Magnetism in Pd Particles

MAGNETISM IN TWO DIMENSIONAL STRUCTURES:
Stacking Faults, Twin Boundaries and Surfaces in Pd

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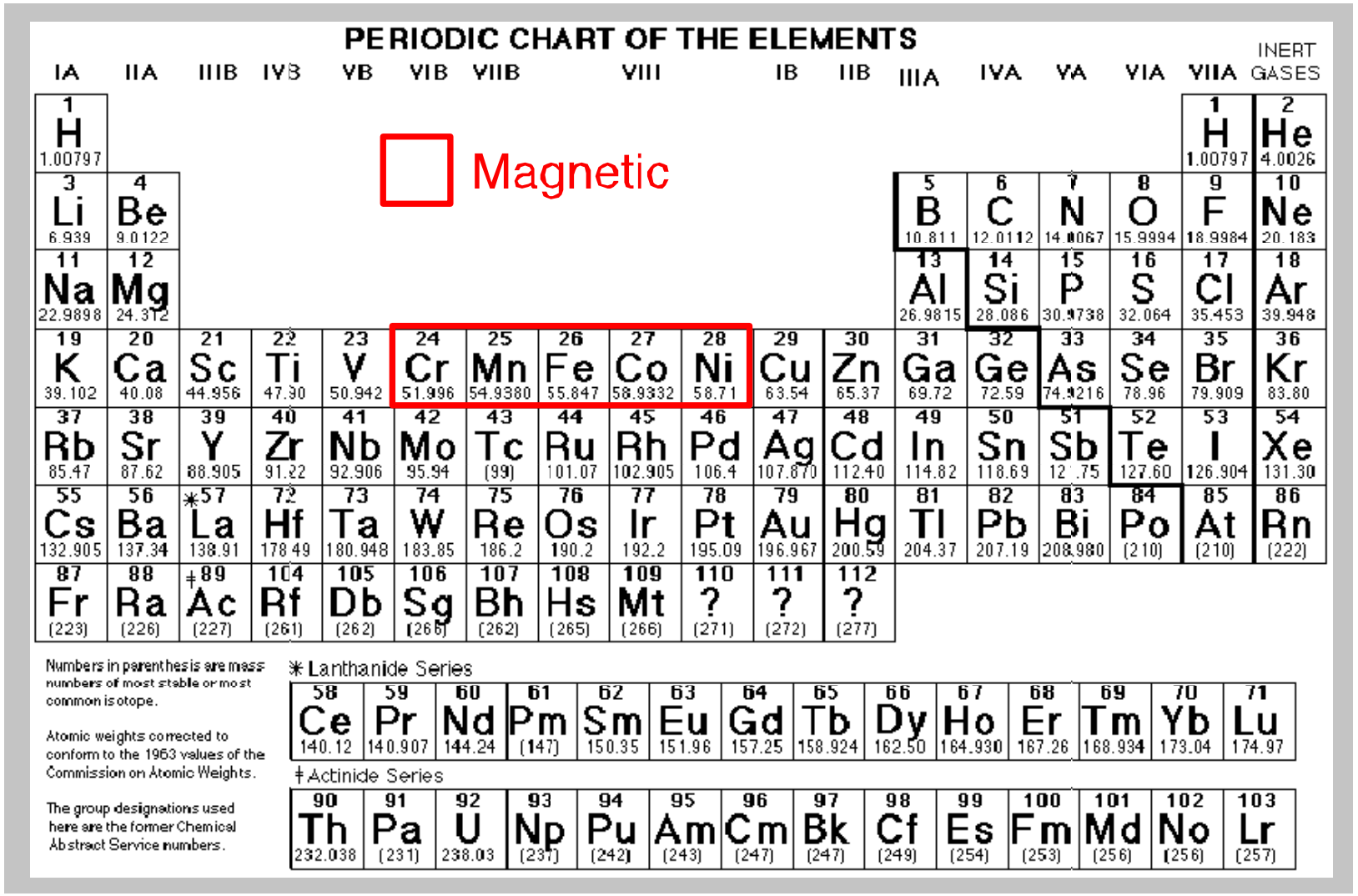
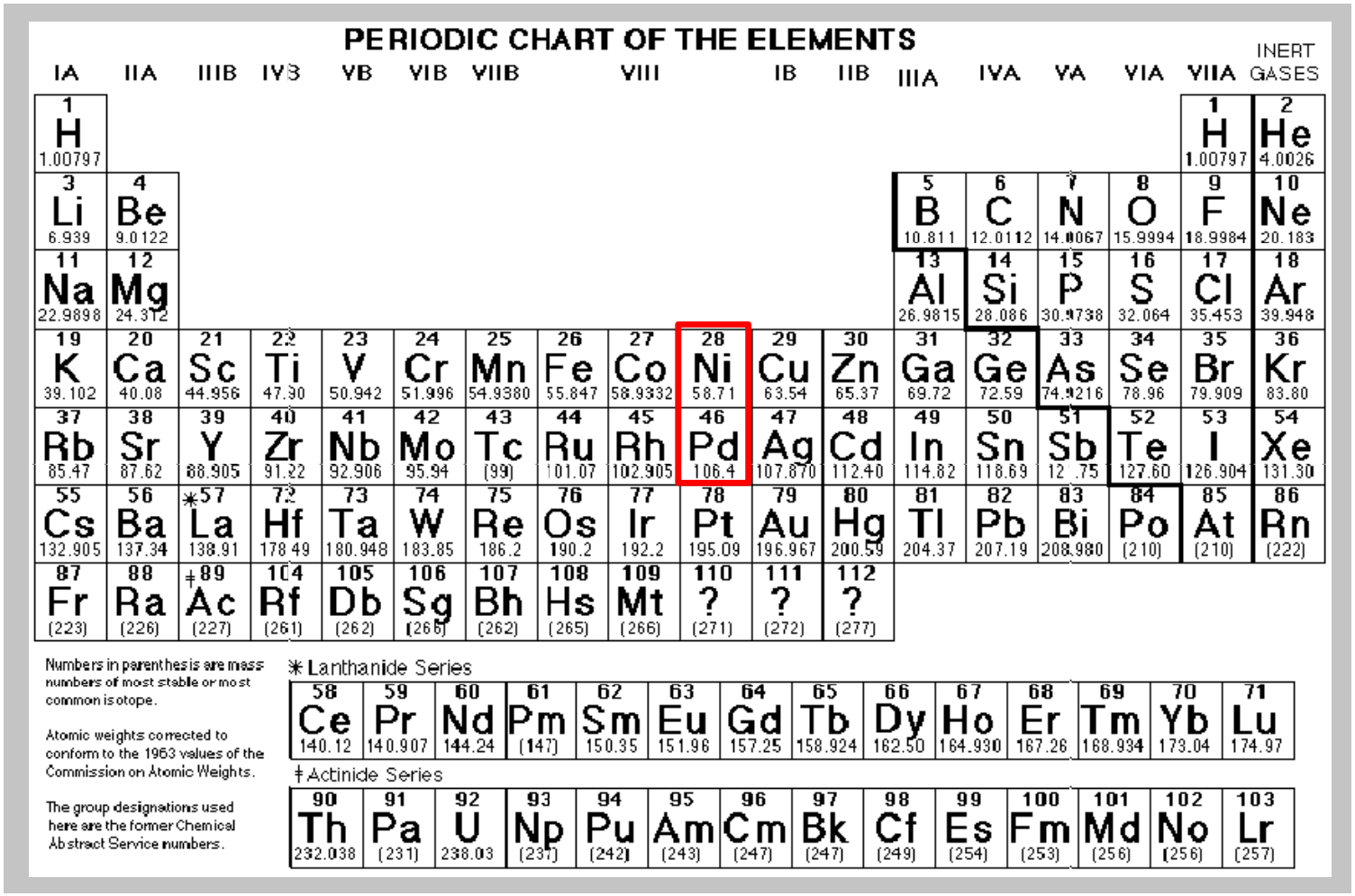
Can small Pd particles have different physical properties than bulk crystals?

Magnetic Metals



Ni (magnetic) and Pd (non-magnetic)

Both with the fcc Structure



Ferromagnetism in fcc Twinned 2.4 nm Size Pd Nanoparticles

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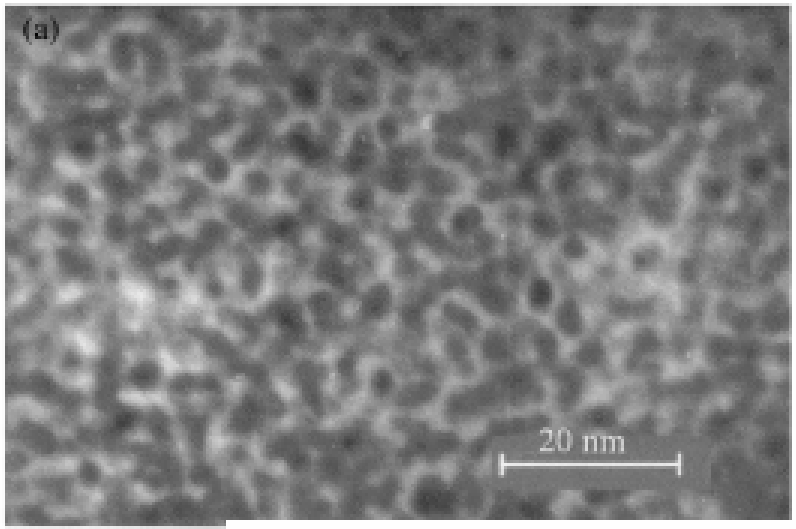

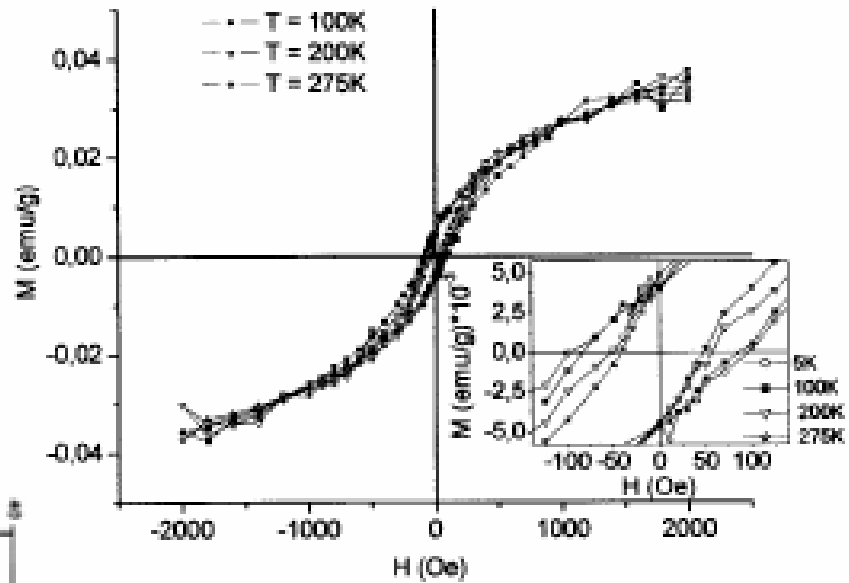

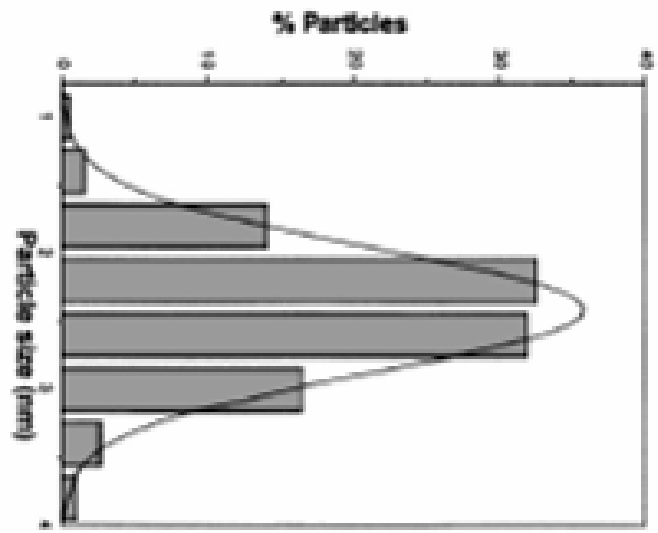

Can two-dimensional defects induce magnetism in Pd?

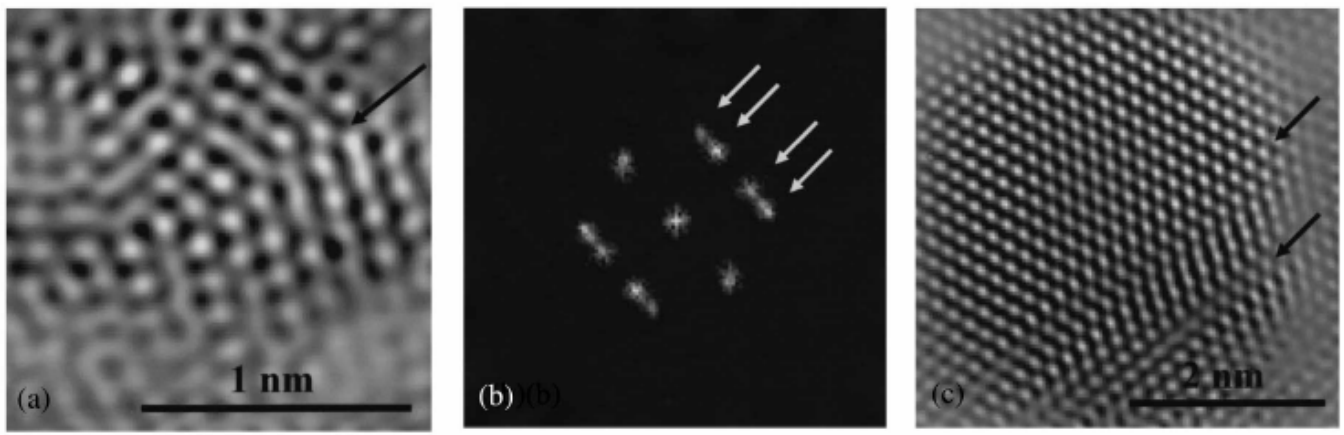

FIG. 2. (a) Fourier filtered HRTEM image of a Pd nanoparticle (diameter = 2 nm). The twin boundary is arrowed. (b) Corresponding FT diffraction pattern along the [111] direction. The splitting of the FT spots due to twinning is indicated. (c) Fourier filtered HRTEM image of a Pd nanocrystal (diameter = 4.4 nm) showing two twin boundaries.

Surface Ferromagnetism of Pd Fine Particles

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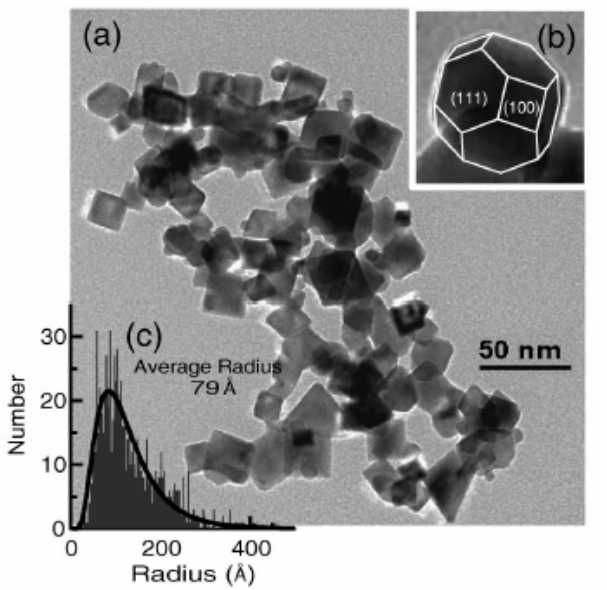
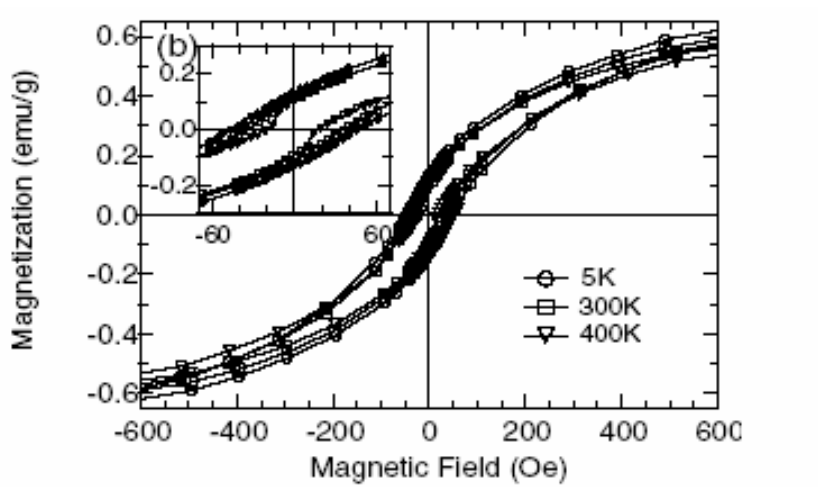
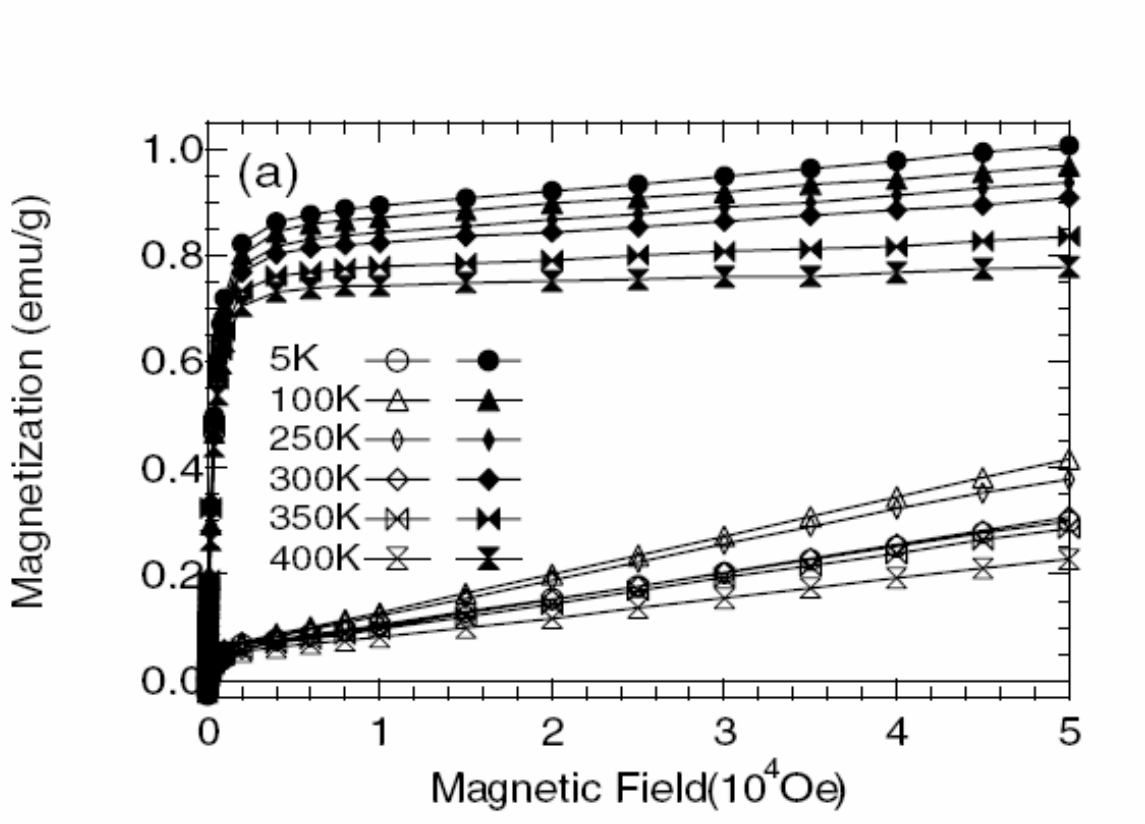
T. Taniyama





Is Magnetism in Pd a Surface Effect?



The field dependence of the magnetization of Pd fine particles with a clean surface (solid symbols, average radius of 115 Å) and after adsorption with O_2 atoms (open symbols, average radius of 108 Å) at various temperatures.

Pd in the form of small particles has

new physical properties

Why?

Method of Calculation: **First Principles Calculations** based on the SIESTA Method

(Spanish Initiative for Electronic Simulations with Thousands of Atoms)

Apart from that of Born and Oppenheimer, the most basic approximations concern the treatment of exchange and correlation (XC), and the use of pseudopotentials.

- Exchange and correlation are treated within Kohn–Sham Density Functional Theory, allowing for both the local (spin) density approximation (LDA/LSD).
- Standard norm-conserving pseudopotentials in their fully nonlocal form are used.
- Localized functions are used as basis to expand the one-electron eigenfunctions.
- Scalar-relativistic effects and the nonlinear partial-core correction to treat XC in the core region can be included.

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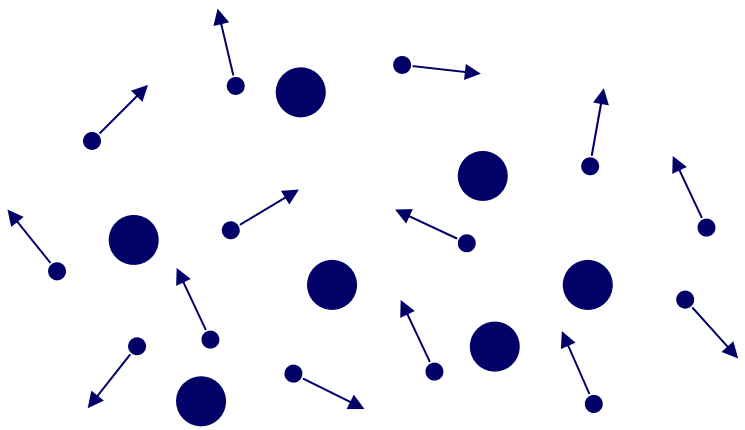
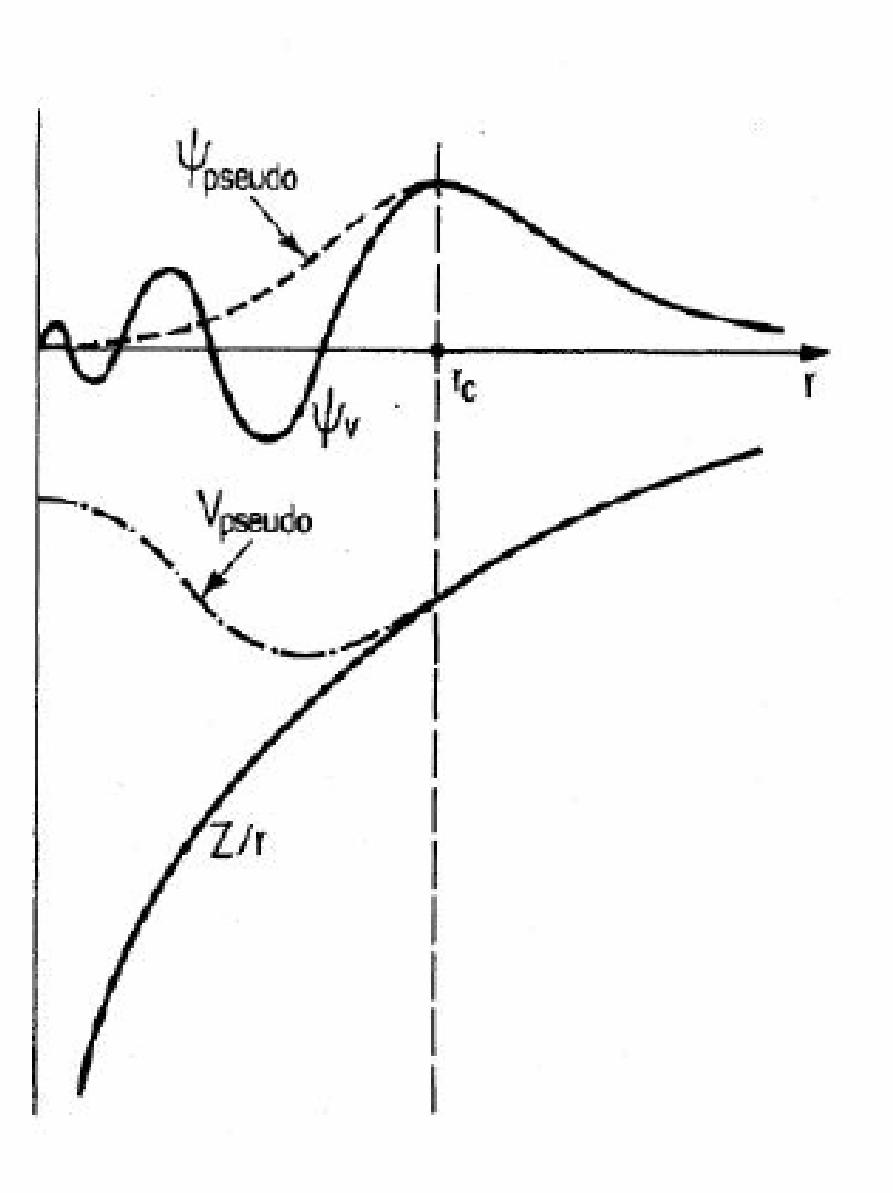
Density-Functional Theory

1. $\Psi(\{\vec{r}_i\}) \rightarrow \rho(\vec{r})$ particle density

2. As if non-interacting electrons in an effective (self-consistent) potential

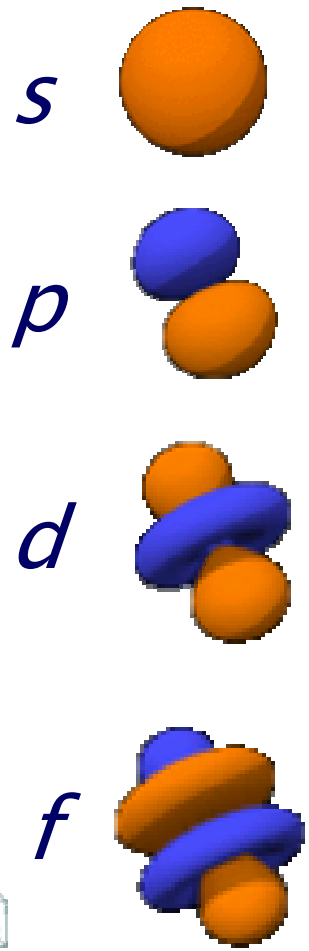


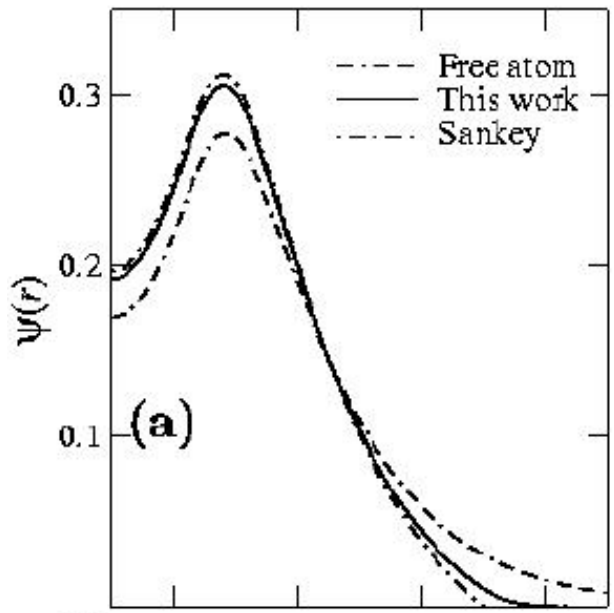
PSEUDOPOTENTIALS: BASIC IDEA



Basis functions:

- Localized Orbitals ← **SIESTA and these calculations**
- Plane Waves ← In some cases to check the SIESTA results





Strictly localised

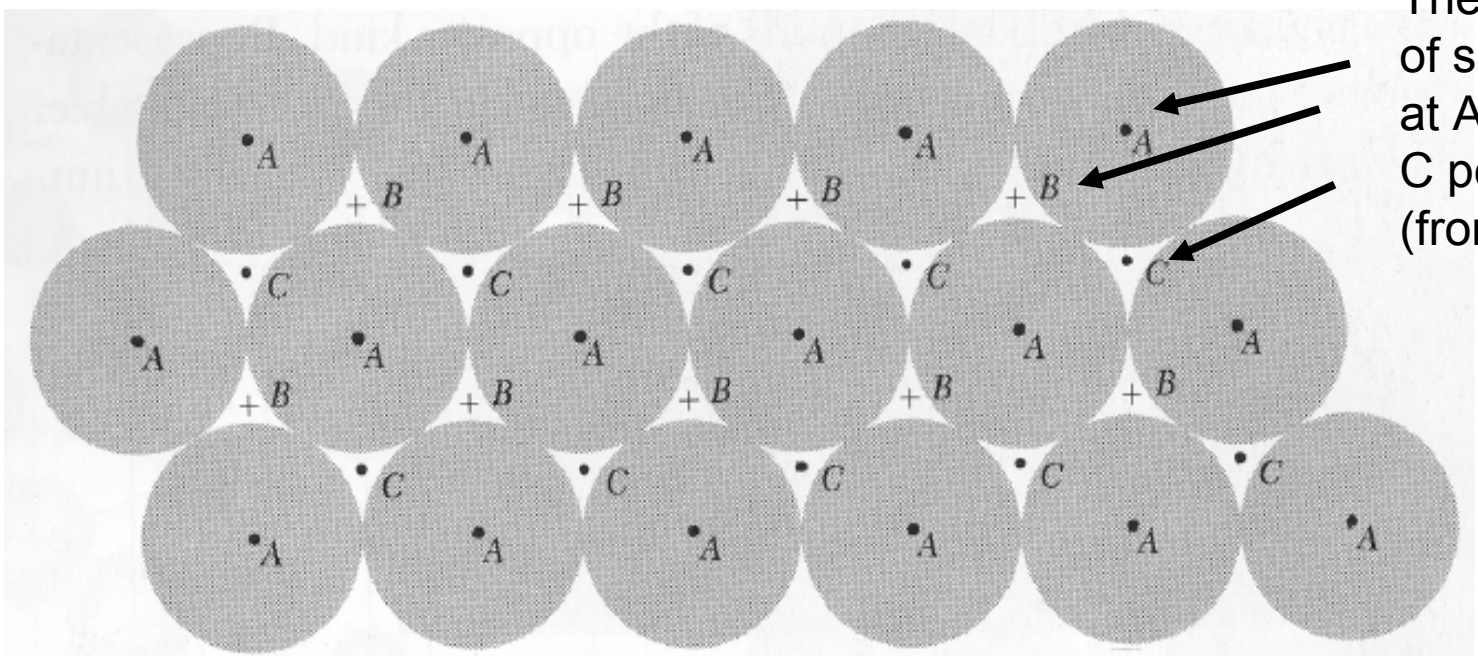
(zero beyond cut-off radius)

Closed-packed structures

(or, what does stacking fruit have to do with solid state physics?)

Closed-packed structures

There are an infinite number of ways to organize spheres to maximize the packing fraction.

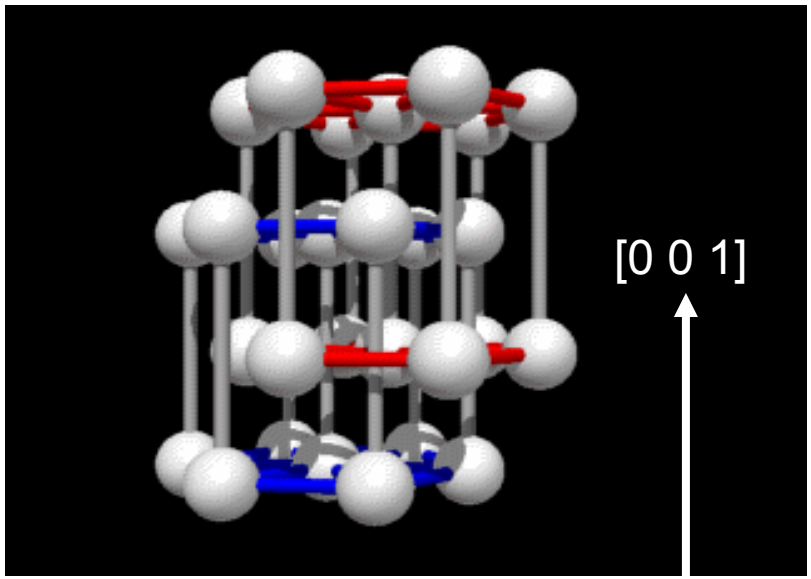


The centres of spheres at A, B, and C positions (from Kittel)

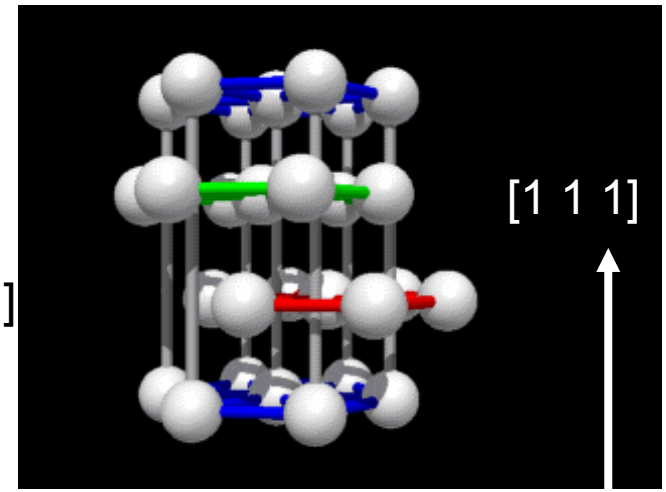
There are different ways you can pack spheres together. This shows two ways, one by putting the spheres in an ABAB… arrangement, the other with ACAC…. (or any combination of the two works)

The fcc and hexagonal closed-packed structures (hcp) are formed from packing in different ways. Cubic fcc has the stacking arrangement of ABCABCABC… hcp has the arrangement ABABAB….

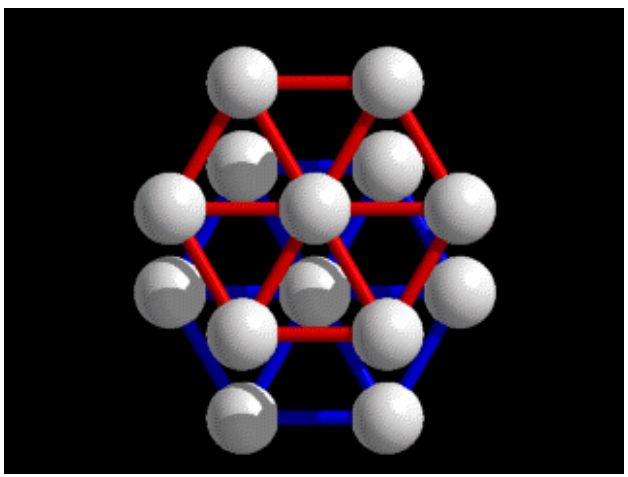
hcp



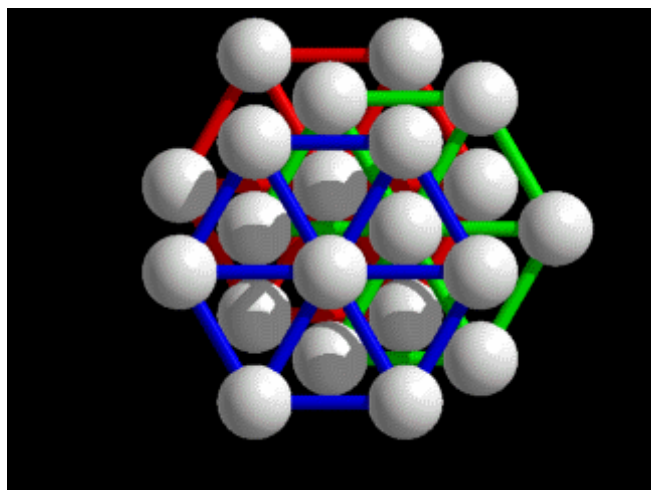
fcc
(looking along [111] direction



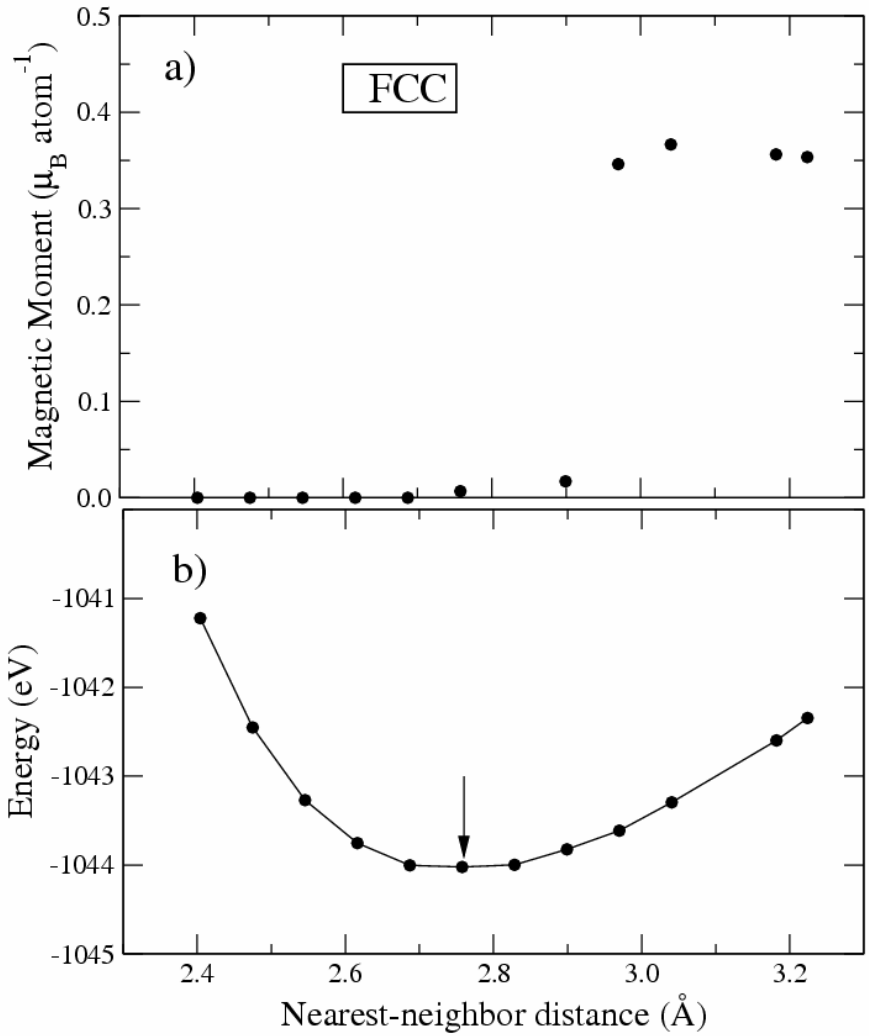
. A B A B .



. A B C A B C .



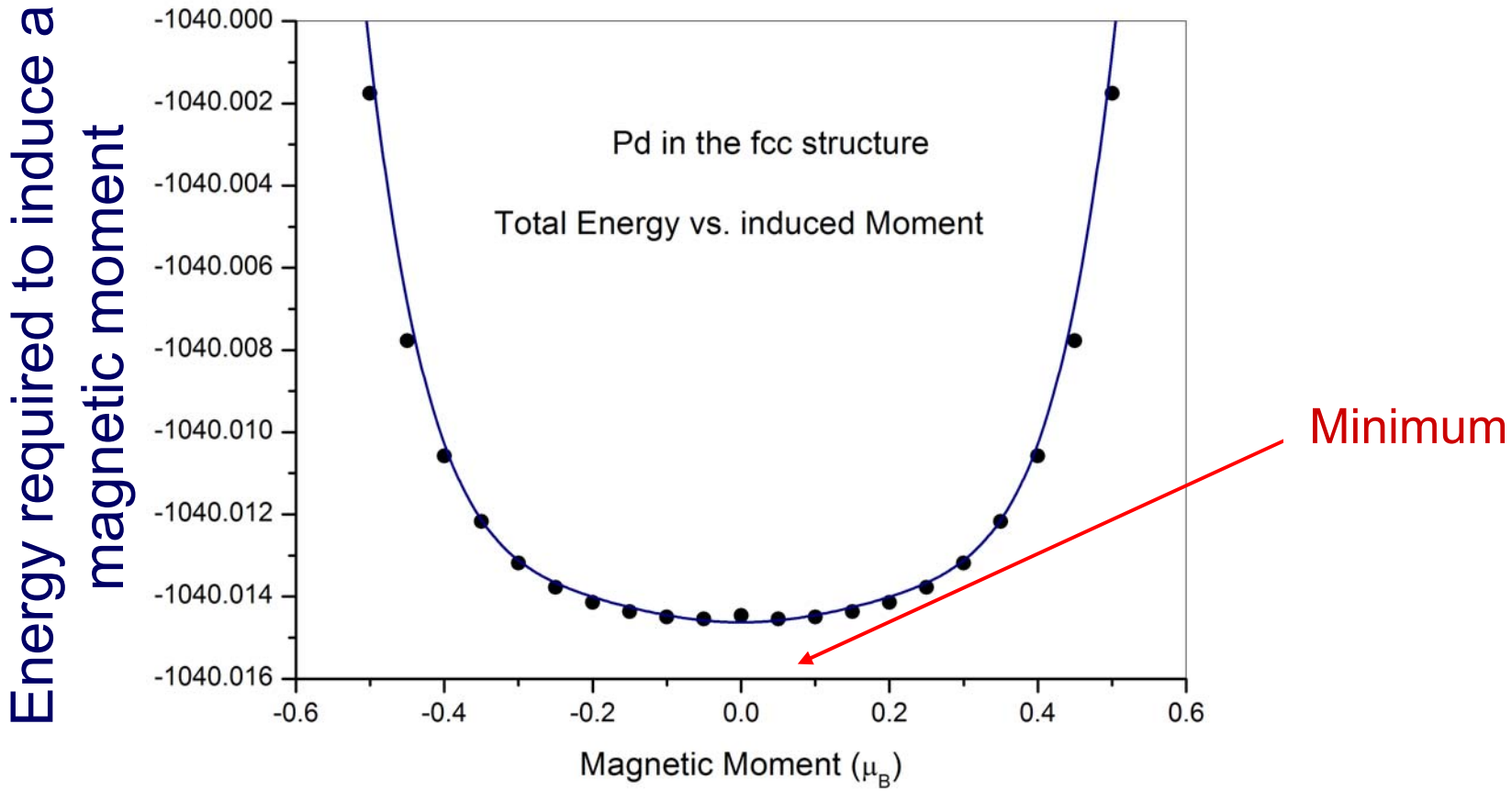
Magnetic moment and total energy of fcc Pd versus lattice constant



Equilibrium n-n distance: 2.76 Å

Exp. 2.75 Å

Pd in the fcc structure, at the equilibrium lattice constant, is paramagnetic

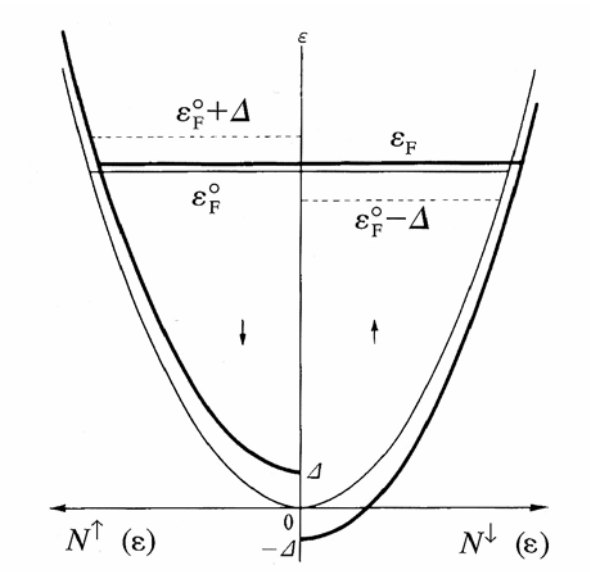


Simple model for itinerant magnetism in transition Metals.

The exchange energy is proportional to the exchange integral J

$$E_X = J \cdot N_\uparrow N_\downarrow = \frac{1}{4} J \cdot (N^2 - M^2)$$

Stoner criterion for Magnetism



Increase of kinetic energy (spin-down):

$$\Delta E_K \approx \left[\frac{1}{4N(E_F)}\right] M^2$$

Decrease of exchange energy:

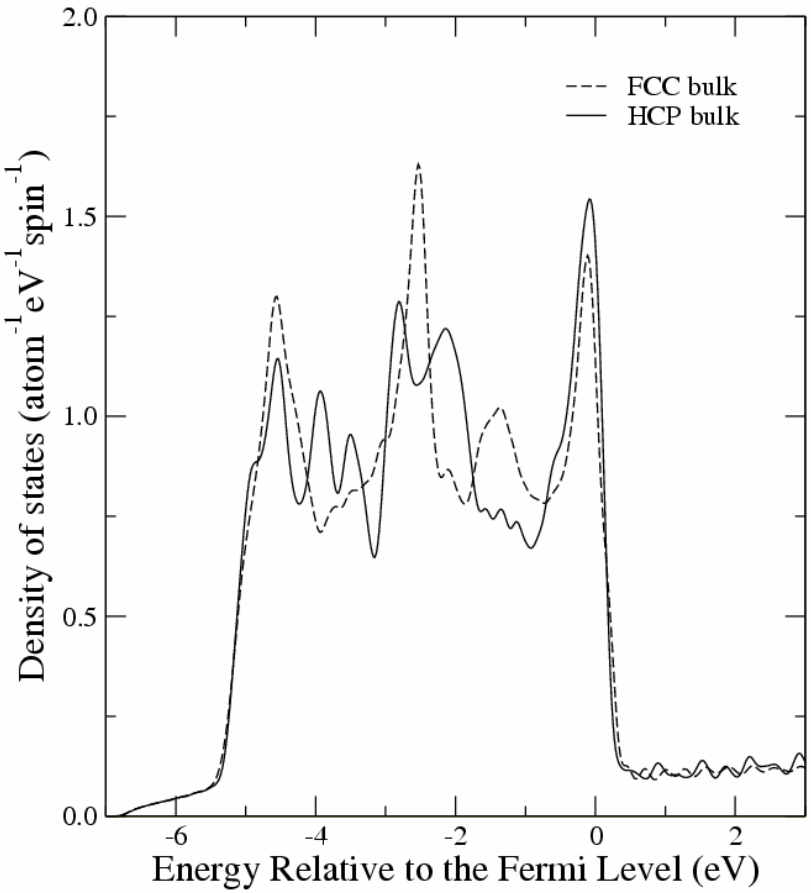
$$\Delta E_X = -J \cdot M^2$$

$$\Delta E = \Delta E_K + \Delta E_X = \frac{1}{4}\left[\frac{1}{N(E_F)} - J\right] M^2$$

Stoner criterion:

$$J \cdot N(E_F) > 1$$

Density of states of paramagnetic Pd in the fcc and hcp structures

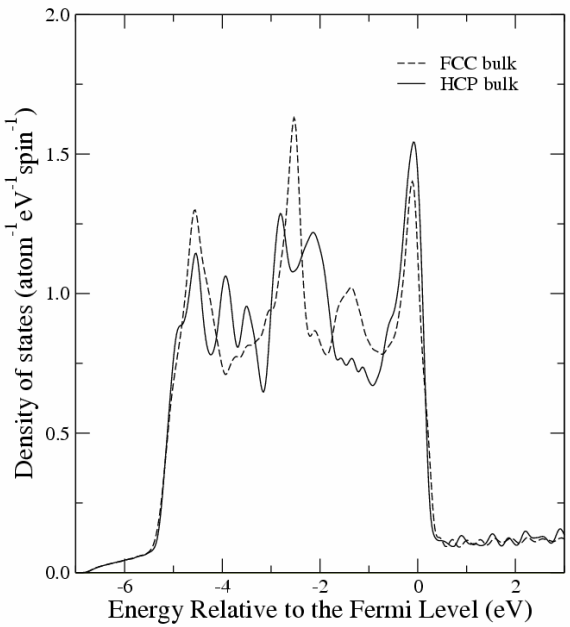


Density of states of paramagnetic Pd in the fcc and hcp structures

a) The d bandwith is almost identical in both structures.

b) The shape of the density of states curves are very different.

c) The density of states at the Fermi level is higher in the case of the hcp structure (1.434 states per atom per eV and per spin) than in the fcc one (1.145 states per atom per eV and per spin).



If Stoner's parameter I~0.71 eV* → hcp can be Magnetic

hcp: $I \times D(E_F) = 1.02 > 1$

fcc: $I \times D(E_F) = 0.81 < 1$

* N. Takano, T. Kai, K. Shiiki, and F. Terasaki, Solid State Commun. **97**, 153 (1996).

Paramagnetic fcc Pd Electronic Structure

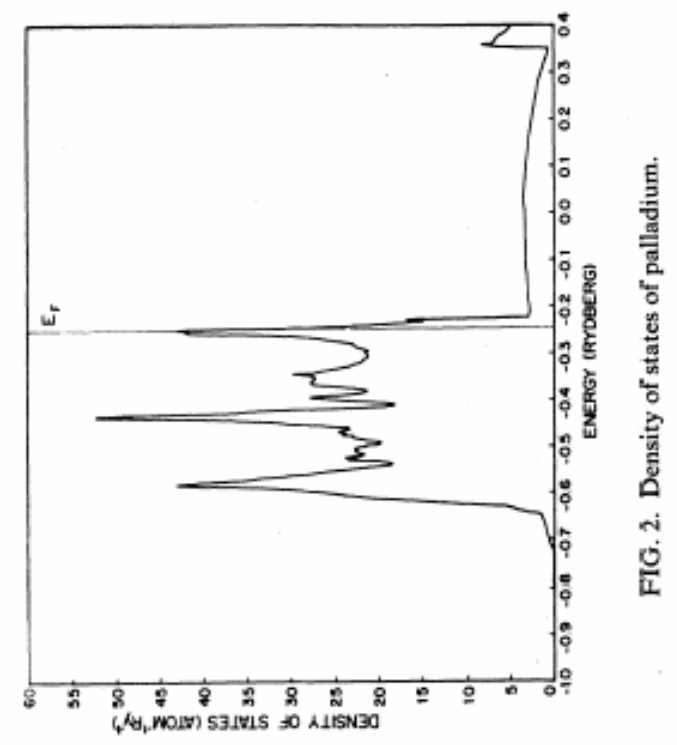


FIG. 2. Density of states of palladium.

H. Chen, N. E. Brener, and J. Callaway

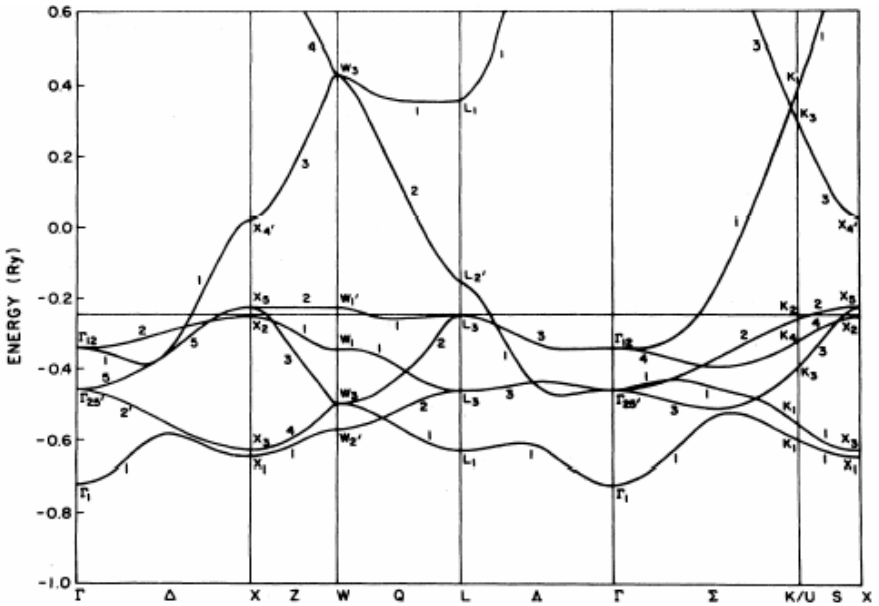
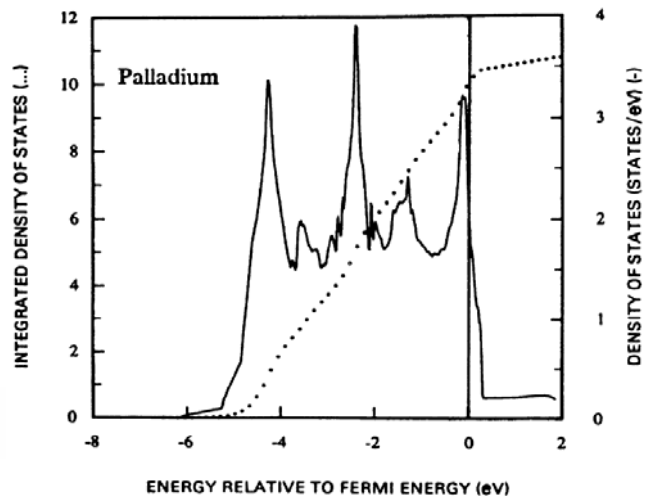
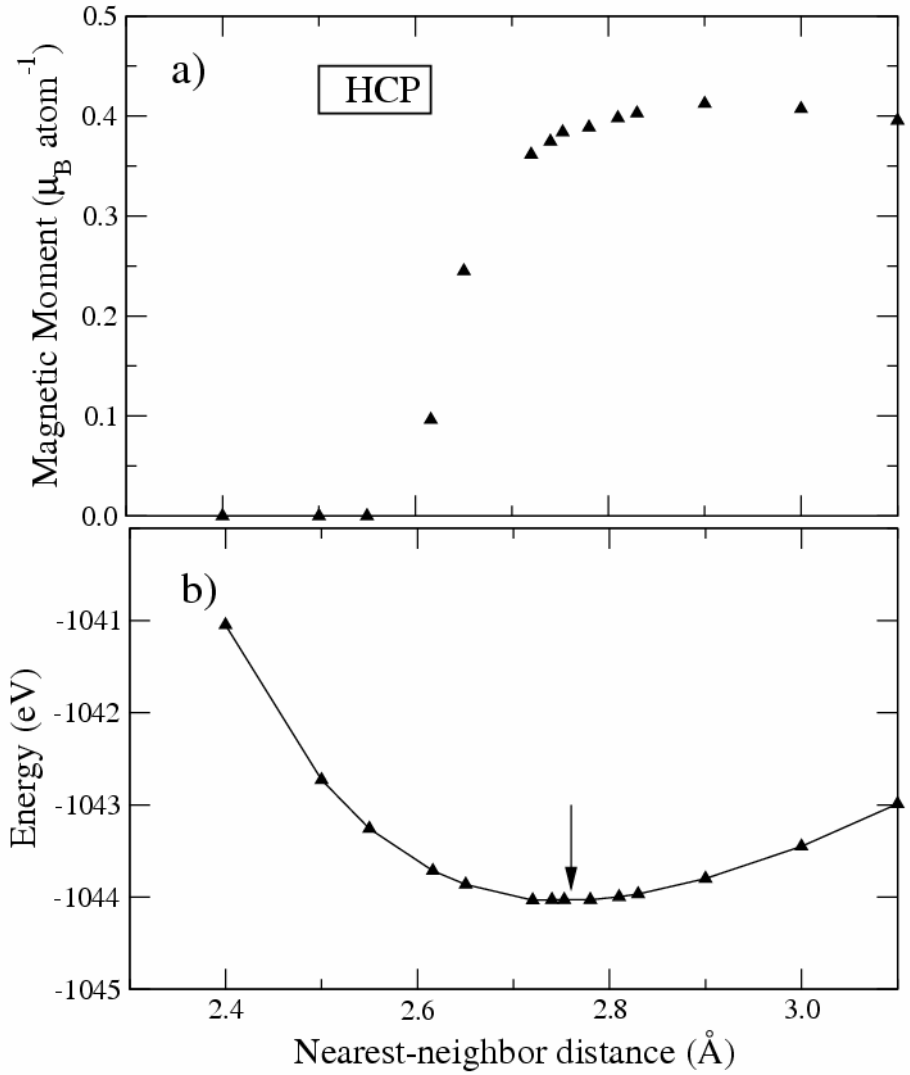


FIG. 1. Energy bands of fcc palladium along symmetry axes.



V. L. Moruzzi and P. M. Marcus

Magnetic moment and total energy of hcp Pd versus lattice constant

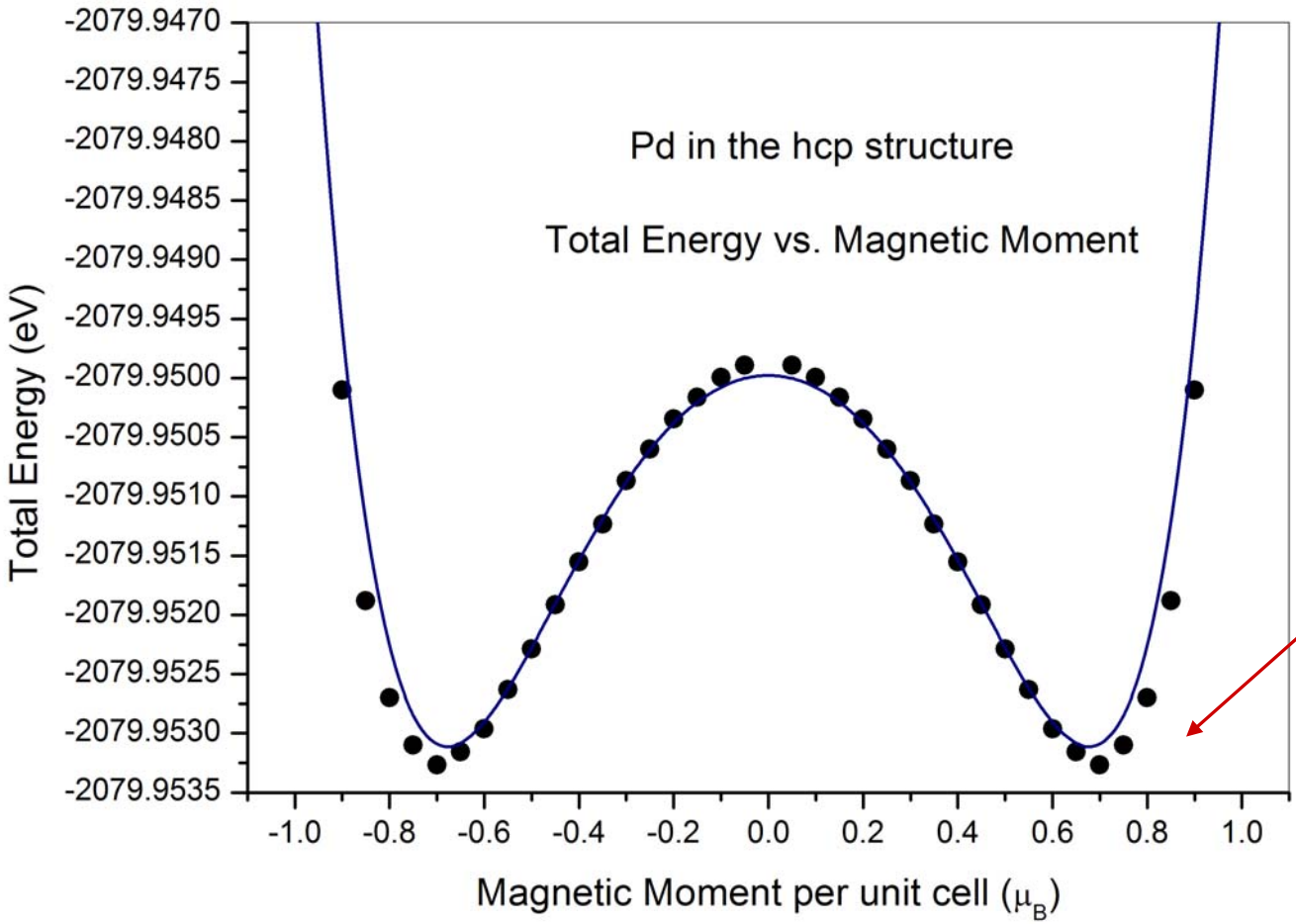


Equilibrium n-n distance: 2.76 Å

Like fcc

Pd in the hcp structure is magnetic

Pd in the hcp structure, at the equilibrium lattice constant, is ferromagnetic

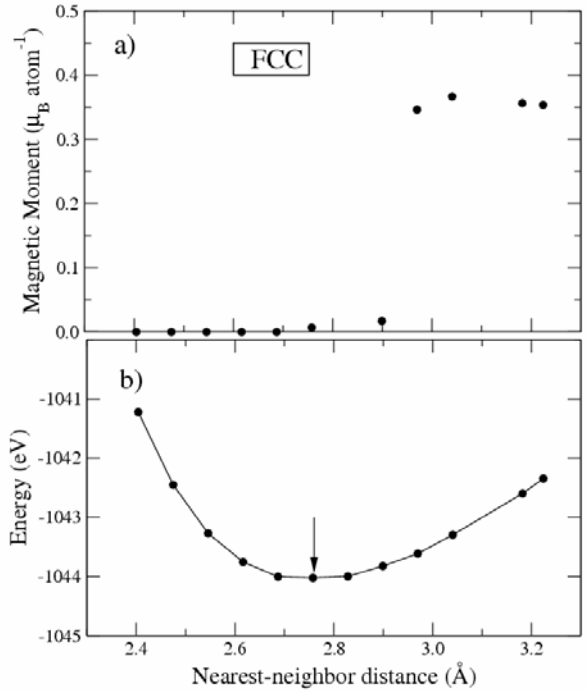


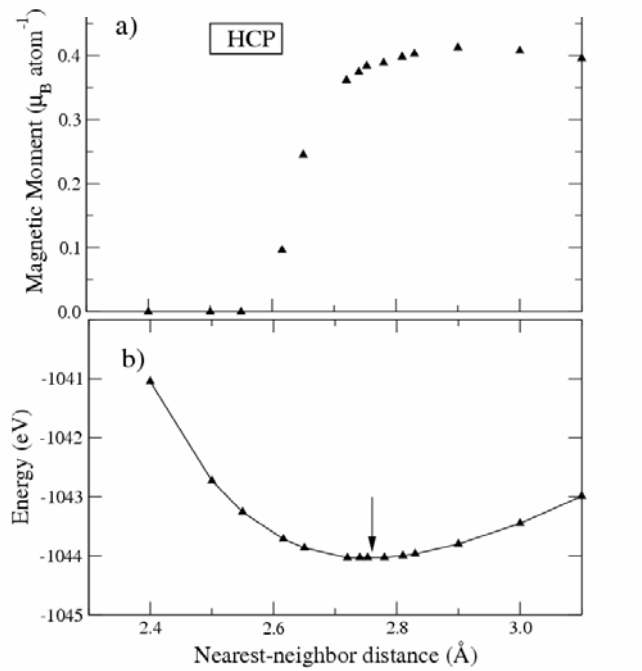
Minimum

Comparison between

fcc and hcp

Same nearest-neighbor distance and bond angles





Different stacking sequences of hexagonal layers

fcc		hcp		St-fault	
.		.		.	
.		.		.	
.		.		Cubic	A
Cubic	A	Hex	A	Cubic	B
Cubic	B	Hex	B	Cubic	C
Cubic	C	Hex	A	Hex	A
Cubic	A	Hex	B	Hex	C
Cubic	B	Hex	A	Cubic	A
Cubic	C	Hex	B	Cubic	B
.		.		Cubic	C
.		.		.	
.		.		.	

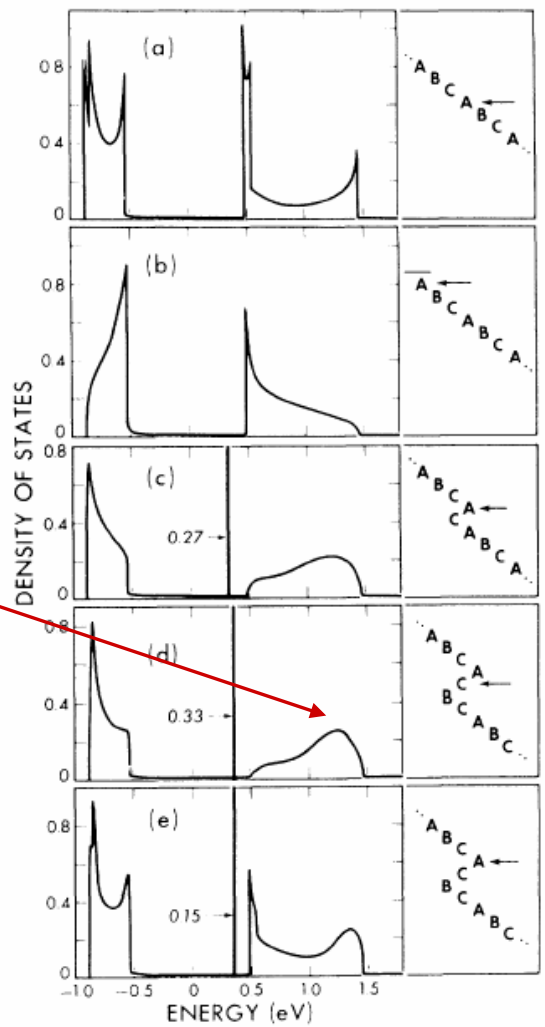
What could we expect near stacking faults?

DOS model calculation (Γ-point)

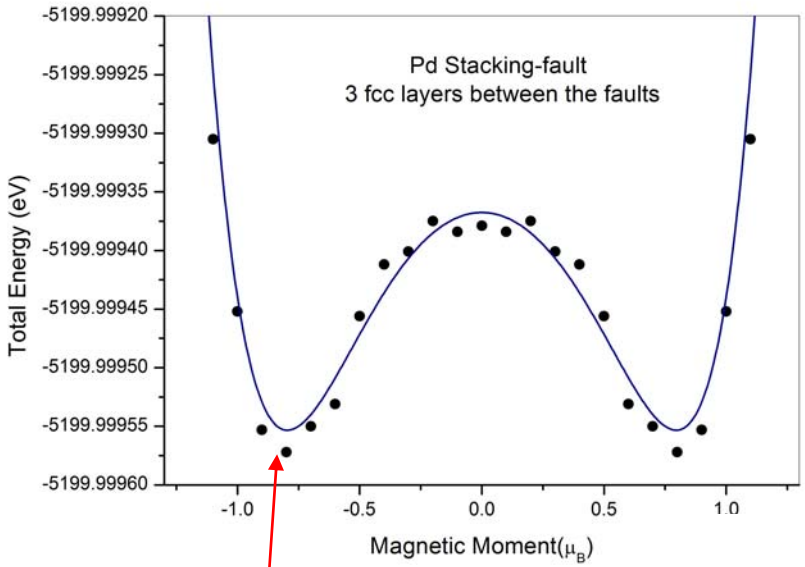
Yndurain & Falicov, Phys. Rev. Lett. 34, 928 (1976)

The Density of States at the top of the d-bands is enhanced:

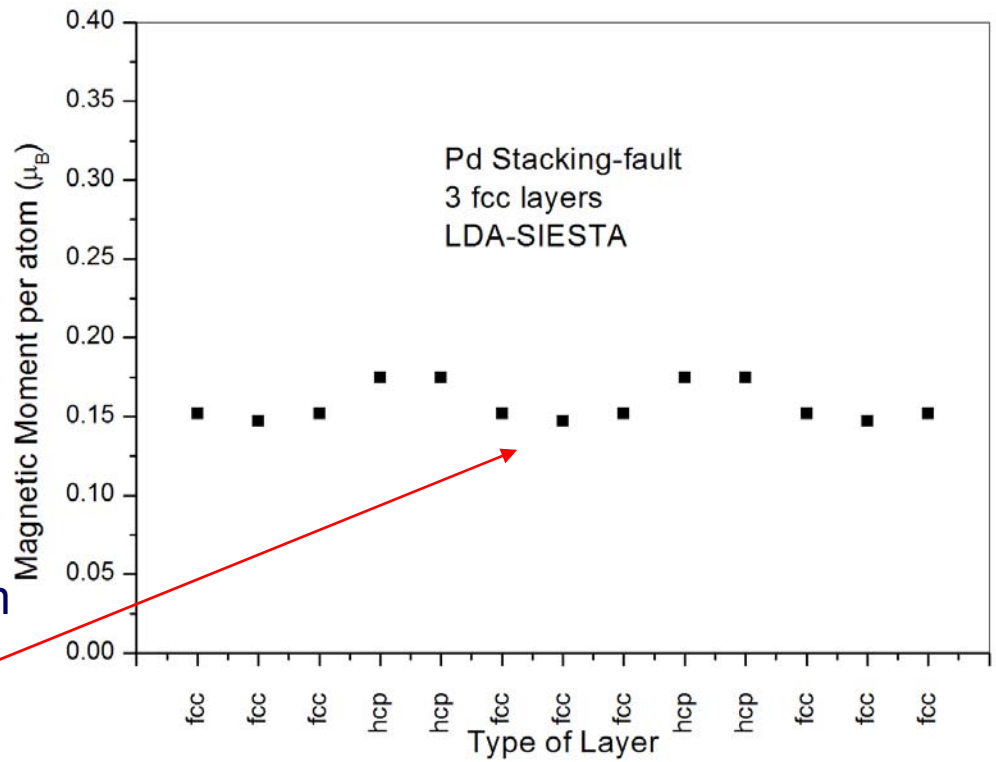
Favors magnetism



Stacking-faults separated by 3 fcc layers

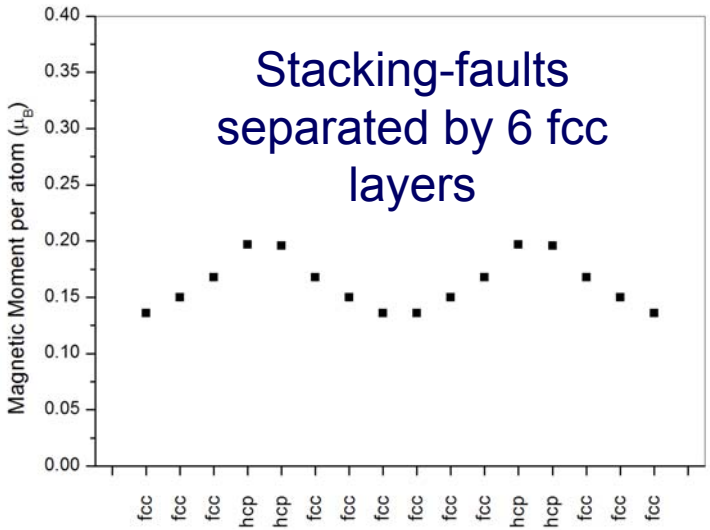


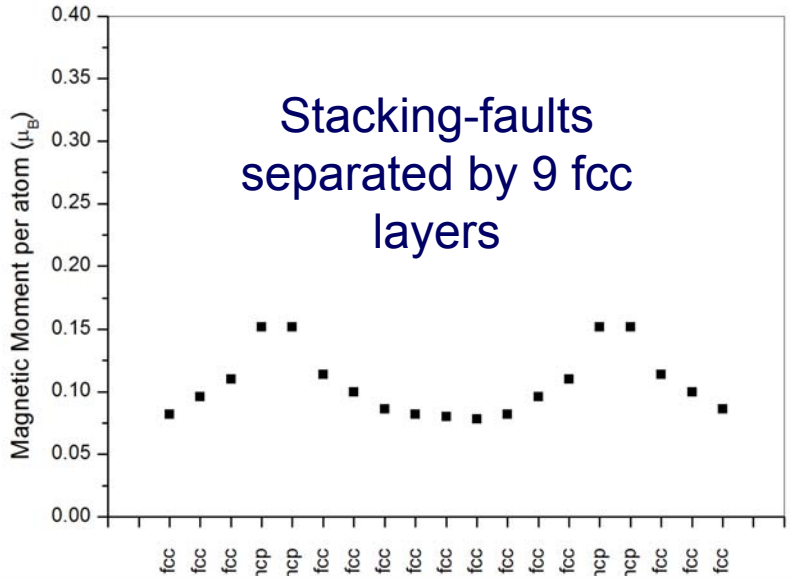
Magnetic solution

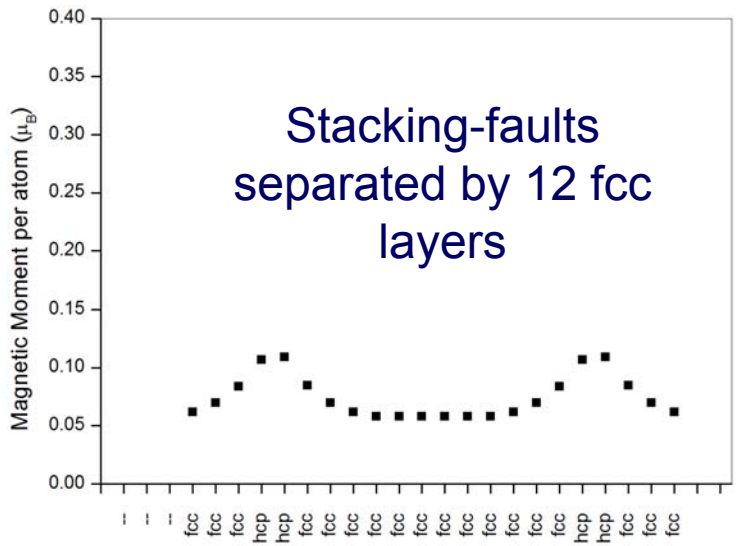


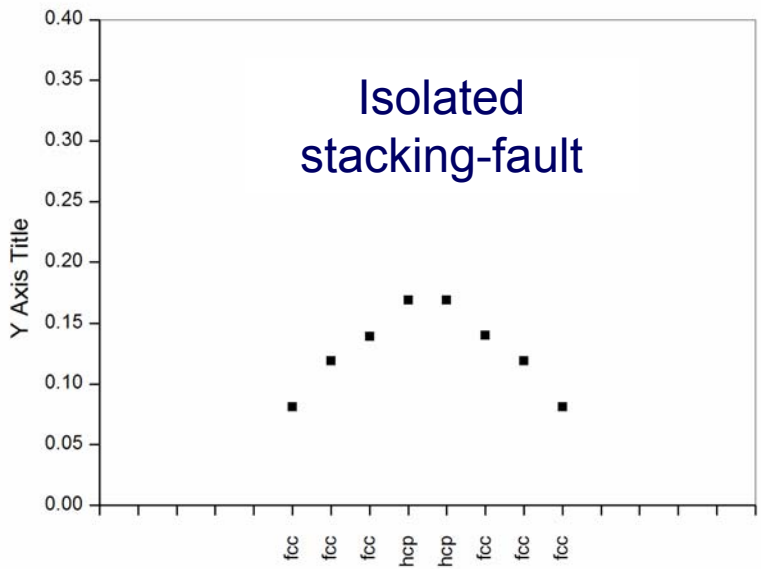
The fault induces magnetism in the fcc layers

DIFFERENT STACKING CONFIGURATIONS









Magnetic anomalies observed experimentally in Co* and Ni** different stackings can be interpreted along similar lines.

*Detecting Electronic States at Stacking Faults in Magnetic Thin Films by Tunneling Spectroscopy. A. L. Vázquez de Parga, F. J. García-Vidal, and R. Miranda, 85, 4365 (2000)

*Spin-Polarized Scaning Tunneling Spectroscopy of Nanoscale Cobalt Islands on Cu (111), O. Pietzsch et al. Phys. Rev. Lett. **92**, 057202 (2004)

Stacking Reversal as a Source of Perpendicular Magnetic Anisotropy in Ni-Pt Multilayers, O. Robach et al. Phys. Rev. B **67, 220405(R) (2003)

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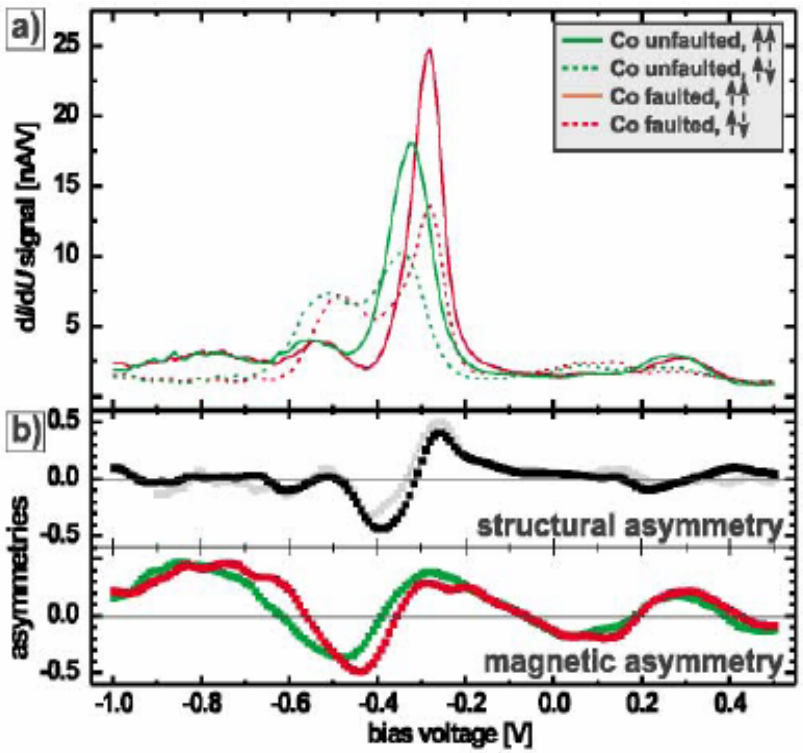
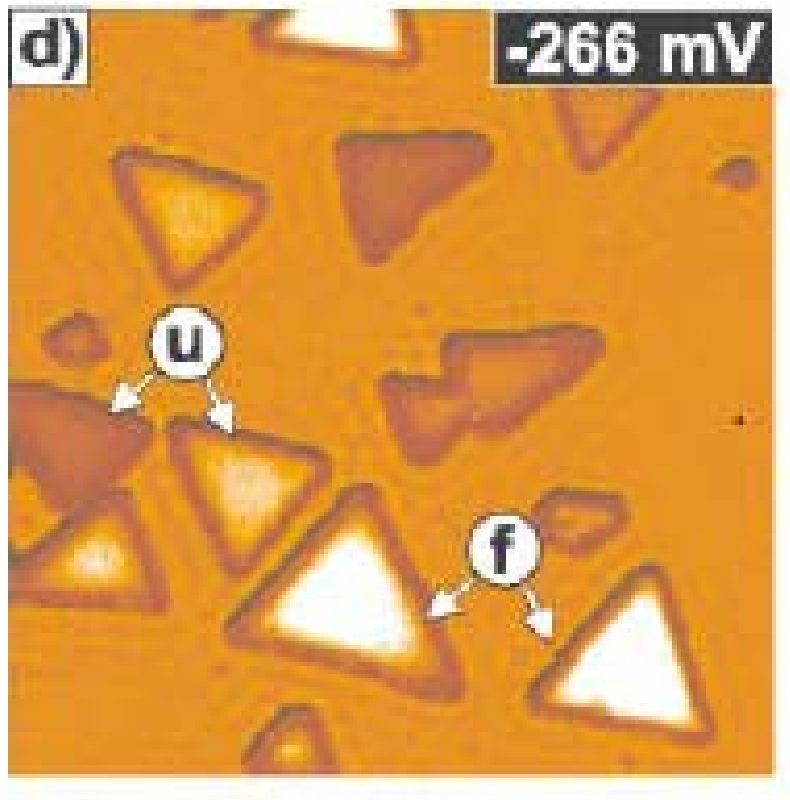
Spin-Polarized Scanning Tunneling Spectroscopy of Nanoscale Cobalt Islands on Cu(111)

O. Pietzsch,* A. Kubetzka, M. Bode, and R. Wiesendanger

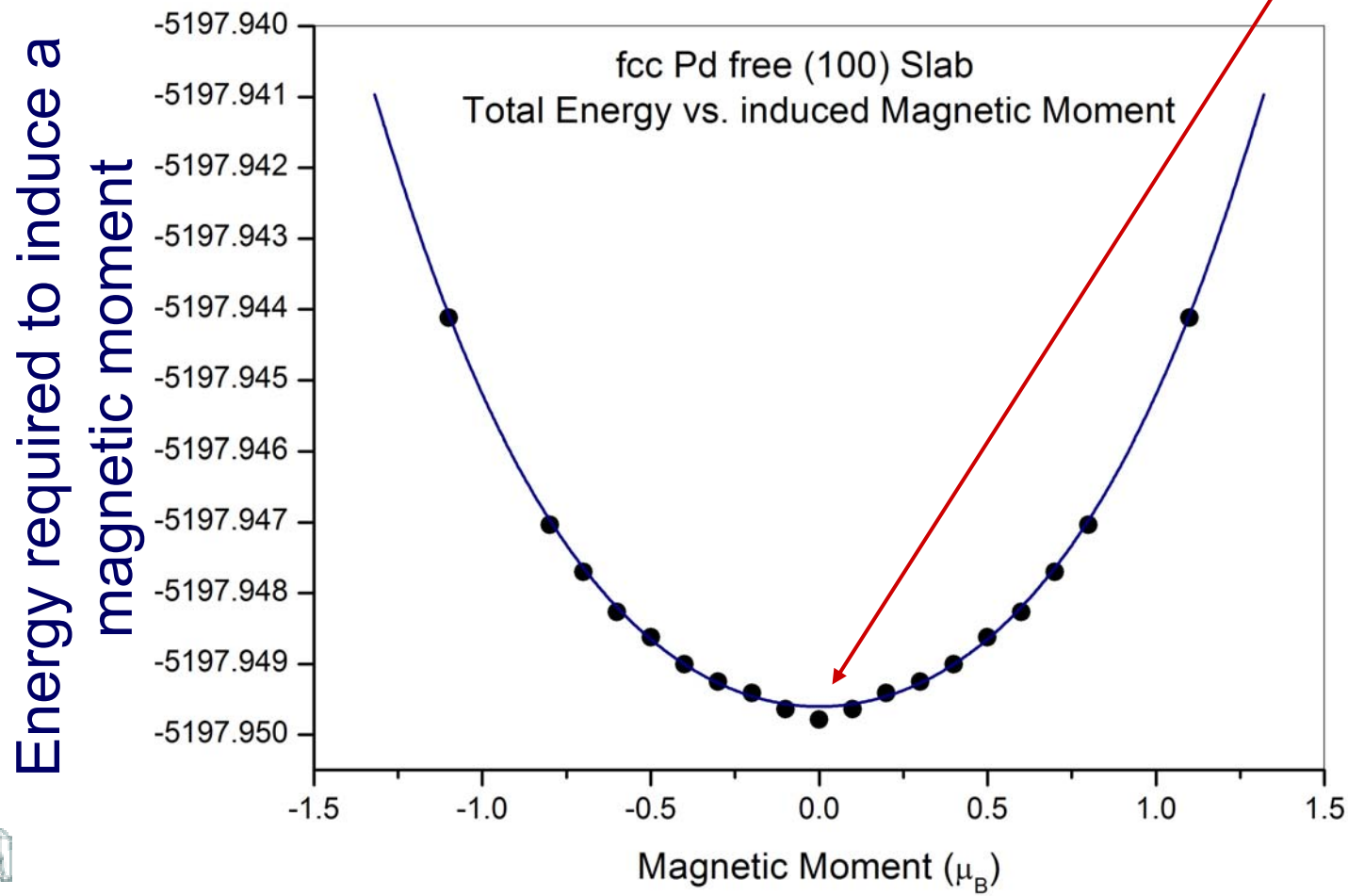
Spin-resolved tunneling spectra



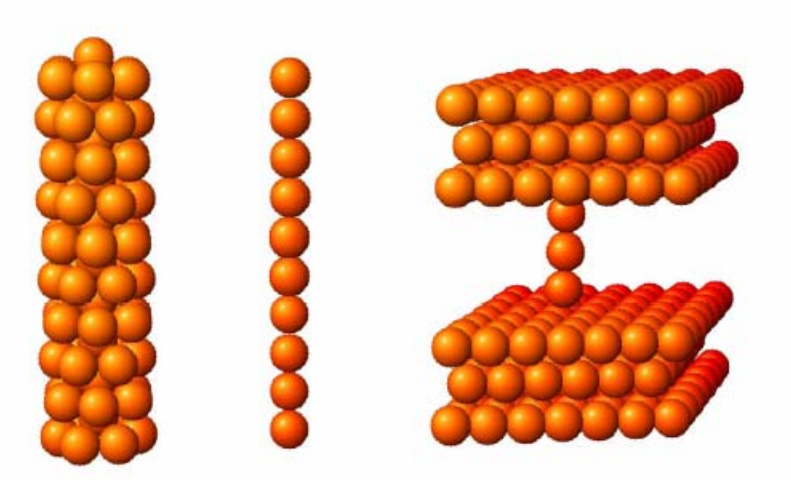


Is Magnetism in Pd a Surface Effect?

A Surface free fcc (100) Pd Slab is Paramagnetic

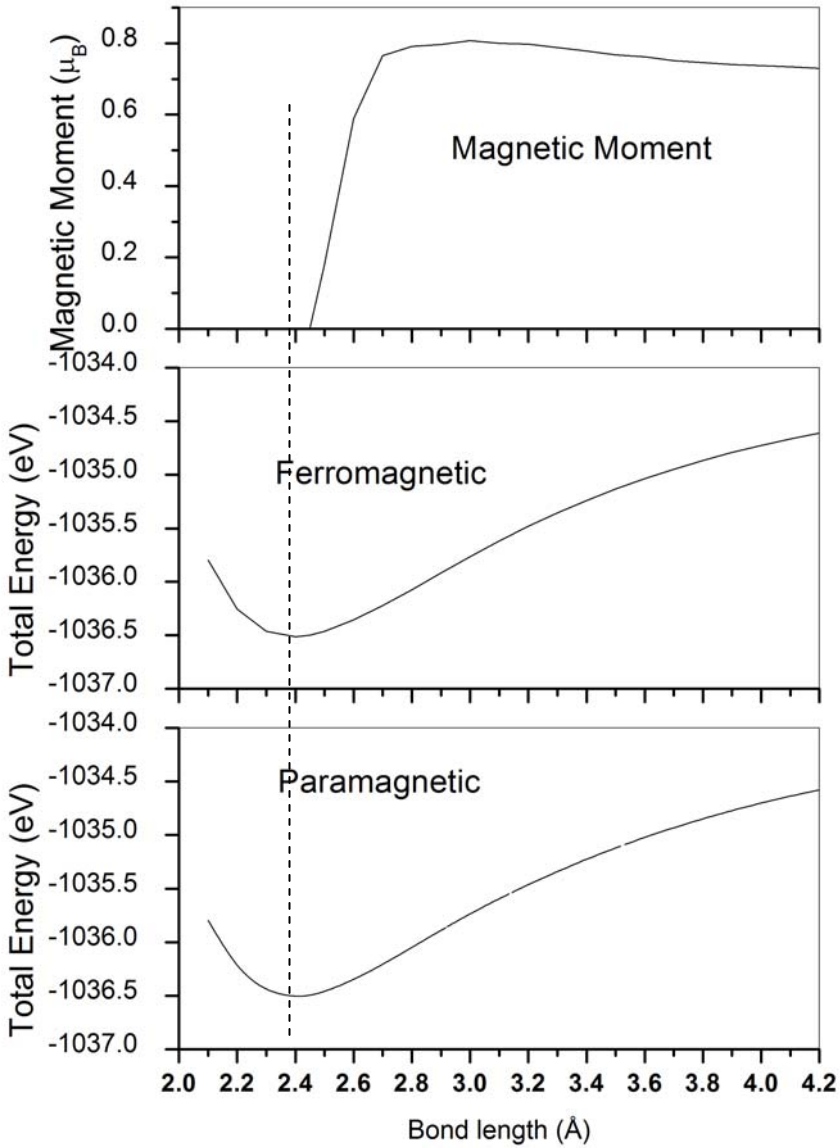


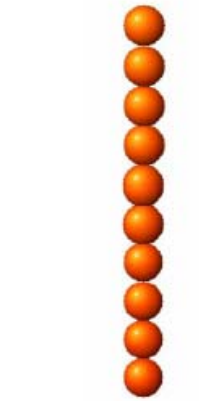
Other Pd NanoStructures

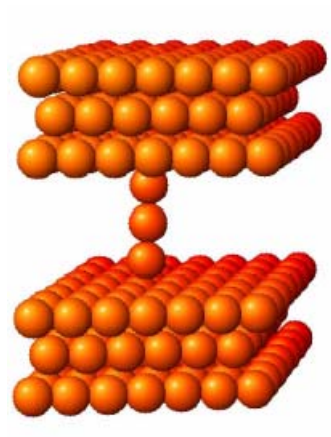


"Magnetism in Atomic-Size Palladium Contacts and Nanowires"
A. Delin,E. Tosatti and R.Weht, Phys. Rev. Lett. **92**, 57201 (2004)

Magnetism in Pd Chains







CONCLUSIONS

- Small Pd particles are magnetic whereas bulk fcc is not
- Pd in the hcp phase (38 meV higher than the fcc) is ferromagnetic
- Stacking-faults in otherwise fcc Pd are magnetic
- Isolated faults are magnetic
- Our results are consistent wit experiments in small clusters
- Free Pd surfaces are not magnetic
- Magnetic anomalies observed experimentally in Co and Ni stacking can be interpreted along similar lines.
- Further study: Pd islands on top of Cu (111) surface

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Acknowledgments

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