Radboud Universiteit

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Mysteries of light rare earths: intrinsic spin glassiness in Nd and nonmagnetic state of Pr

Mikhail Katsnelson

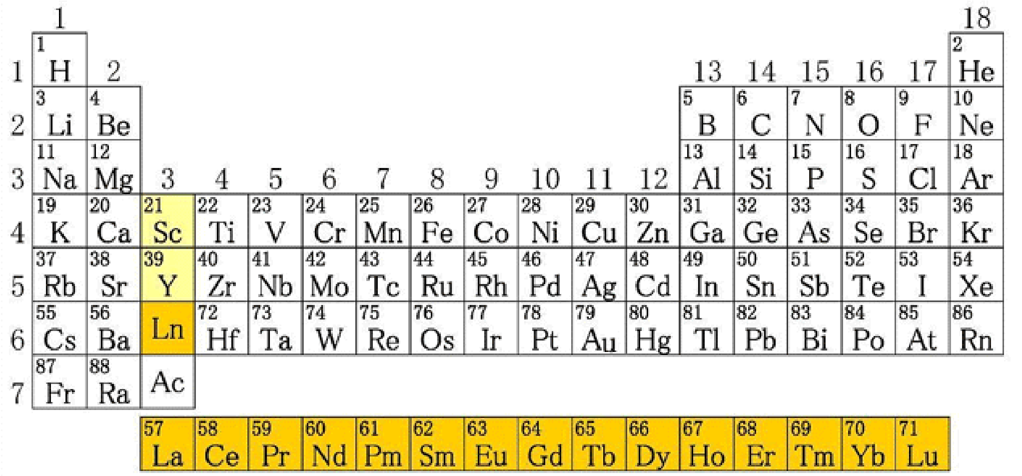
erc Synergy Grant

Wallenberg Initiative Materials Science for Sustainability

Outline

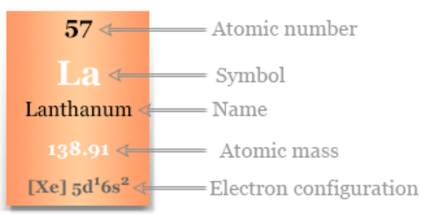
- How to treat rare earths in general?
- Self-induced spin-glass concept and application to Nd
- Crystal-field against exchange interactions: tale of Pr

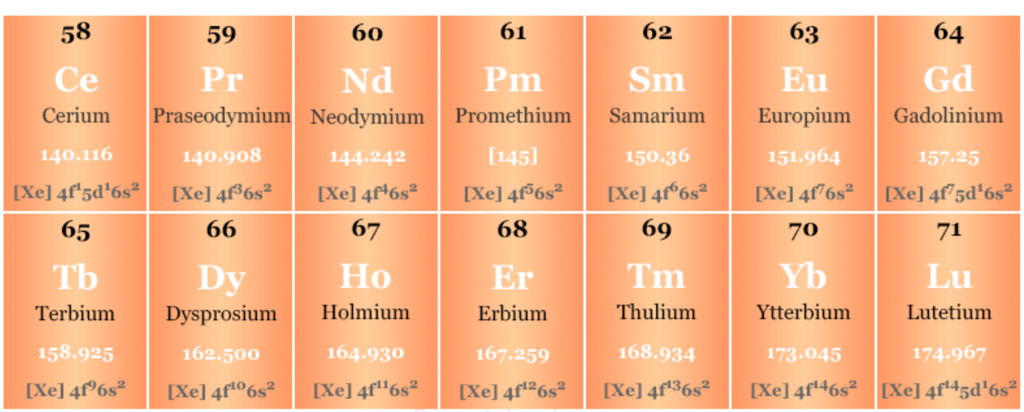
Magnetism of elemental rare-earths



From the point of view of geology and chemistry "rare earths" include also Sc and Y but I will be interested only in elements with partially occupied 4f shell, that is, from Ce to Yb

- **Multiplet notation:** The ground state is represented by the notation ${}^{2S+1}L_J$, where $2S+1$ is the spin multiplicity, L is the total orbital angular momentum, and J is the total angular momentum.
- **Degeneracy:** The ground state multiplet is degenerate, with the degeneracy equal to $2J+1$.
- **Examples:**
  - f^0 (La^{3+}): ${}^1S_0$
  - f^1 (Ce^{3+}): ${}^2F_{5/2}$
  - f^2 (Pr^{3+}): ${}^3H_4$
  - f^3 (Nd^{3+}): ${}^4I_{9/2}$
  - f^4 (Pm^{3+}): ${}^5I_4$
  - f^5 (Sm^{3+}): ${}^6H_{5/2}$
  - f^6 (Eu^{3+}): ${}^7F_0$
  - f^7 (Gd^{3+}): ${}^8S_{7/2}$
  - f^8 (Tb^{3+}): ${}^7F_6$
  - f^9 (Dy^{3+}): ${}^6H_{15/2}$
  - f^{10} (Ho^{3+}): ${}^5I_8$
  - f^{11} (Er^{3+}): ${}^4I_{15/2}$
  - f^{12} (Tm^{3+}): ${}^3H_6$
  - f^{13} (Yb^{3+}): ${}^2F_{7/2}$
  - f^{14} (Lu^{3+}): ${}^1S_0$





Magnetism of elemental rare-earths II

Elemental RE metals have frequently quite complicated magnetic structures

Journal of the Less-Common Metals, *93* (1983) 15–30

THE MAGNETIC STRUCTURES OF THE RARE EARTH METALS— A HISTORICAL SURVEY*

W. C. KOEHLER
Oak Ridge National Laboratory, Oak Ridge, TN 37830 (U.S.A.)

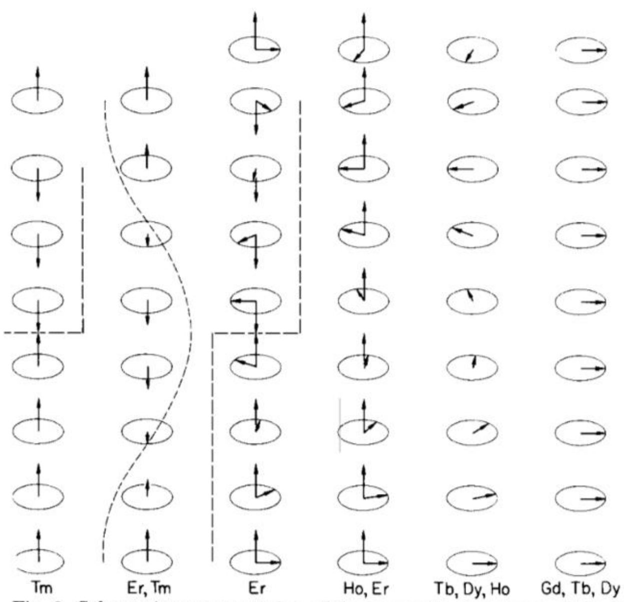


Fig. 3. Schematic representation of the magnetic structures of the heavy rare earth metals. The moments are assumed to be parallel in a given hexagonal layer. The different structures are found in different temperature ranges (see ref. 16).

Magnetic Structures of Samarium

W. C. Koehler and R. M. Moon

Show more

Phys. Rev. Lett. **29**, 1468 – **Published 20 November, 1972**

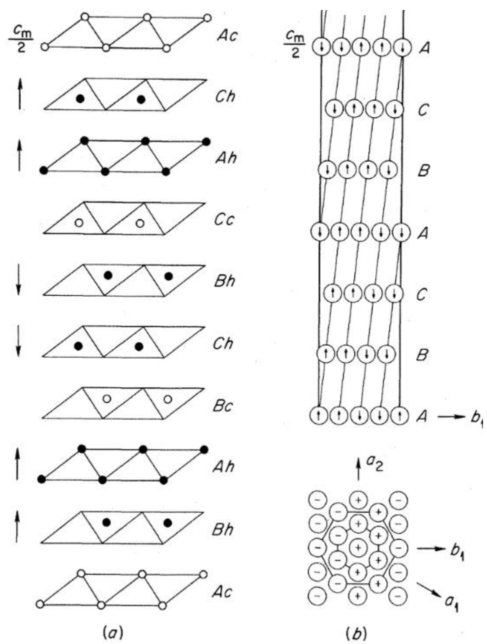
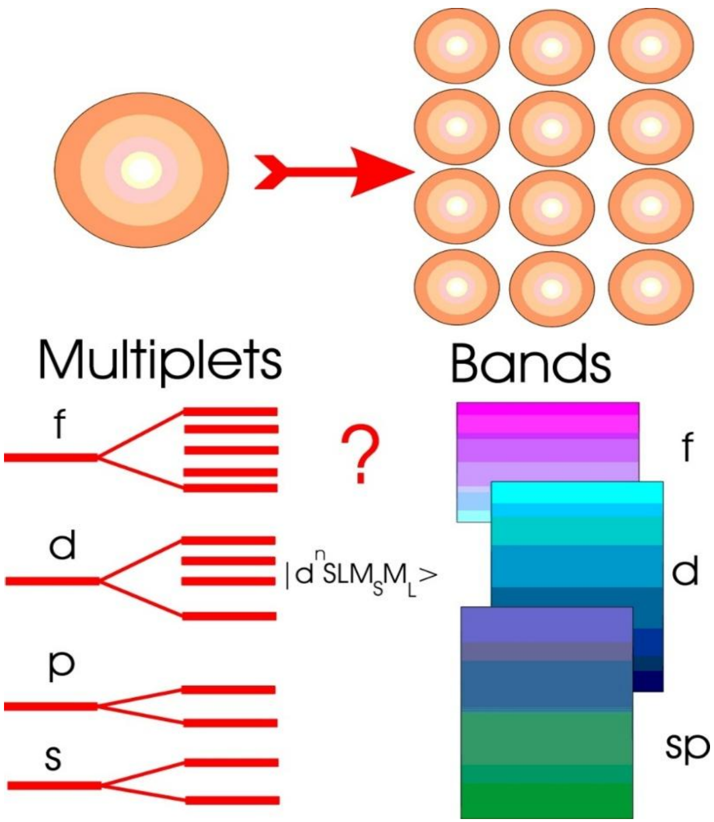


FIG. 1. (a) High-temperature magnetic structure involving only the hexagonal-site ions. Closed circles, hexagonal sites (*h*); open circles, cubic sites (*c*). The hexagonal sites are coupled ferromagnetically within layers normal to the *c* axis. The moment direction within each layer is indicated by the arrows. Only half of the magnetic unit cell is shown. The upper half is the same as the lower half, but with all moments reversed. (b) Low-temperature magnetic structure involving only cubic-site ions. In the lower part is shown the antiferromagnetic structure within a single layer with nearest- and next-nearest-neighbor coordination emphasized. In the upper part is shown a projection of the magnetic unit cell onto the plane containing $\vec{c}$ and $\vec{b}_1$. The arrows stand for rows of atoms along the $\vec{a}_2$ direction with moments directed along the arrows. The layers containing hexagonal sites are not shown. Only half of the magnetic cell is shown. The upper half is generated by translating the lower half by $\vec{c}_M/2$ and reversing the direction of all moments.

How to describe electronic structure?

4f electrons are atomlike,
spd electrons are itinerant



How to combine?

PHYSICAL REVIEW B VOLUME 57, NUMBER 12 15 MARCH 1998-II

***Ab initio* calculations of quasiparticle band structure in correlated systems: LDA++ approach**

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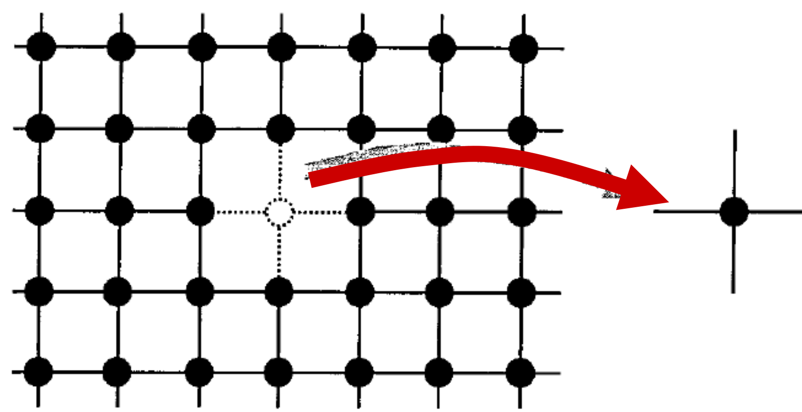
M. I. Katsnelson
Institute of Metal Physics, Ekaterinburg 620219, Russia
(Received 11 July 1997)

"Hubbard I" approximation: insert free atom into crystal lattice

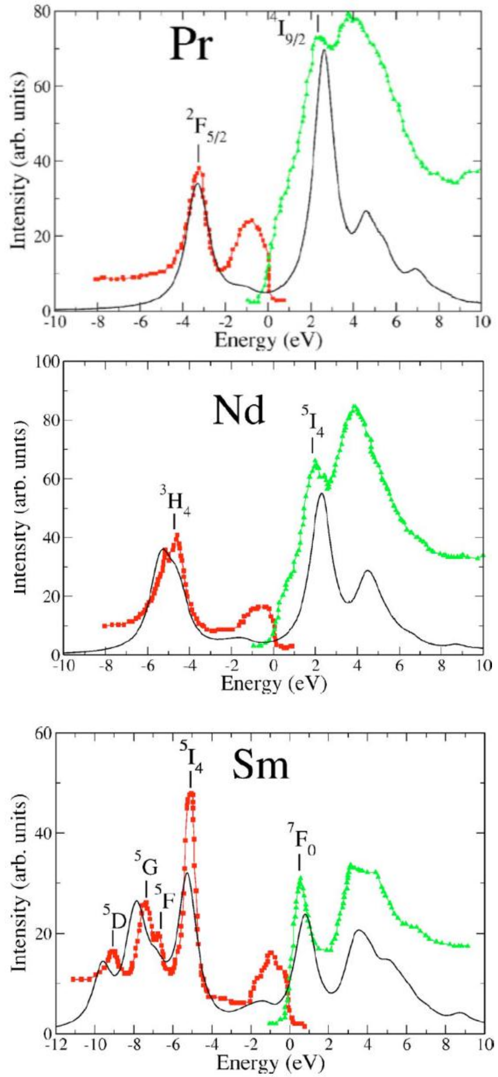


Electronic structure of elemental rare-earths

PHYSICAL REVIEW B **74**, 045114 (2006)

Multiplet effects in the electronic structure of light rare-earth metals

S. Lebègue,[1,2] A. Svane,[3] M. I. Katsnelson,[4] A. I. Lichtenstein,[5] and O. Eriksson[1]

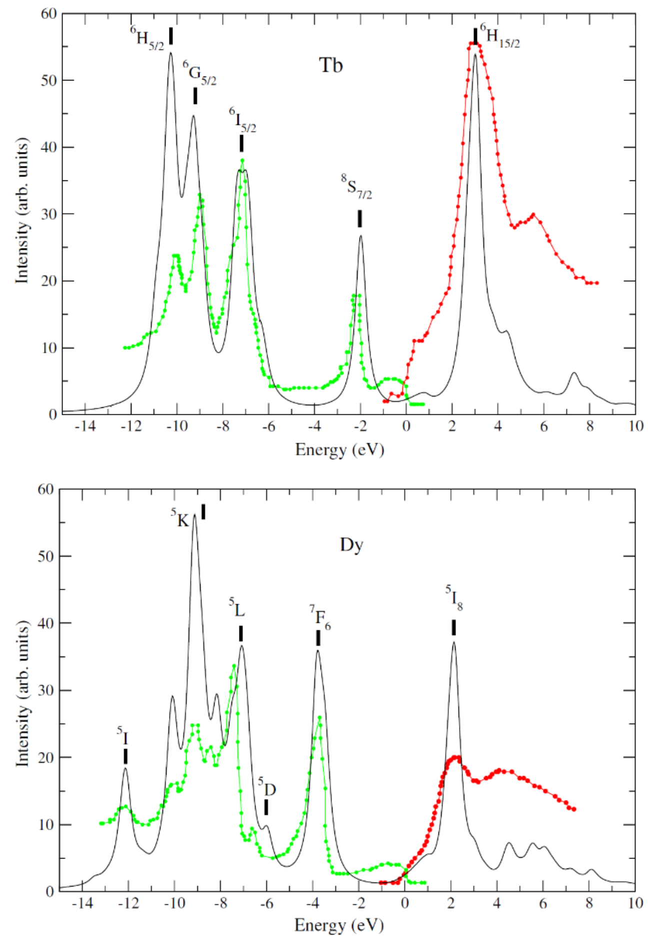


J. Phys.: Condens. Matter **18** (2006) 6329–6335

doi:10.1088/0953-8984/18/27/015

Multiplet effects in the electronic structure of heavy rare-earth metals

S Lebègue[1,2], A Svane[3], M I Katsnelson[4], A I Lichtenstein[5] and O Eriksson[1]

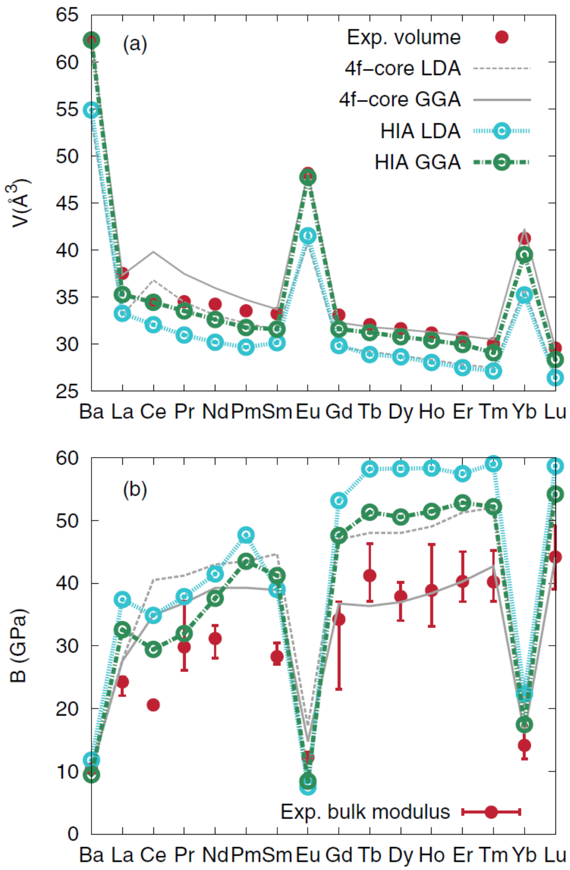


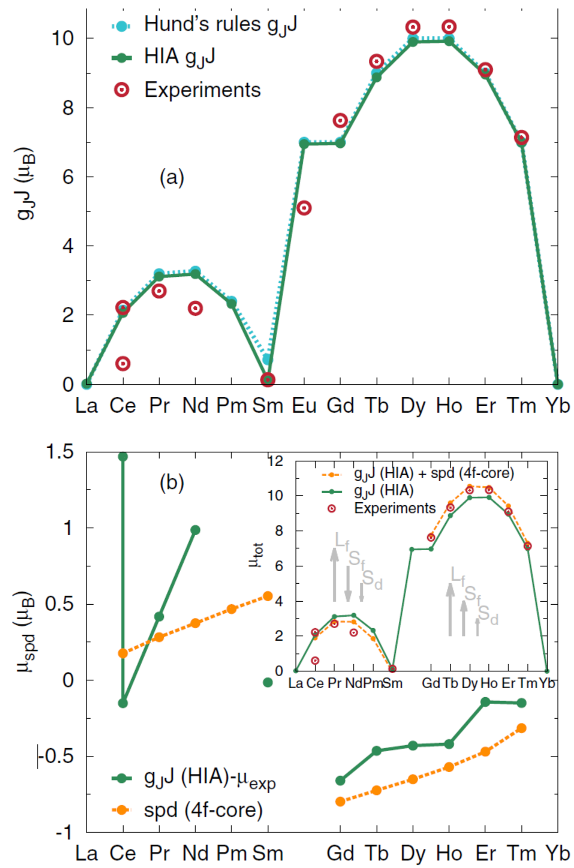
“Standard model” for rare earths

PHYSICAL REVIEW B **94**, 085137 (2016)

Standard model of the rare earths analyzed from the Hubbard I approximation

I. L. M. Locht,[1,2] Y. O. Kvashnin,[1] D. C. M. Rodrigues,[1,3] M. Pereiro,[1] A. Bergman,[1] L. Bergqvist,[4,5] A. I. Lichtenstein,[6]
M. I. Katsnelson,[2] A. Delin,[1,4,5] A. B. Klautau,[3] B. Johansson,[1,7] I. Di Marco,[1] and O. Eriksson[1]





Not only spectroscopy but also energetics

Exchange interactions

General tool: “magnetic force theorem” (a.k.a. “LKAG formula”)

REVIEWS OF MODERN PHYSICS, VOLUME 95, JULY–SEPTEMBER 2023

Quantitative theory of magnetic interactions in solids

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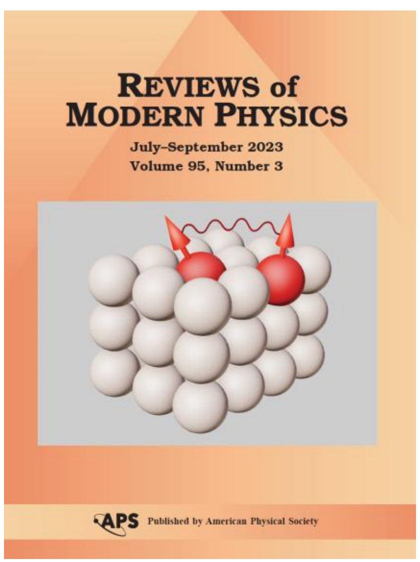
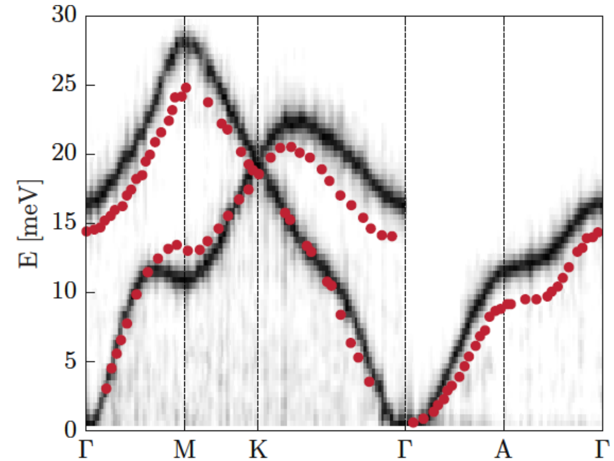
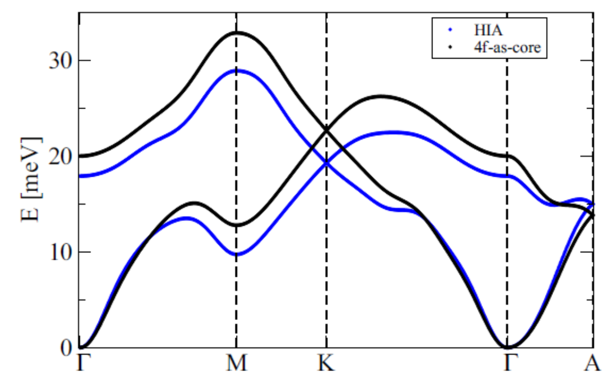
(published 11 September 2023)



Turns out: 4f electrons can be put into the core!



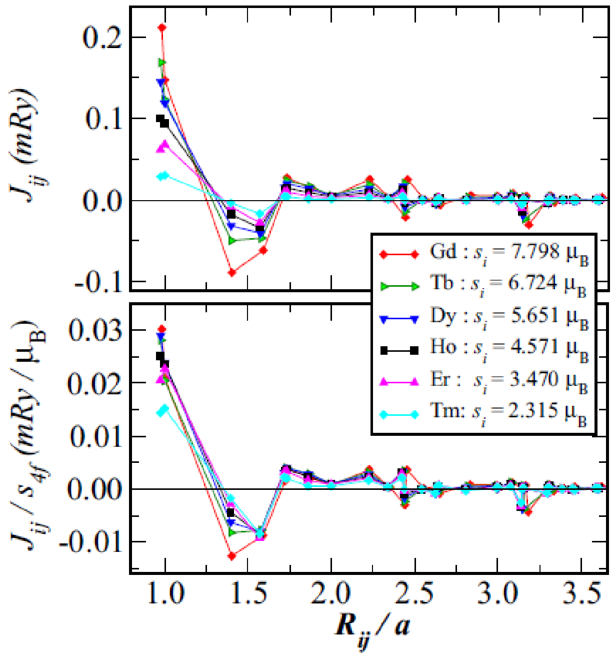
(a)Spin wave dispersion spectrum.



(b)Adiabatic magnon spectrum.

FIG. 6. Spin wave dispersion spectrum of hcp Gd. (a) Simulated spectrum using ASD (black) along with experimental data (red solid circles) from Ref. [12]. (b) A comparison between adiabatic magnon spectra calculated with exchange parameters obtained with HIA (blue) and with 4*f*-as-core (black).

Exchange interactions II



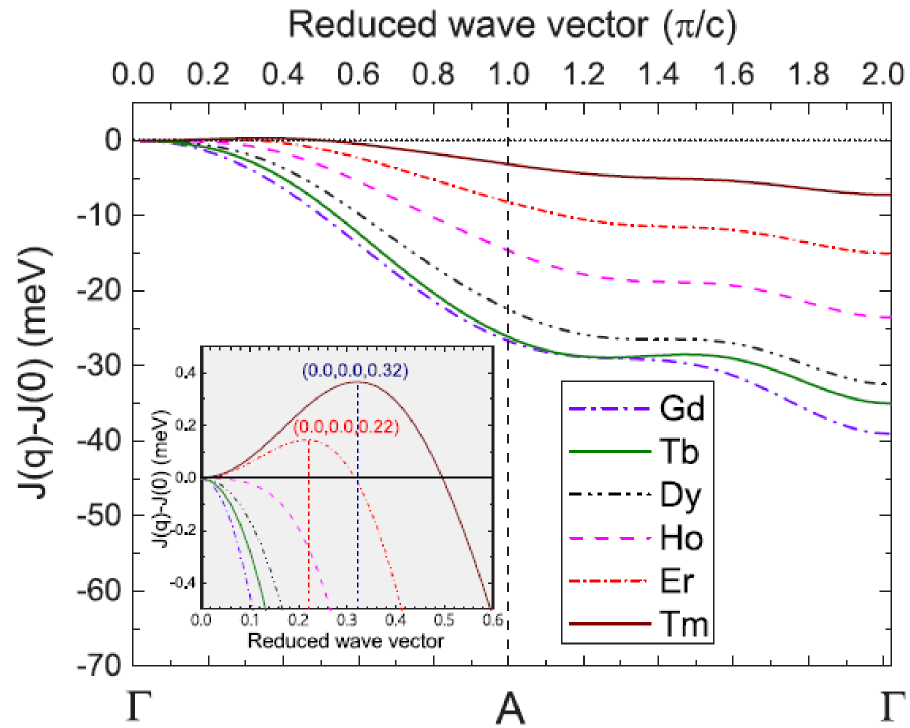
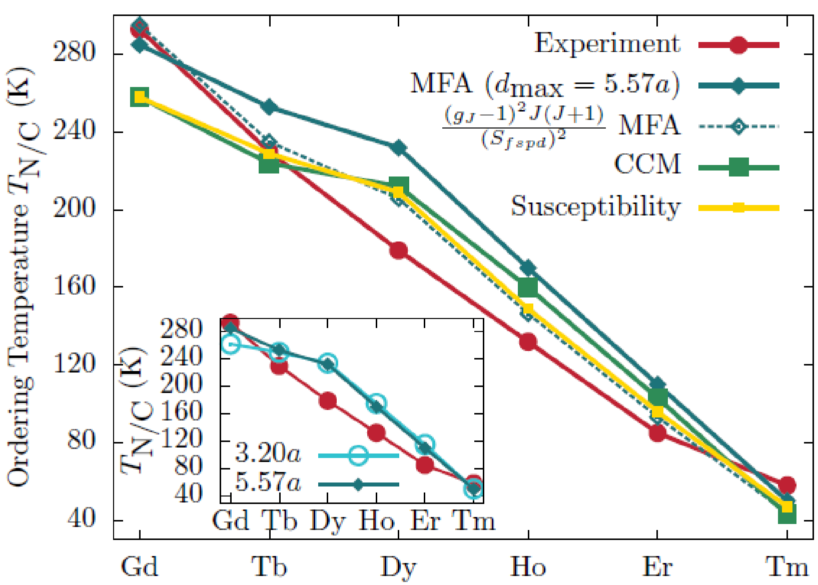


FIG. 5. Fourier transform of the exchange interaction $J(q) - J(0)$ for heavy rare-earth metals plotted along the Γ-A-Γ line. The inset shows a magnification of the figure for the reduced wave vector in the interval [0, 0.6]. In the inset we also indicated the pitch vector for Er and Tm, showing that the ferromagnetic reference state is unstable for both metals.



Self-induced spin glasses

PHYSICAL REVIEW B **93**, 054410 (2016)

Stripe glasses in ferromagnetic thin films

Alessandro Principi* and Mikhail I. Katsnelson

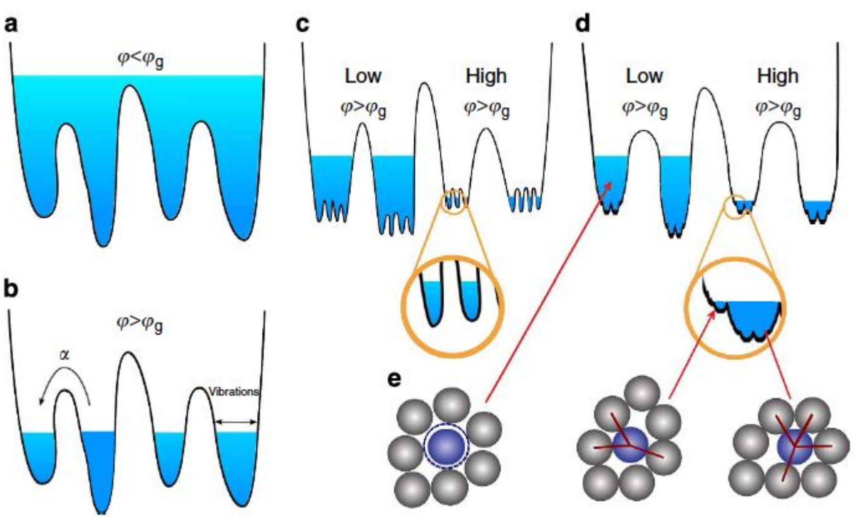
PRL **117**, 137201 (2016) PHYSICAL REVIEW LETTERS week ending 23 SEPTEMBER 2016

Self-Induced Glassiness and Pattern Formation in Spin Systems Subject to Long-Range Interactions

Alessandro Principi* and Mikhail I. Katsnelson

Development of idea of stripe glass, J. Schmalian and P. G. Wolynes, PRL 2000

Glass: a system with an energy landscape characterizing by infinitely many local minima, with a broad distribution of barriers, relaxation at "any" time scale and **aging** (at thermal cycling you never go back to *exactly* the same state)



Picture from P. Charbonneau et al,

DOI: 10.1038/ncomms4725

Intermediate state between equilibrium and non-equilibrium, opportunity for history and memory ("stamp collection")

Glassiness without disorder?

Giorgio Parisi, Nobel Prize in physics 2021
"for the discovery of the interplay of disorder and fluctuations in physical systems from atomic to planetary scales."

Actually, disorder may be not needed, frustrations are enough (self-induced spin glass state in Nd)

Can we have something more or less exactly solvable?! – Yes!

PHYSICAL REVIEW B **109**, 144414 (2024)

Frustrated magnets in the limit of infinite dimensions: Dynamics and disorder-free glass transition

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(Received 16 November 2023; accepted 27 March 2024; published 18 April 2024)

The prototype theory: dynamical mean-field theory (DMFT) for strongly correlated systems (Metzner, Vollhardt, Georges, Kotliar and others)

Glassiness in infinite dimensions

Frustrations are necessary

$$H = -\frac{1}{2}\sum_{i,j} J_{ij}^{\alpha\beta} S_i^\alpha S_j^\beta + \sum_i V(\mathbf{S}_i)$$

$$\mathbf{S}_i^2 = S_i^\alpha S_i^\alpha = 1$$

The limit of large dimensionality *d*

$$J_{ij}^{\alpha\beta} = [f^{\alpha\beta}(\hat{t}/\sqrt{2d})]$$ e.g.

$$f^{\alpha\beta}(x) = J_0^{\alpha\beta} + J_1^{\alpha\beta} x + J_2^{\alpha\beta} x^2 + J_4^{\alpha\beta} x^4$$ means

$$J_{ij}^{\alpha\beta} = J_0^{\alpha\beta}\delta_{ij} + \frac{J_1^{\alpha\beta}}{\sqrt{2d}} t_{ij} + \frac{J_2^{\alpha\beta}}{2d}\sum_k t_{ik}t_{kj} + \frac{J_4^{\alpha\beta}}{4d^2}\sum_{k,l,m} t_{ik}t_{kl}t_{lm}t_{mj} \, .$$

$$J^{\alpha\beta}(\mathbf{k}) = \sum_i \mathrm{e}^{-i\mathbf{k}\cdot(\mathbf{x}_i - \mathbf{x}_j)} J_{ij}^{\alpha\beta} = f^{\alpha\beta}(\varepsilon_{\mathbf{k}})$$

with $\varepsilon_{\mathbf{k}} = \sqrt{2/d}\sum_{a=1}^d \cos(k_a)$. Thus, $J^{\alpha\beta}(\mathbf{k})$ depends on the wave vector $\mathbf{k}$ only through $\varepsilon_{\mathbf{k}}$. This implies that, for many choices of the function $f^{\alpha\beta}(x)$ the interaction can develop degenerate surfaces of maxima in momentum space.

The simplest frustrated model: $f^{\alpha\beta}(\varepsilon) = \delta^{\alpha\beta} f(\varepsilon)$ $\quad f(\varepsilon) = J(\varepsilon^2 - 1)$

Mean-field ordering temperature tends to zero at $d \to \infty$ in this model

Glassiness in infinite dimensions II

Cavity construction and mapping on effective single impurity

Purely dissipative Langevin dynamics

$$\dot{\mathbf{S}}_i = -\mathbf{S}_i \times (\mathbf{S}_i \times (\mathbf{N}_i + \boldsymbol{\nu}_i)) = \mathbf{N}_i + \boldsymbol{\nu}_i - \mathbf{S}_i(\mathbf{S}_i \cdot (\mathbf{N}_i + \boldsymbol{\nu}_i))$$

$$\mathbf{N}_i = -\frac{\partial H}{\partial \mathbf{S}_i} = \mathbf{b}_i + \mathbf{F}_i \qquad b_i^\alpha = \sum_j J_{ij}^{\alpha\beta} S_j^\beta \qquad F^\alpha(\mathbf{S}_i) = -\partial V(\mathbf{S}_i)/\partial S_i^\alpha$$

$$\langle \nu_i^\alpha(t) \nu_j^\beta(t') \rangle = 2k_{\mathrm{B}} T \delta^{\alpha\beta} \delta_{ij} \delta(t - t')$$

Exactly mapped to a single-impurity dynamics with nonlocal in time "memory function"

Edwards-Anderson criterion of glassiness (local spin-spin correlation function tends to nonzero value in the limit of infinite time difference)

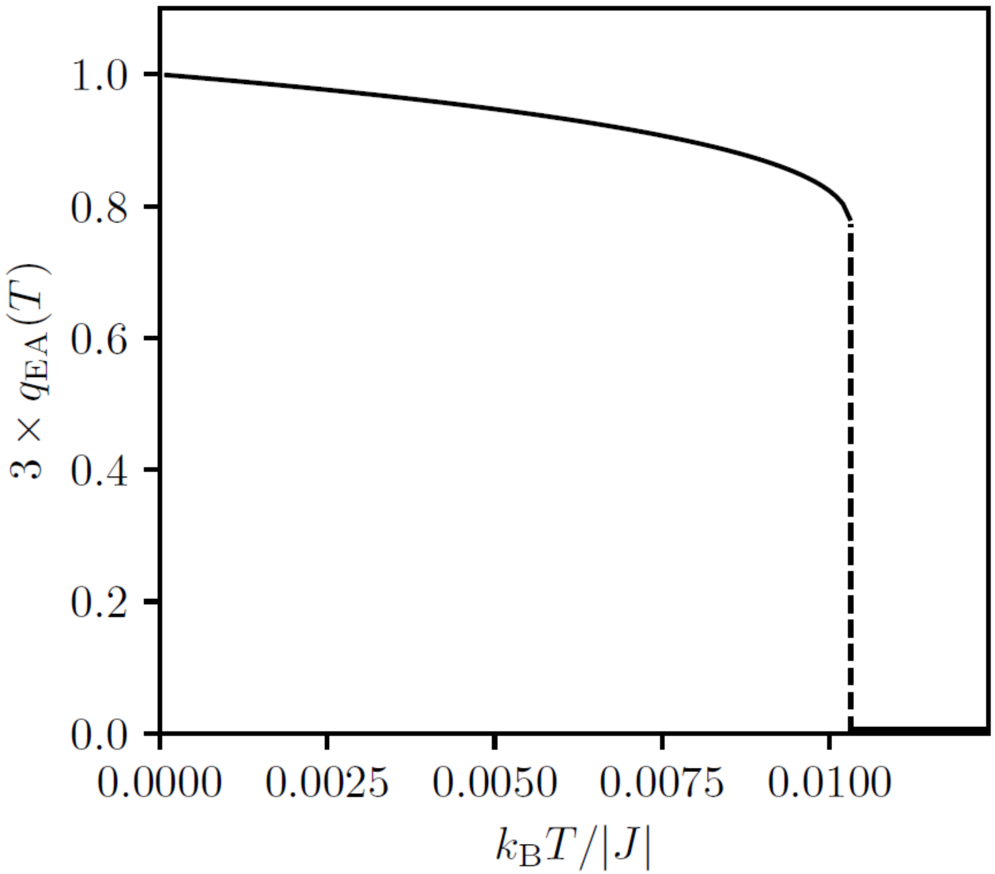
$$3q_{\mathrm{EA}}(T) = \lim_{|t-t'|\to\infty} \langle S^\alpha(t) S^\alpha(t') \rangle$$

Glassiness in infinite dimensions III

Isotropic model $f(\varepsilon) = J(\varepsilon^2 - 1)$

nonzero below the glass transition temperature $T_g \simeq 0.0103|J|/k_B$

First-order transition $q_{EA}(T_g) \simeq 0.2575$



Glassiness without disorder is theoretically possible if exchange energy reaches optimum on the whole (hyper)line!

Experimental observation of self-induced spin glass state: elemental Nd

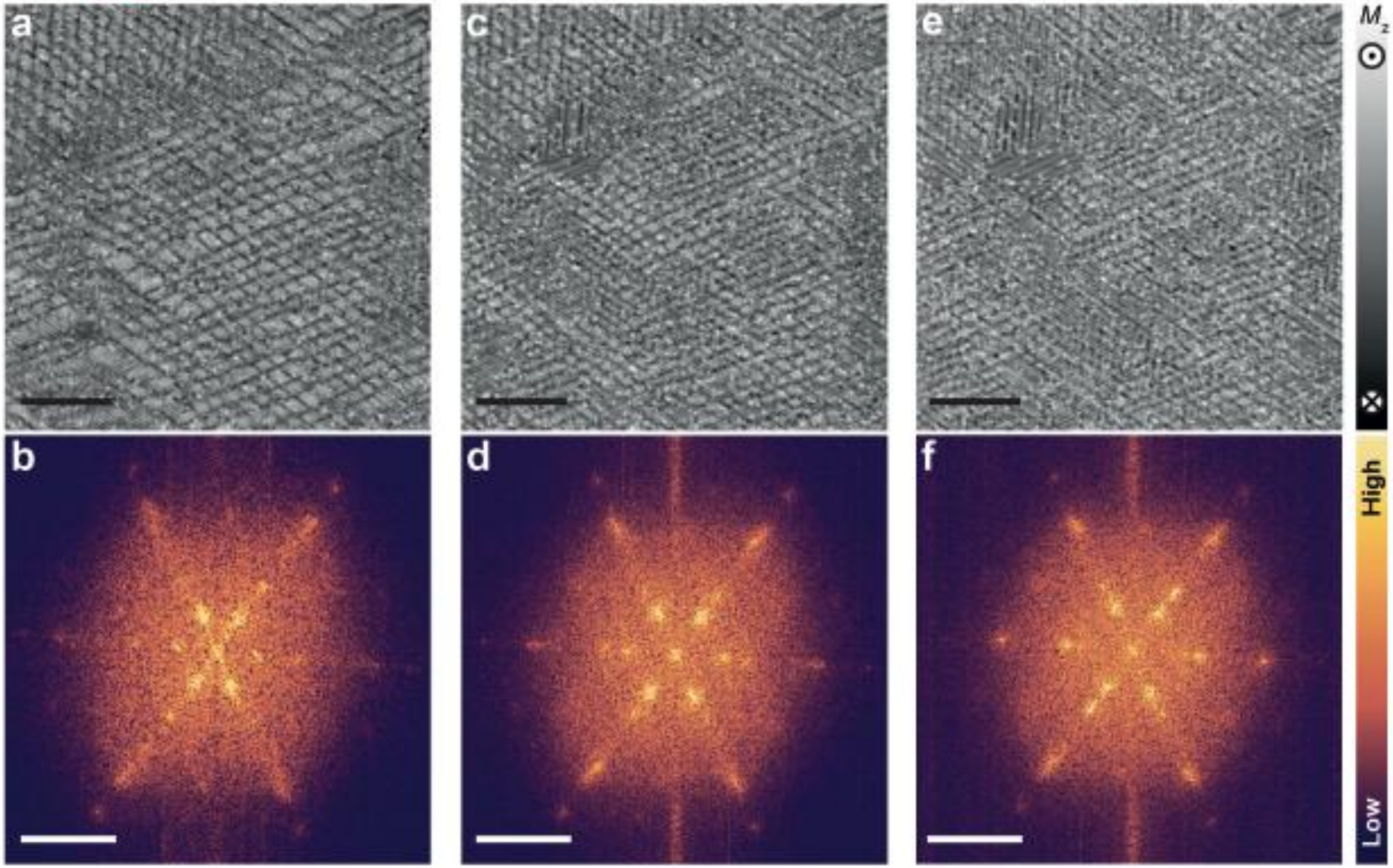
Self-induced spin glass state in elemental and crystalline neodymium

Science **368**, 966 (2020)

Umut Kamber, Anders Bergman, Andreas Eich, Diana Iuşan, Manuel Steinbrecher, Nadine Hauptmann, Lars Nordström, Mikhail I. Katsnelson, Daniel Wegner*, Olle Eriksson, Alexander A. Khajetoorians*

Spin-polarized STM experiment, Radboud University

Magnetic structure: local correlations

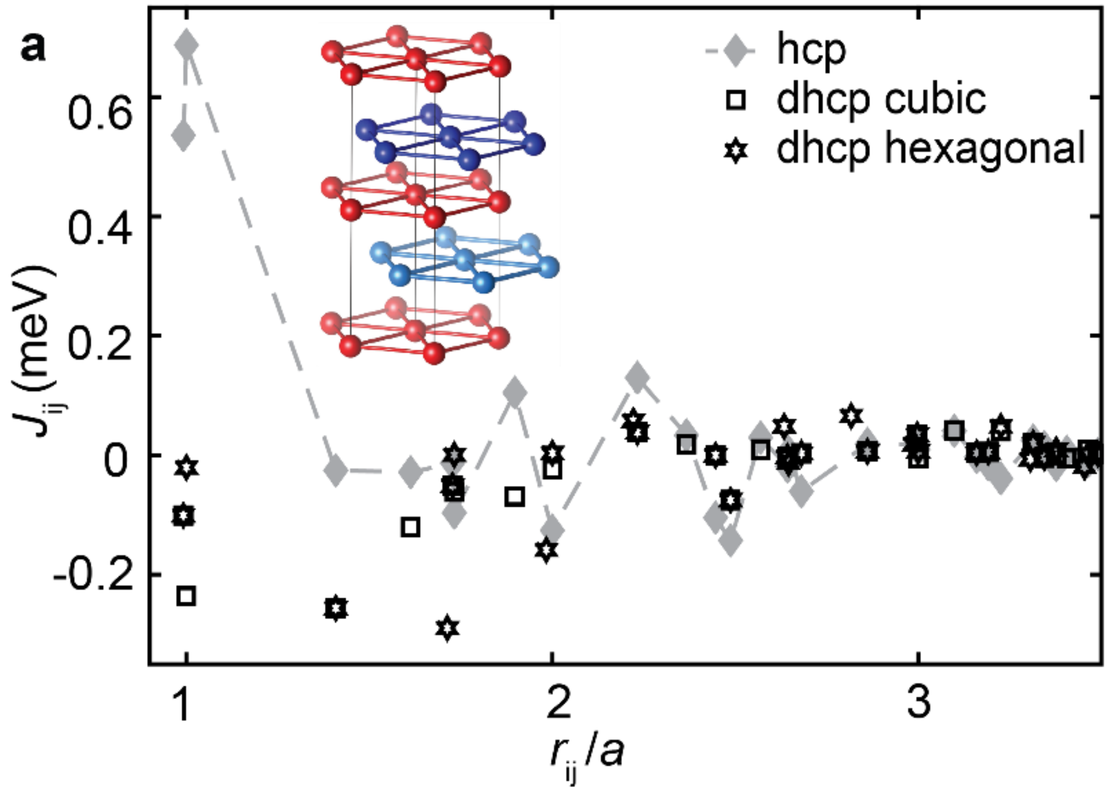


The most important observation: aging. At thermocycling (or cyling magnetic field) the magnetic state is not exactly reproduced

Ab initio: magnetic interactions in bulk Nd

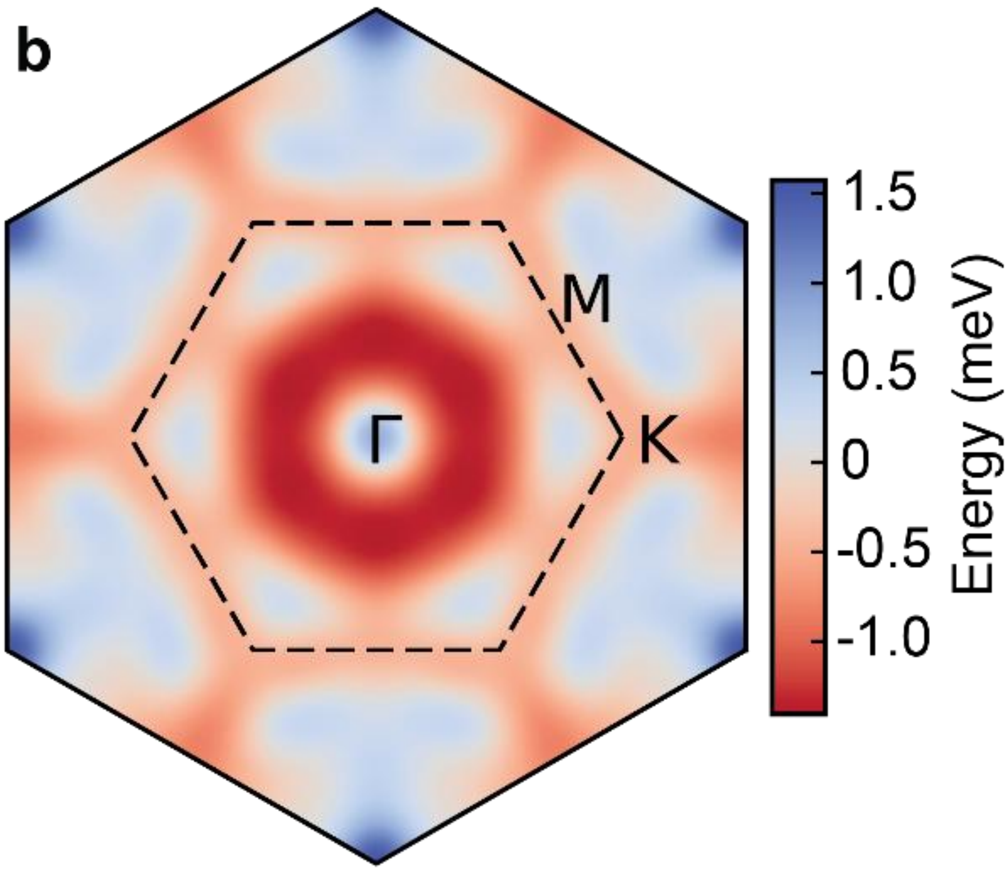
Method: magnetic force theorem (Lichtenstein, Katsnelson, Antropov, Gubanov JMMM 1987)

Calculations: Uppsala team (Olle Eriksson group)



- Dhcp structure drives competing AFM interactions
- Frustrated magnetism

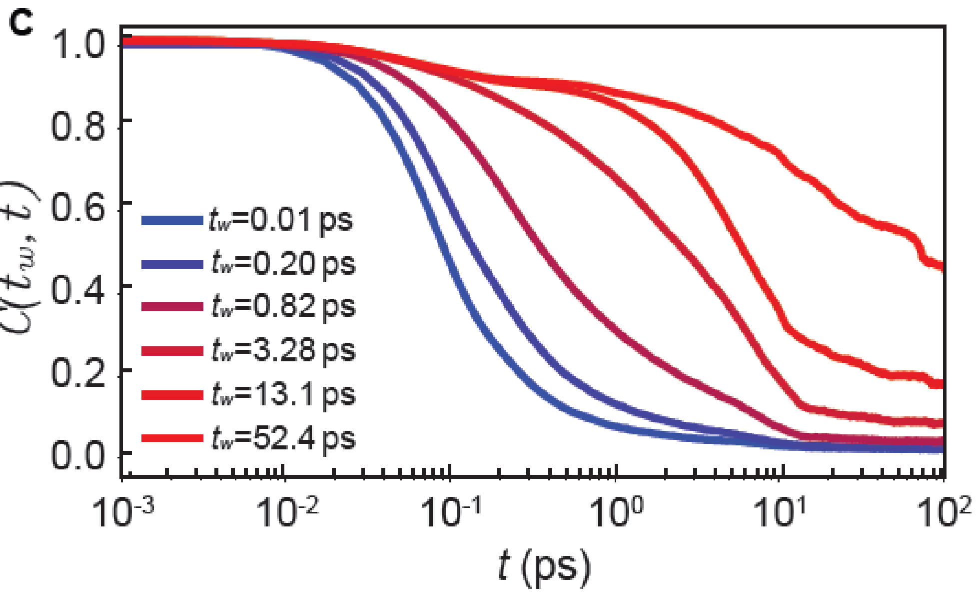
Ab initio bulk Nd: energy landscape



- E(Q) landscape features flat valleys along high symmetry directions

See A. Principi, M.I. Katsnelson, PRB/PRL (2016)/(2017)

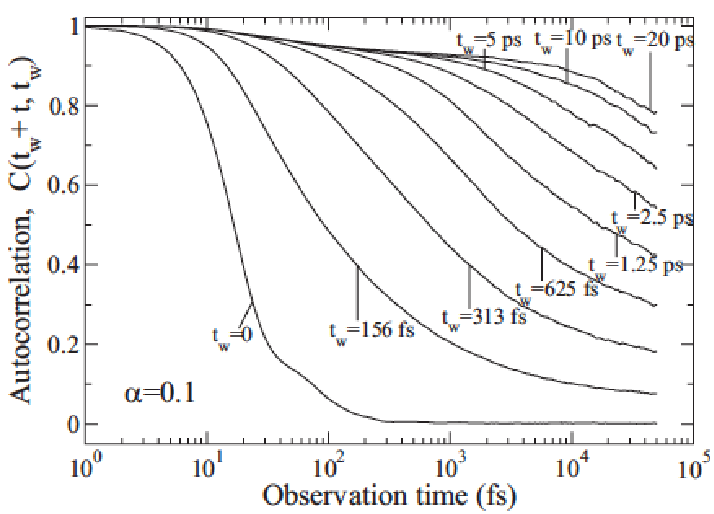
Spin-glass state in Nd: spin dynamics



Atomistic spin dynamics simulations

Typically spin-glass behavior

Autocorrelation function $C(t_w, t) = \langle \boldsymbol{m}_i(t + t_w) \cdot \boldsymbol{m}_i(t_w) \rangle$ for dhcp Nd at T = 1 K



To compare: the same for prototype *disordered* spin-glass Cu-Mn

B. Skubic et al, PRB 79, 024411 (2009)

Order from disorder

Thermally induced magnetic order from glassiness in elemental neodymium

NATURE PHYSICS | VOL 18 | AUGUST 2022 | 905–911

Benjamin Verlhac[1], Lorena Niggli[1], Anders Bergman[2], Umut Kamber[1], Andrey Bagrov[1,2], Diana Iuşan[2], Lars Nordström[2], Mikhail I. Katsnelson[1], Daniel Wegner[1], Olle Eriksson[2,3] and Alexander A. Khajetoorians[1]

Glassy state at low T and long-range order at T increase

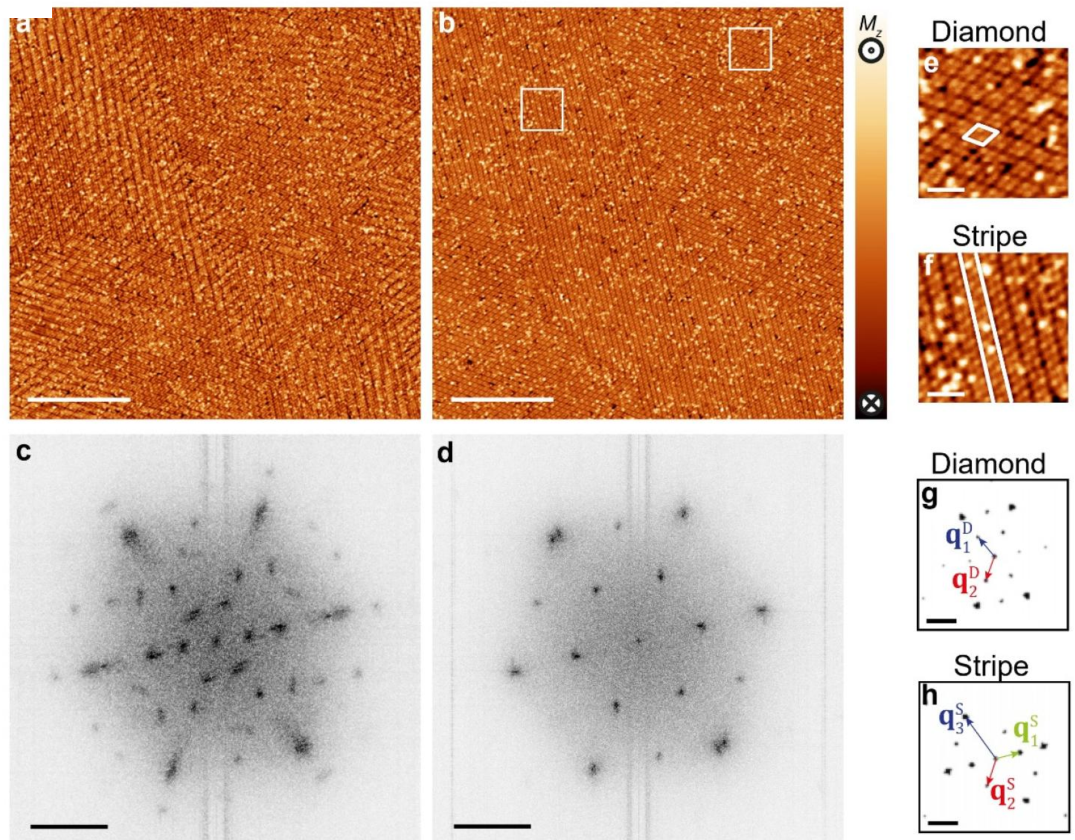
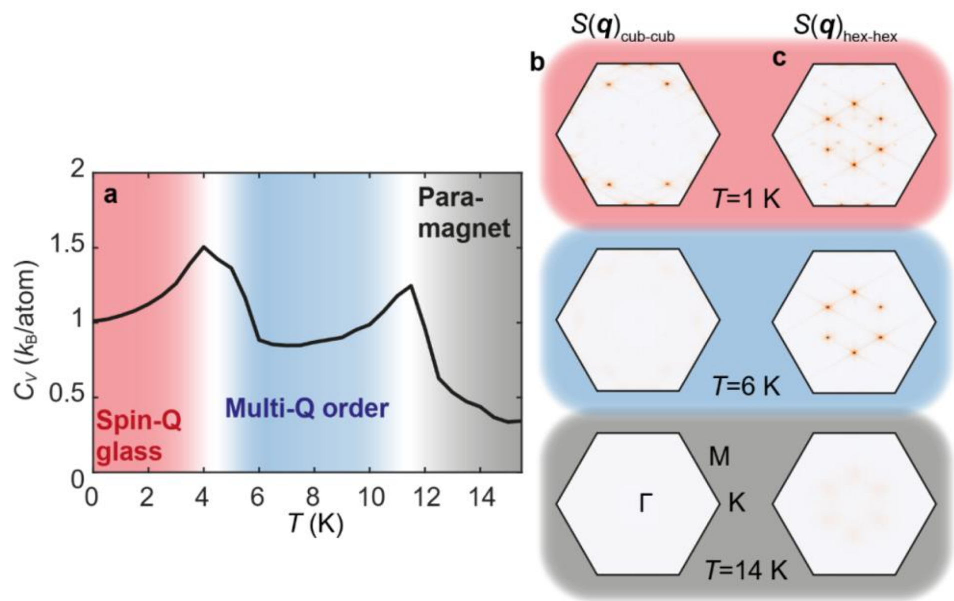
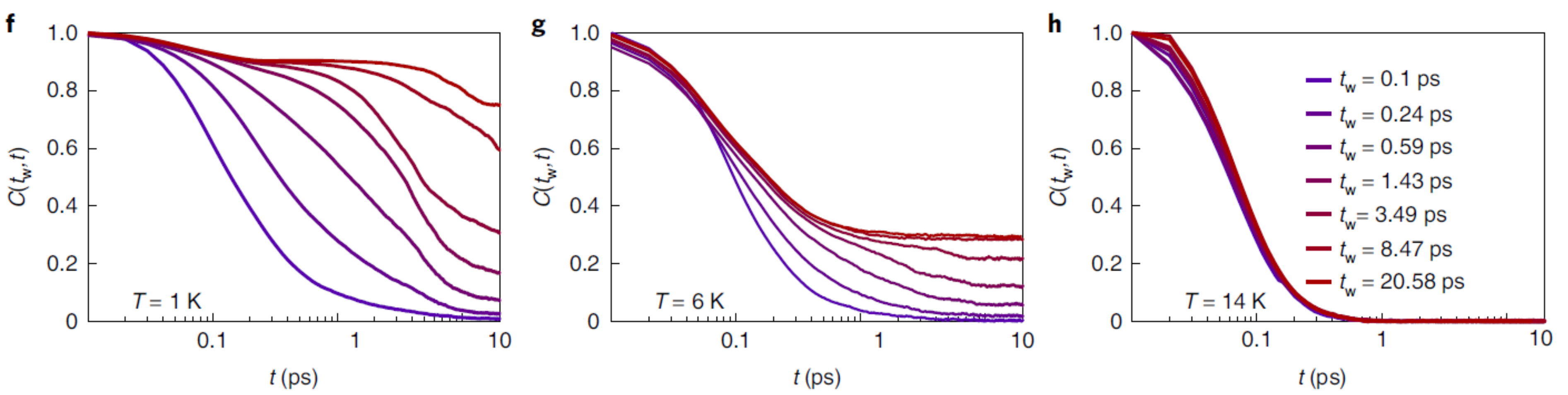


Figure 2: Emergence of long-range multi-Q order from the spin-Q glass state at elevated temperature. a,b. Magnetization images of the same region at T = 5.1 K and 11 K, respectively (I_t = 100 pA, a-b, scale bar: 50 nm). c,d. Corresponding Q-space images (scale bars: 3 nm^{-1}), illustrating the changes from strong local (i.e. lack of long-range) Q order toward multiple large-scale domains with well-defined long-range multi-Q order. e,f. Zoom-in images of the diamond-like (e) and stripe-like (f) patterns (scale bar: 5 nm). The locations of these images is shown by the white squares in b. g,h. Display of multi-Q state maps of the two apparent domains in the multi-Q ordered phase, where (g)

T=5K (a,c): spin glass
T=11K(b,d): (noncollinear) AFM

Order from disorder II





Theory: Atomistic simulations

Pr: nonmagnetic ground-state?!

f^2 configuration of Pr^{3+} The ground state multiplet is $S = 1$, $L = 5$, $J = 4$

Experimentally: no magnetic ordering at "normal" temperatures and nuclear magnetic ordering at millikelvins!

Magnetic ordering in praseodymium at millikelvin temperatures

To cite this article: K A McEwen and W G Stirling 1981 *J. Phys. C: Solid State Phys.* **14** 157

Abstract. Using thermal neutron scattering techniques, the development of magnetic ordering in single-crystal DHCP praseodymium has been studied over the temperature range 0·03–4·2 K. The intensity of the broad elastic peak around the wavevector 0·11 τ_{100} (which has been observed in previous studies of Pr) increased steadily as the temperature was reduced. In addition, new satellite reflections originating from a sinusoidally modulated magnetic structure with wavevector 0·13 τ_{100} were observed at temperatures well below 1 K. The magnetic transition is believed to be driven by an enhancement of the exchange interaction via the hyperfine interaction. No temperature dependence of the magnetic excitation energies between 4·2 K and 0·03 K was detected.

General explanation are known: crystal-field splitting of $^3H_4$ multiplet with singlet ground state but (1) interionic interactions can change energetics making magnetic state favorable; (2) what is the role of various sites is unknown; (3) what is on the surface – neither theory nor experiment; (4) quantitative theory is absent

Article | Open access | Published: 03 November 2025

Quantitative theory of magnetic properties of elemental praseodymium

Leonid V. Pourovskii, Alena Vishina, Olle Eriksson & Mikhail I. Katsnelson

npj Computational Materials **11**, Article number: 326 (2025) | Cite this article

In spirit of our "standard model"; Hubbard-I-like approach for crystal field and f-electron-in-the core calculations of exchange parameters

Crystal field splittings

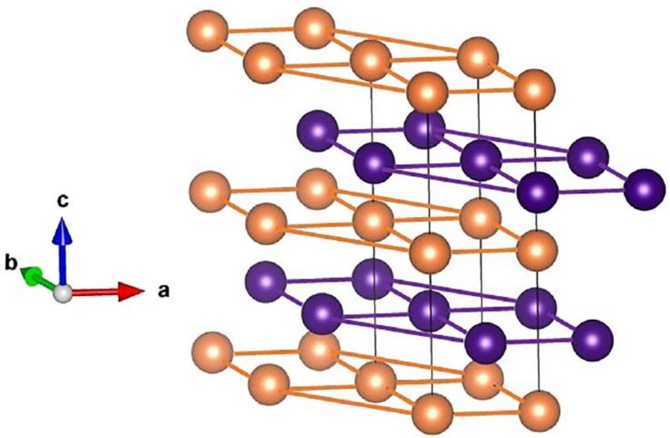


Fig. 1 | The crystal structure of dhcp Pr. The cubic (hexagonal) sites are depicted with orange (violet) spheres.

$$H^{\mathrm{CF}} = \sum_{kq} B_k^q O_k^q$$

Table 1 | Calculated CF parameters for bulk and (0001) relaxed surface of dhcp Pr (in meV)

Bulk						
	$B_2^0 \times 10^2$	$B_4^0 \times 10^4$	$B_4^3 \times 10^4$	$B_6^0 \times 10^4$	$B_6^3 \times 10^4$	$B_6^6 \times 10^4$
Hex. site	14.0	−4.17	–	0.82	–	10.3
Hex. site (EE)	19 ± 4	−5.7 ± 5	–	1.0 ± 0.1	–	9.6
Cub. site	3.05	11.6	−462	0.9	10.0	11.2
Cub. site (EE)		29	*−820*	0.8	*10*	*8*
(0001) surface						
Hexagonal termination						
surf. l. (h)	−2.26	−6.17	−15.07	0.97	3.06	4.20
subsurf. l. (c)	−3.93	8.06	−182.09	0.81	13.45	8.81
Cubic termination						
surf. l. (c)	−5.76	2.48	81.1	1.1	5.89	3.92
subsurf. l. (h)	4.88	−3.96	141	0.86	6.68	7.61

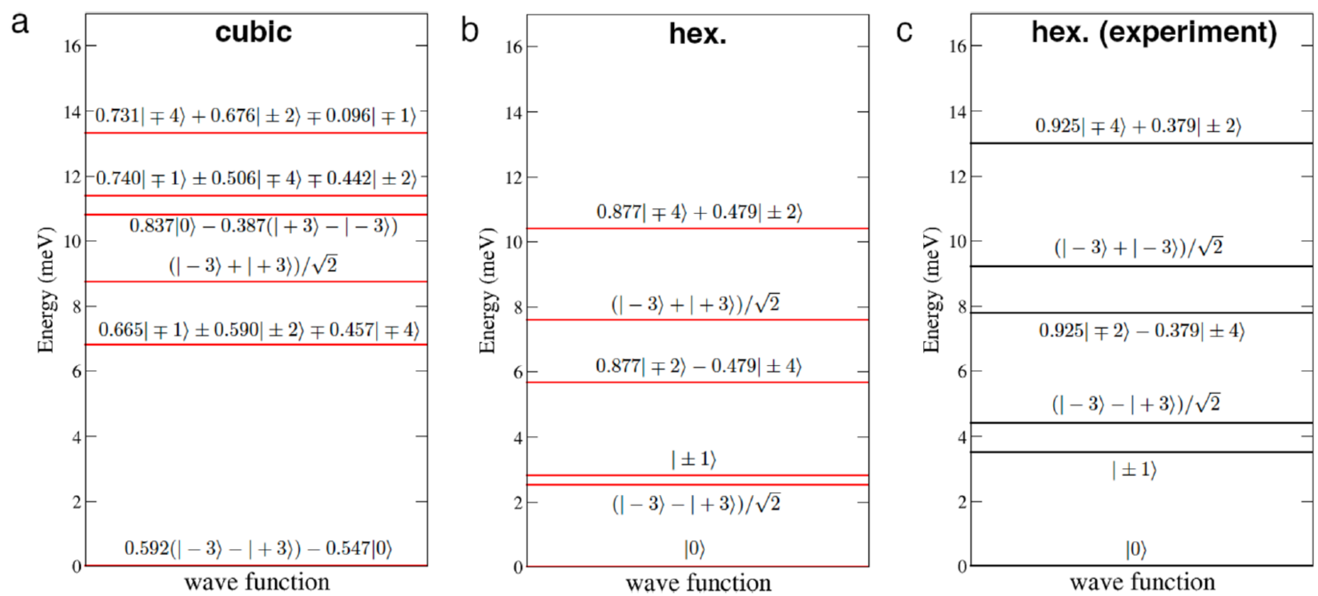


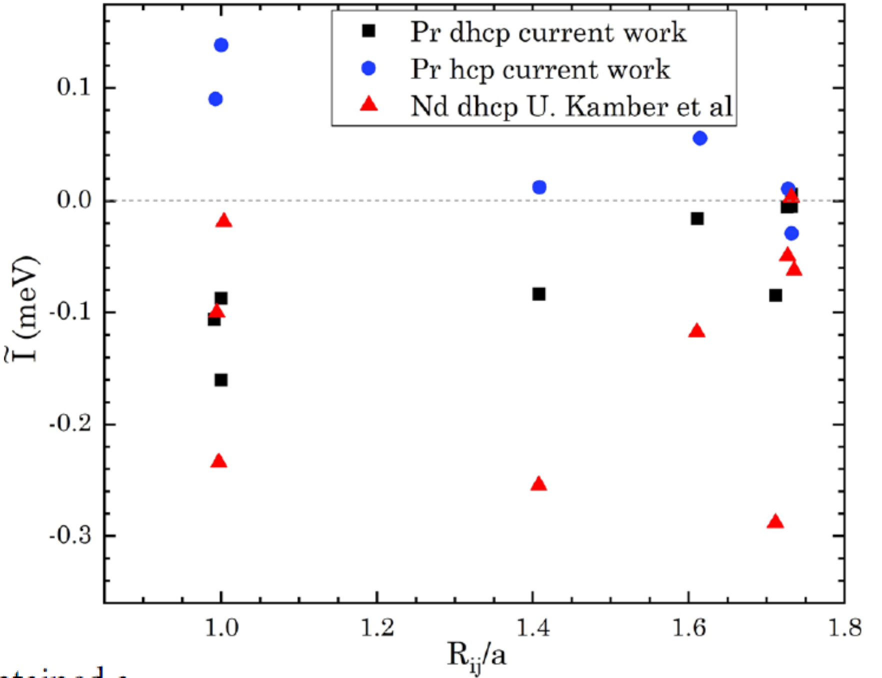
Fig. 2 | Calculated crystal-field splitting of the Pr $^3H_4$ configuration for the cubic (**a**) and hexagonal (**b**) site in bulk dhcp Pr. The CF wavefunctions are written in the $|M\rangle \equiv |J=4; M_J\rangle$ basis and are defined in the same coordination frame as the CFPs in Table 1. In panel (**c**), we reproduce the experimentally inferred CF level scheme of ref. 17 for the hexagonal site.

Exchange interactions in Pr

$$H_{\text{eff}} = \sum_i H_i^{\text{CF}} - \sum_{ij} I_{ij} \mathbf{J}_i \cdot \mathbf{J}_j;$$

$$\sum_{ij} I_{ij} \mathbf{J}_i \cdot \mathbf{J}_j \rightarrow \sum_{ij} I'_{ij} \mathbf{S}_i \cdot \mathbf{S}_j;$$

$$\sum_{ij} I'_{ij} \mathbf{S}_i \cdot \mathbf{S}_j \rightarrow \sum_{ij} \tilde{I}_{ij} \mathbf{e}_i \cdot \mathbf{e}_j.$$



Solving $\hat{H}_{\text{eff}}$, Eq. (1), for the bulk dhcp phase we correctly obtained a nonmagnetic state, with both crystallographic sites having the same singlet ground state as shown in Fig. 2. It agrees with experimental observations and illustrates the competition between interatomic exchange, which favors a magnetically ordered state, and crystal field effects, which for Pr favor a non-magnetic, singlet state. Following the experimental observations, the singlet state has the lowest energy. It means that the energy gain that would come from a magnetically ordered state, as quantified by the second term of Eq. (1), is smaller than the gain of the singlet crystal field effect that arises due to the Coulombic interaction of the $J = 4$ state of Pr in the dhcp crystal structure. In the Supplementary Section 3, we analyze the magnetic contribution to the specific heat, and a Schottky anomaly that occurs due to the excited CF levels of Pr.

Exchange energies are smaller than CF splitting, the ground state of the crystal remains nonmagnetic (without nuclear spins)

Surface of Pr: prediction

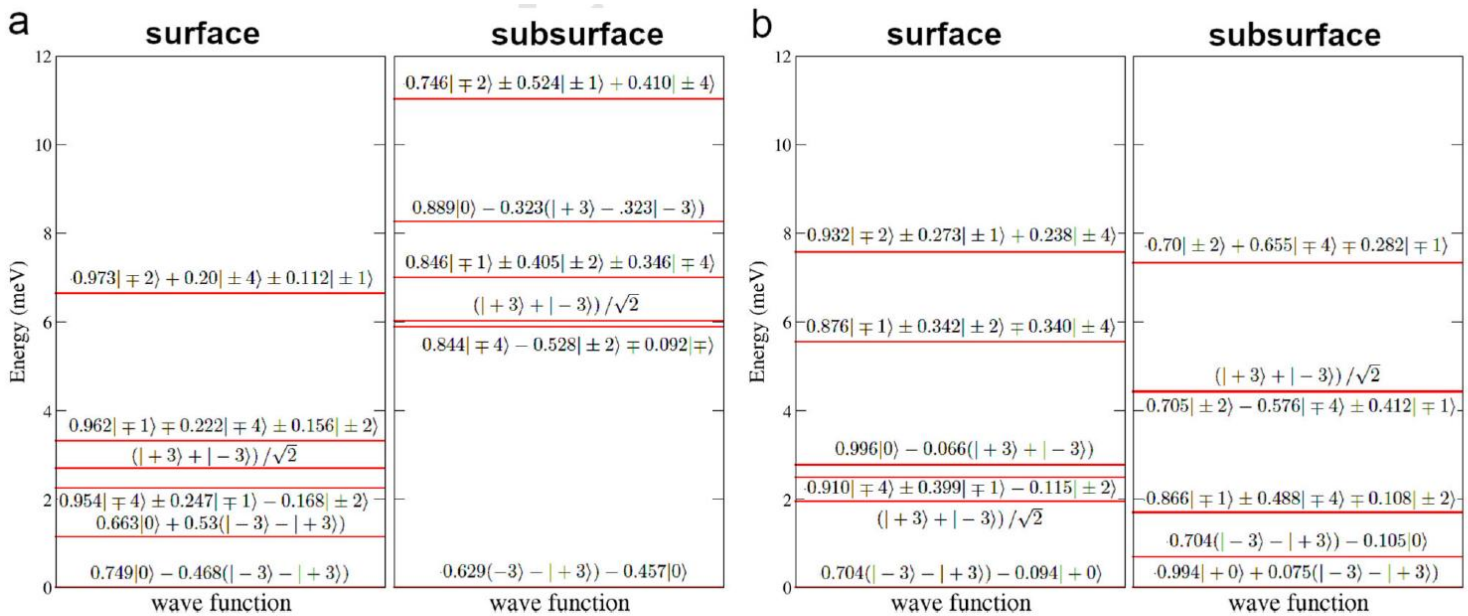


Fig. 5 | Calculated crystal-field level splitting of the Pr $^3H_4$ multiplet at the (0001) dhcp surfaces with hexagonal (**a**) and cubic (**b**) termination. The CF wavefunction representation and coordination frame are the same as in Fig. 2. For both cases, we show the levels for the surface and subsurface site. In the subsurface layer the site symmetries are reversed with respect to the surface one, becoming cubic in (**a**) and hexagonal in (**b**), respectively.

Crystal field splittings are smaller than in the bulk but still, singlet ground state wins, exchange interactions are not sufficient to change it, (0001) surface of Pr should be nonmagnetic

To conclude

- We have a very satisfactory quantitative theory for rare-earth elements (mixed valent and Kondo systems should be discussed separately!)

- Even behavior of pure elements can be complicated and counterintuitive (well… after graphene I am not very surprised)

Too many collaborators to mention all of them but special thanks to

Sasha Lichtenstein for very long (> 40 years) collaboration

Olle Eriksson and the whole Uppsala group

Alex Khajetoorians and the whole SPM group in Nijmegen

Achille Mauri (now EPFL) for spin-glass theory

Leonid Pourovskii (EP Paris and College de France) for Pr

…

MANY THANKS FOR YOUR ATTENTION