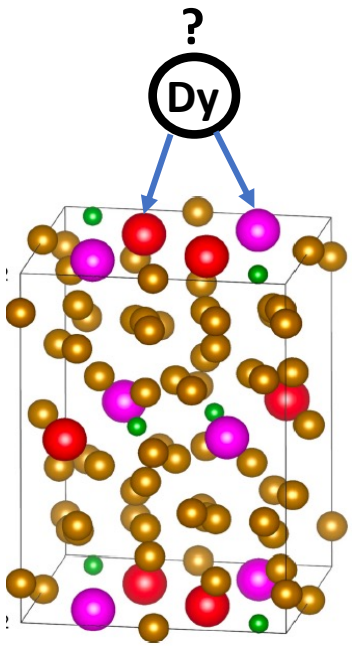




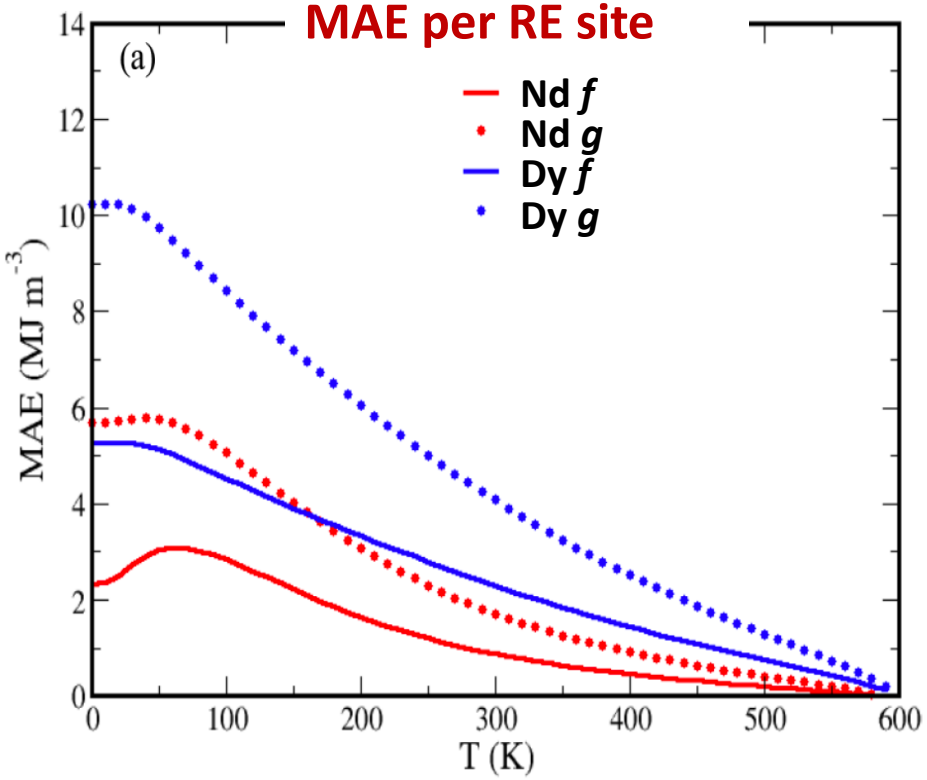
- **Good agreement with experiment for MAE=$F(M||a) - F(M||c)$**
- **Ce-at-*f* MAE by about 10% higher than for exp. occupancies**

experiment: ~60% of Ce at *f*
Colin et al. APL 108, 242415 (2016)

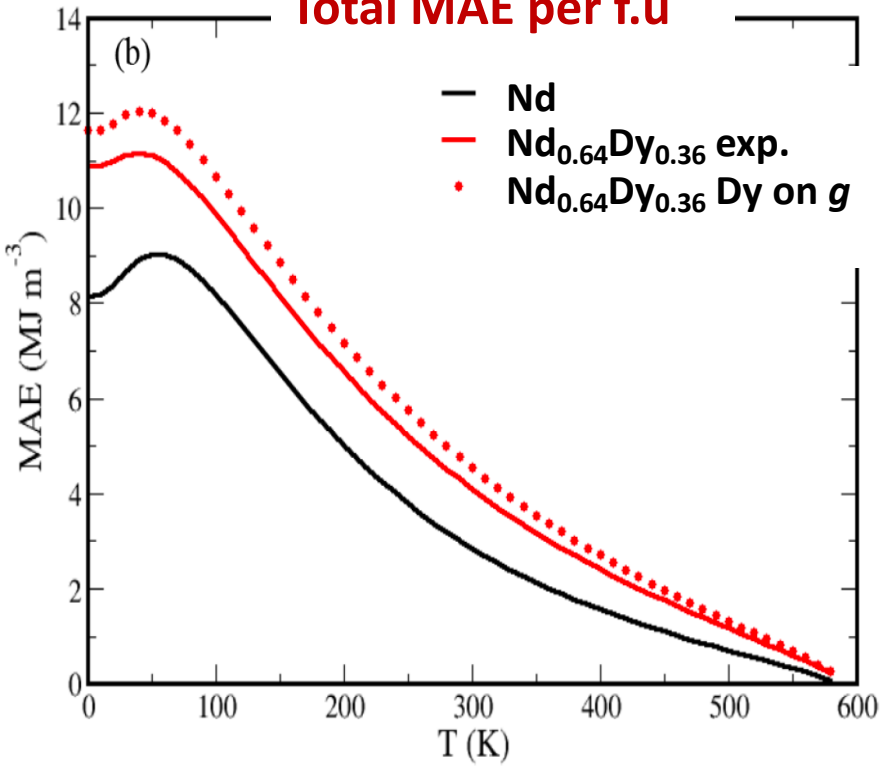
Preferential RE occupancy in $(Nd,Dy)_2Fe_{14}B$



MAE per RE site



Total MAE per f.u



***r*(Dy 3+) < r(Nd 3+)**
[rare-earth contraction]

Dy likely go to ***f*** site
[exp: 2/3 Dy goes to *f* site
Saito et al. J. Alloys Compd. 721, 476 (2017)]

- **Much larger *g*-site MAE for both Nd and Dy cases (larger for Dy)**
- **$\mathbf{MAE}(f) - \mathbf{MAE}(g)$ is similar for Nd and Dy → moderate effect on total MAE**
  [~10% at 300 K]

Challenges and perspectives

- **Improving treatment of RE-TM exchange coupling**
  [*f-f* interaction, interplay of 4f-5d and 3d-5d couplings ?]

- **Ab initio approach to TM magnetization and TM anisotropy at finite T**
  [Force-theorem exchange interactions + Monte-Carlo?]

- **Ce beyond DFT: intermediate valence and its impact on anisotropy**

- **Realistic compositions, defects, integration with micromagnetic and machine-learning models**

B_{exc} (T)	
535	exp.
506±5	
470±30	
252	theory
292	
558	exp.

$NdCo_5$ (from arXiv:2306.00821)

npj | Quantum Materials

npj Quantum Materials (2021)6:2

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Intrinsically weak magnetic anisotropy of cerium in potential hard-magnetic intermetallics

Anna Galler[1✉], Semih Ener[2], Fernando Maccari[2], Imants Dirba[2], Konstantin P. Skokov[2], Oliver Gutfleisch[2], Silke Biermann[1,3,4,5] and Leonid V. Pourovskii[1,3]

Coauthors and acknowledgments

Theory

CPHT-Ecole Polytechnique

Pascal Delange

James Boust

Silke Biermann

AIST, Tsukuba

Takashi Miyake

Experiment

Institut Néel (Grenoble)

Dominique Givord

Rafik Ballou

Gabriel Gomez Eslava

AGENCE NATIONALE DE LA RECHERCHE ANR DPG

DFG-ANR grant «RE-MAP »

Technical University of Darmstadt

Konstantin Skokov

Alex Aubert

Bahar Fayyazi

Yurii Skourski

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