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" ELECTRONIC STRUCTURE OF DISORDERED SURFACES AND ITS APPLICATIONS "

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These are preliminary lecture notes, intended only for distribution to participants.

ELECTRONIC STRUCTURE OF DISORDERED SURFACES AND ITS APPLICATIONS

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MOTIVATION: surface disorder occurs frequently

- disordered / incomplete overlayers on substrates: (Ag, Pd) on Ag(110); gases on TM surfaces (catalysis)
- surface disordering: $Cu_{50} Au_{50}$ (001)
- surfaces of TM alloys with non-uniform composition: (Ni, Pt) or (Cu, Ni) low-index surfaces
- semiconductor interfaces / superlattices: CdTe | (Cd, Hg) Te

Electronic structure is <u>key</u> to microscopic understanding

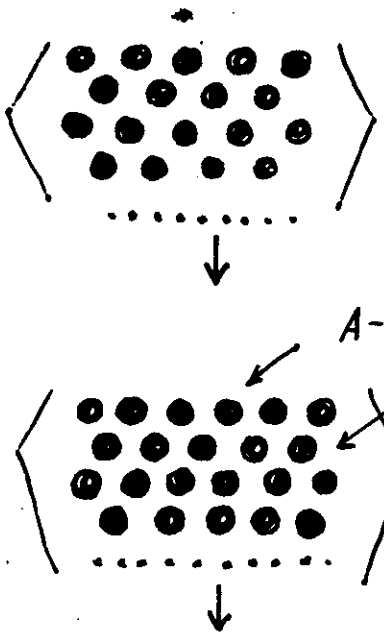
AIM: develope electronic theory of systems with disordered surfaces / interfaces which

- starts from first principles ...
- semiinfinite sample geometry
- describes reliably concentration trends

To this end we combine

- TB-LMTO to describe electron states
- SGF method within the PL concept
- CPA to include disorder (inhomogeneous CPA)
- LSDA to account for electron correlations
- Empty spheres to describe vacuum

STUDIED SYSTEMS



random overlayer

non-random substrate

{ LDA and CPA }

bulk-alloy layer composition

● A-atom
● B-atom

Basic approximation (in addition to LDA & CPA):
Sample inhomogeneity in conjunction with LDA and CPA implies that each layer has different properties and layers are coupled each other → ∞ set of equations

Surface-bulk approximation: only first N-top layers have different properties to be found selfconsistently, remaining layers have bulk properties

Typically concentrations / potentials differ from bulk ones in few top layers for metallic systems

GREEN'S FUNCTION

To facilitate simultaneous treatment of disorder and surface we transform from original (γ) to new (β) LMTO representation

ORIGINAL $\rightarrow \gamma_{RL}$

$$G(z) = (z - H)^{-1}$$

$$H = C + \Delta^{1/2} S^{\gamma} \Delta^{1/2}$$

$$S^{\gamma} = S^{0}(1 - \gamma S^{0})^{-1}$$

- off diagonal disorder
- large spatial extent of S^{γ}

NEW $\rightarrow \beta_{RL} \equiv \beta_{L}$

$$g^{\beta}(z) = (P^{\beta}(z) - S^{\beta})^{-1}$$

$$P^{\beta}(z) = (z - C)/\{\Delta + (\gamma - \beta)(z - C)\}$$

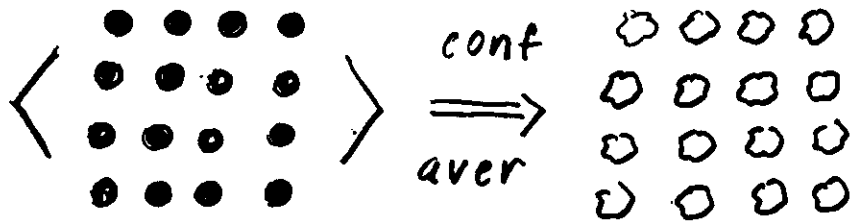
$$S^{\beta} = S^{0}(1 - \beta S^{0})^{-1}$$

- site diagonal disorder {KKR-CPA like}
- shortest possible spatial extent of S^{β}

Basic trick: we perform CPA averaging / introduce surface in β and final results transform back to physical γ using scaling relation of $G(z)$ and $g^{\beta}(z)$

$$G_{RL,R'L'}(z) = \lambda^{\beta}_{RL}(z)\,\delta_{RR'}\delta_{LL'} + \mu^{\beta}_{RL}(z)\, g^{\beta}_{RL,R'L'}(z)\, \mu^{\beta}_{R'L'}(z)$$

COHERENT POTENTIAL APPROXIMATION



after averaging TS is restored

A ● B ● ○ effective potential

$$c_A \left(\begin{smallmatrix} \circ & \circ & \circ \\ \circ & \bullet & \circ \\ \circ & \circ & \circ \end{smallmatrix}\right) + c_B \left(\begin{smallmatrix} \circ & \circ & \circ \\ \circ & \bullet & \circ \\ \circ & \circ & \circ \end{smallmatrix}\right) = \left(\begin{smallmatrix} \circ & \circ & \circ \\ \circ & \circ & \circ \\ \circ & \circ & \circ \end{smallmatrix}\right)$$ CPA equation

CPA concept applied to <u>each layer</u> in question ($i = 1, 2, \ldots N$)

$$\mathcal{P}_i^{\beta}(z) = \langle P_i^{\beta}(z) \rangle + \left[P_i^{\beta,A}(z) - \mathcal{P}_i^{\beta}(z) \right] \Phi_{ii}^{\beta}(z) \left[P_i^{\beta,B}(z) - \mathcal{P}_i^{\beta}(z) \right]$$

$$\Phi_{ii}^{\beta}(z) = \frac{1}{N_{11}} \sum_{k_{11}}^{SBZ} \mathcal{G}_{ii}^{\beta}(k_{11}, z \mid \{ \mathcal{P}_j^{\beta}(z) \})$$ – layer GF central quantity

$\mathcal{P}_i^{\beta}(z)$ – coherent potential function (non-random) determined from above coupled set of Eqs. (coupled via $\Phi_{ii}^{\beta}(z)$)

Properties of $\mathcal{P}_i^{\beta}(z)$:

- site diagonal, complex function
- non diagonal with respect to orbital index $L = lm$ due to lowering symmetry at the surface (bulk!)

PRINCIPAL LAYERS (PL)

Localized nature of S^{β} allows to define naturally PL which is very useful tool to determine layer GF (TB-LMTO !)

Def.: solid is divided into PL (p) such that only nn PL are coupled by S^{β} (site off-diagonal part of problem, P^{β} - diagonal one)

$$S^{\beta}_{pq} = S^{\beta}_{01}\,\delta_{p,q+1} + S^{\beta}_{10}\,\delta_{p,q-1}\,, \qquad S^{\beta}_{pp} = S^{\beta}_{00}$$

(bulk S^{β} are assumed)

Thus only $S^{\beta}_{00}(k_{\parallel})$, $S^{\beta}_{01}(k_{\parallel}) = \left[S^{\beta}_{10}(k_{\parallel})\right]^{+}$ fully describe our system [and $S^{\beta,\lambda\lambda}$, $S^{\beta,\lambda 0} = \left[S^{\beta,0\lambda}\right]^{+}$ for overlayer]

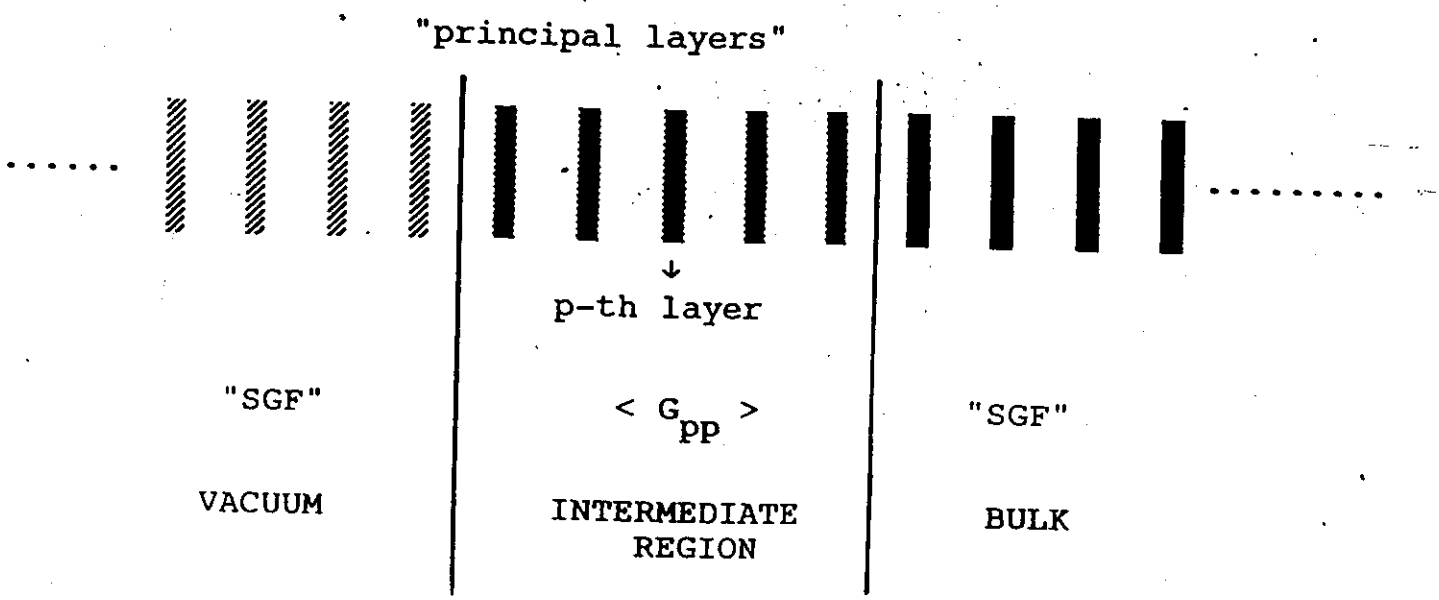
PL includes 1 to few atomic layers depending on lattice type, sample face & spatial extent of S^{β}

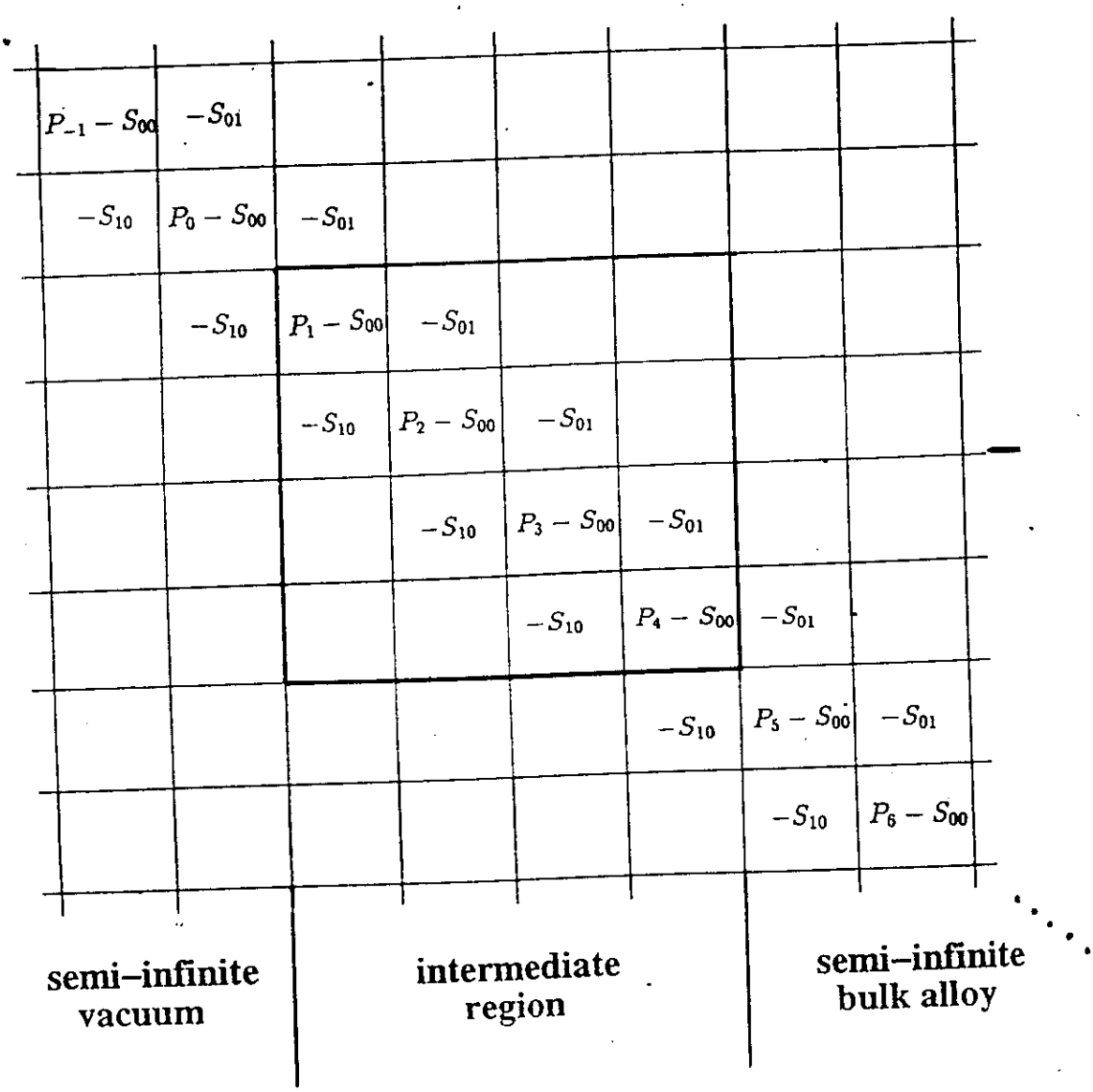
Example: fcc (001), fcc (111), bcc (110) $\longrightarrow$ PL $\equiv$ 1 at. layer
fcc (110), bcc (100) $\longrightarrow$ PL $\equiv$ 2 at. layers

fcc - 1st nn, bcc - 2nd nn : most-localized MTO repres.

Remark: if p-th PL includes more atomic layers, ϕ^{β}_{ii} in the CPA set is a superdiagonal element of ϕ^{β}_{DD} ,

Description of the semi–infinite geometry



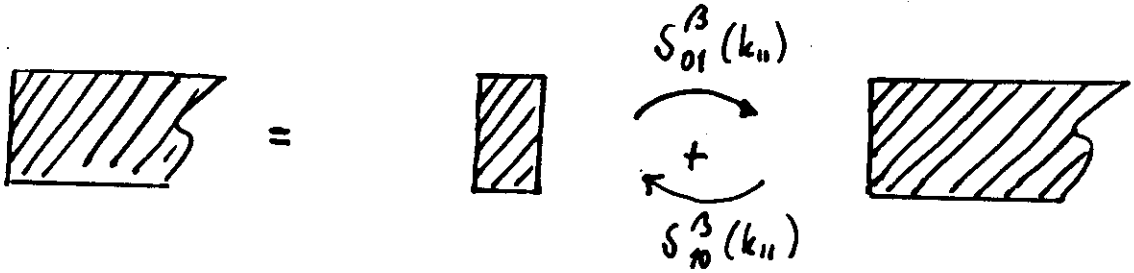


Remark: $P_5 = P_6 = \cdots P^{bulk}$, $P_0 = P_{-1} = \cdots P^{vac}$

SURFACE GREEN's FUNCTION (SGF)

We determine SGF employing removal invariance principle (RIP) avoiding knowledge of bulk GF and necessity of $k_\perp$-integration of corresponding Dyson equation (cleavage perturbation method)

SGF by definition relates to ideal substrate, i.e. all layers have identical properties



$$\mathcal{G}^{\beta,\sigma}(k_\parallel z) = \left\{ \mathcal{P}^{\beta,b}(z) - S_{00}^{\beta}(k_\parallel) - S_{01}^{\beta}(k_\parallel)\, \mathcal{G}^{\beta,\sigma}(k_\parallel z)\, S_{10}^{\beta}(k_\parallel) \right\}^{-1}$$

Remarks:

(i) selfconsistent equation for $\mathcal{G}^{\beta,\sigma}(k_\parallel z)$ is solved iteratively in complex energy plane followed by deconvolution to real axis at the end

(ii) simple and effective alternative to layer-doubling (RDT) and RS-MST techniques

(iii) serves as an exact identity to simplify expressions for interfaces, superlattices, etc.

Summary:

originally infinite problem in PL-indices is reduced to a finite one using surface GF to describe the semi-infinite bulk / vacuum

$P_1 - S_{00} - S_{10}\mathcal{G}^v S_{01}$	$-S_{01}$	0	0
$-S_{10}$	$P_2 - S_{00}$	$-S_{01}$	0
0	$-S_{10}$	$P_3 - S_{00}$	$-S_{01}$
0	0	$-S_{10}$	$P_4 - S_{00} - S_{01}\mathcal{G}^b S_{10}$

surface Green's functions $\mathcal{G}^v$ and $\mathcal{G}^b$ are found from removal invariance principle

$$\mathcal{G}^b(k_{11}, z) = \left[P^b(z) - S_{00}(k_{11}) - S_{01}(k_{11}) \cdot \mathcal{G}^b(k_{11}, z)\, S_{10}(k_{11}) \right]^{-1}$$

$$\mathcal{G}^v(k_{11}, z) = \left[P^v(z) - S_{00}(k_{11}) - S_{10}(k_{11}) \cdot \mathcal{G}^v(k_{11}, z)\, S_{01}(k_{11}) \right]^{-1}$$

LAYER-RESOLVED $k_\parallel$-INTEGRATED GF:

$$\Phi_p(z) = \frac{1}{N_\parallel} \sum_{k_\parallel} \langle g(k_\parallel z) \rangle_{pp} = f(\{\mathcal{P}_p(z)\})$$

(i) depends on all $\mathcal{P}_p$ relating them via a set of coupled layer-CPA equations

(ii) enters also LDA part thus making necessary link of both CPA and LDA

LAYER-RESOLVED LDA-POTENTIAL $V_p^\alpha(r)$: $\alpha = A, B$

$$V_p^\alpha(r) = -\frac{Z^\alpha}{r} + V_p^{\alpha,H}(\tilde{\rho}(r)) + V_p^{\alpha,ex}(\tilde{\rho}(r)) + \sum_L \sum_q M_{pq}^{sL} \bar{Q}_q^L$$

$\bar{\rho}$ – spherical part of $\rho^\alpha(r)$

Q_p – net charge in a given layer

monopole & dipole terms of multipole expansion of $\rho^\alpha(r)$

$$\bar{Q}_p^L \propto \sum_\alpha c_p^\alpha \left\{ \int_0^{s^\alpha} Y_L(\hat{r}) \left(\frac{r}{s^\alpha}\right)^\ell \rho_p^\alpha(r)\, dr - Z^\alpha \delta_{\ell,0} \right\} \qquad \begin{matrix} \ell=0 & \text{mono} \\ \ell=1 & \text{dipole} \end{matrix}$$

$\bar{Q}_p^{\ell=0}$ from $\phi_p^{LL}(z)$ $\qquad$ $\bar{Q}_p^{\ell=1}$ from $\phi_p^{L,L'}(z)$

M_{pq}^{sL} are intra- and inter-layer Madelung constants describing elst interaction of mono/dipo charges

ITERATION LOOP:

$$V_p^{\alpha,inp}(r) \quad \boxed{\text{CPA}} \Longrightarrow \bar{Q}_p^\ell \Longrightarrow \left(\text{LDA}\right) \Rightarrow V_p^{\alpha,out}(r)$$

WORK FUNCTION:

(i) Clean Ag (001)

theory 4.78 eV (present)

4.74 eV (FLAPW: Surf. Sci. 243, 317 (1991))

4.95 eV (SEGF: PRB 37, 6682 (1988))

experiment: 4.2 - 4.64 eV (surface roughness)

Model: 'sandpaper'-like => ~ 20% vacancies

4.45 eV

Dipole barrier: 8 Ag + 10 ES (9 Ag + 9 ES) } 7.1 - 7.2 eV

$M_{pq}^{s,\ell=1} = 0$

(ii) Clean Pd (001)

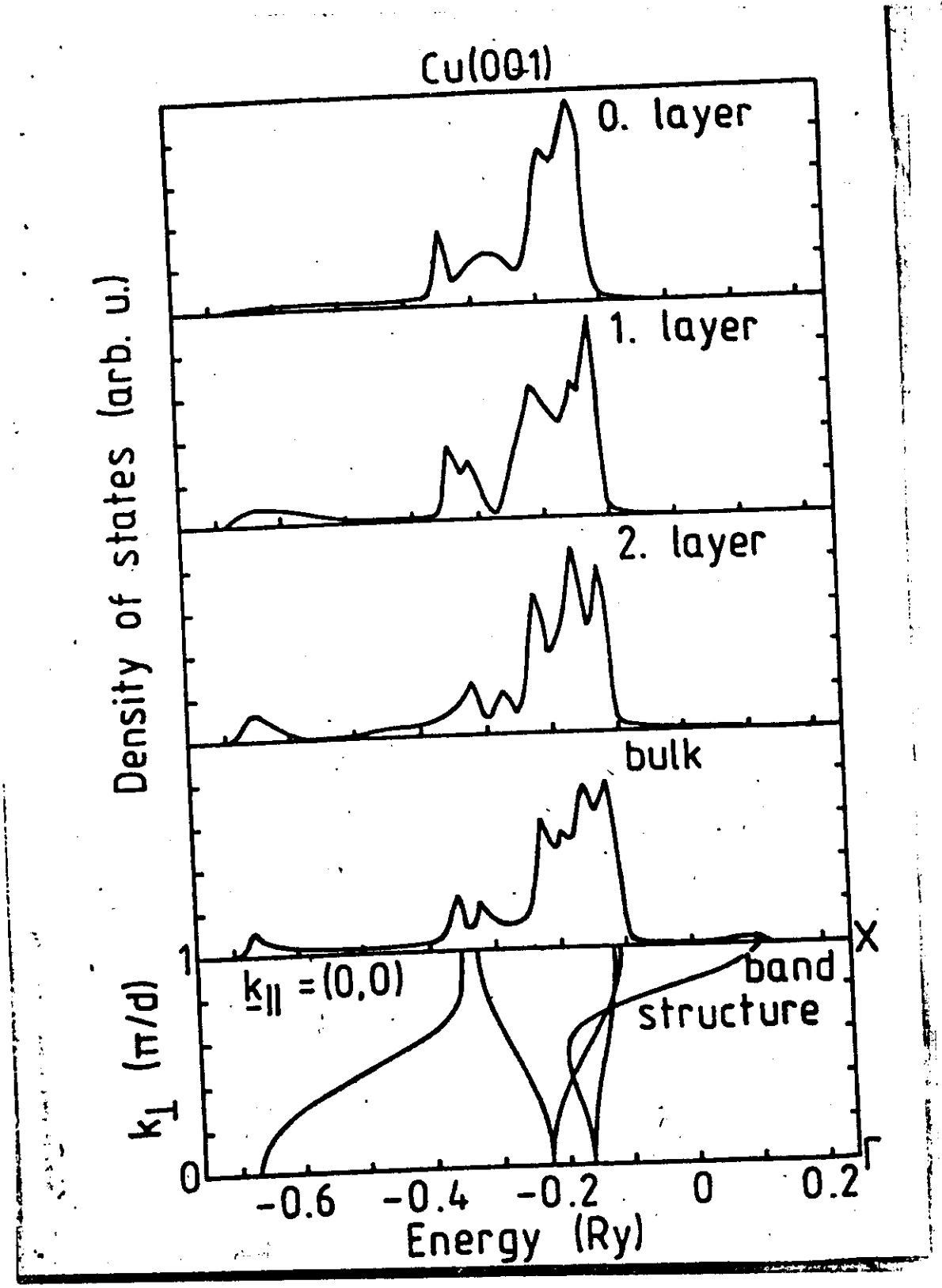
theory equilibrium: 5.83 eV expanded (Ag): 5.61 eV

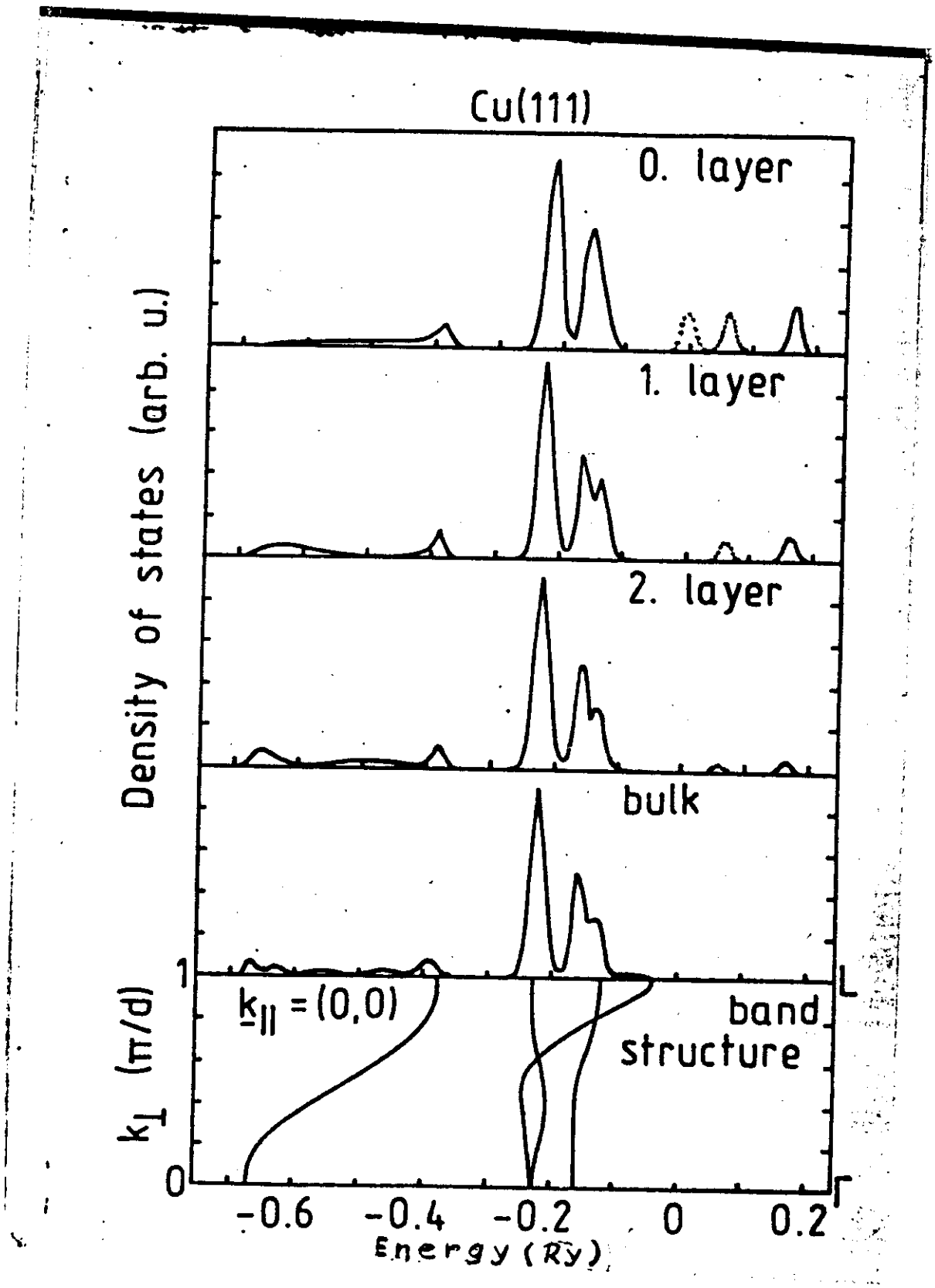
experiment: 5.8 eV

(iii) (Ag, Pd) overlayer on Ag (001)

monotonic increase from 4.78 eV (clean Ag (001)) to

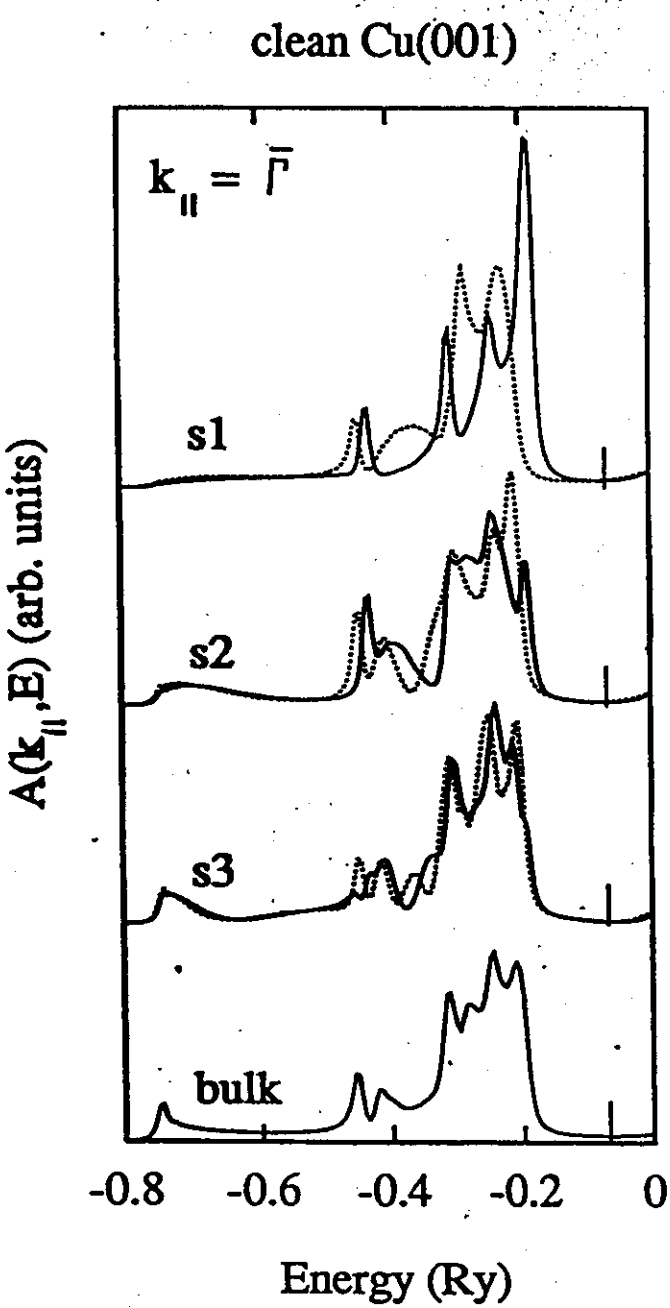
5.67 eV (Pd monolayer) ⟶ expanded Pd (001)


Cu(001)
0. layer
1. layer
2. layer
bulk
Density of states (arb. u.)
X
Γ
band
structure
$\underline{k}_{\parallel}$ = (0,0)
$k_\perp$ (π/d)
1
0
-0.6
-0.4
-0.2
0
0.2
Energy (Ry)


Cu(111)
0. layer
1. layer
2. layer
bulk
Density of states (arb. u.)
$k_\perp$ (π/d)
1
0
$\underline{k}_{||}$ = (0,0)
band structure
L
Γ
-0.6
-0.4
-0.2
0
0.2
Energy (Ry)

—— scf calculations

..... nscf calculations: bulk potentials up to the surface



Intermediate region: 2 ES + overlayer + 2 substrate layers

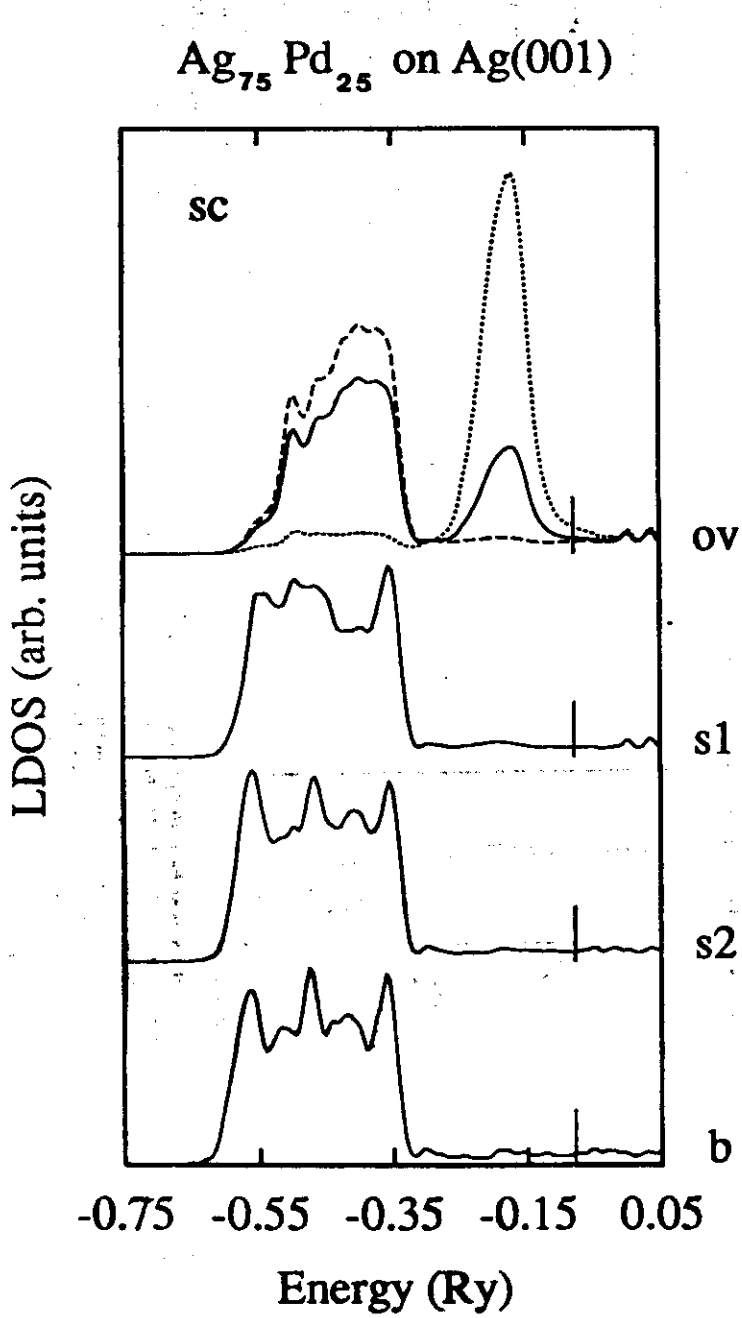
SBZ integration: 21 special $k_{\parallel}$-points

Layer-resolved DOS

— total DOS

---- Ag LDOS

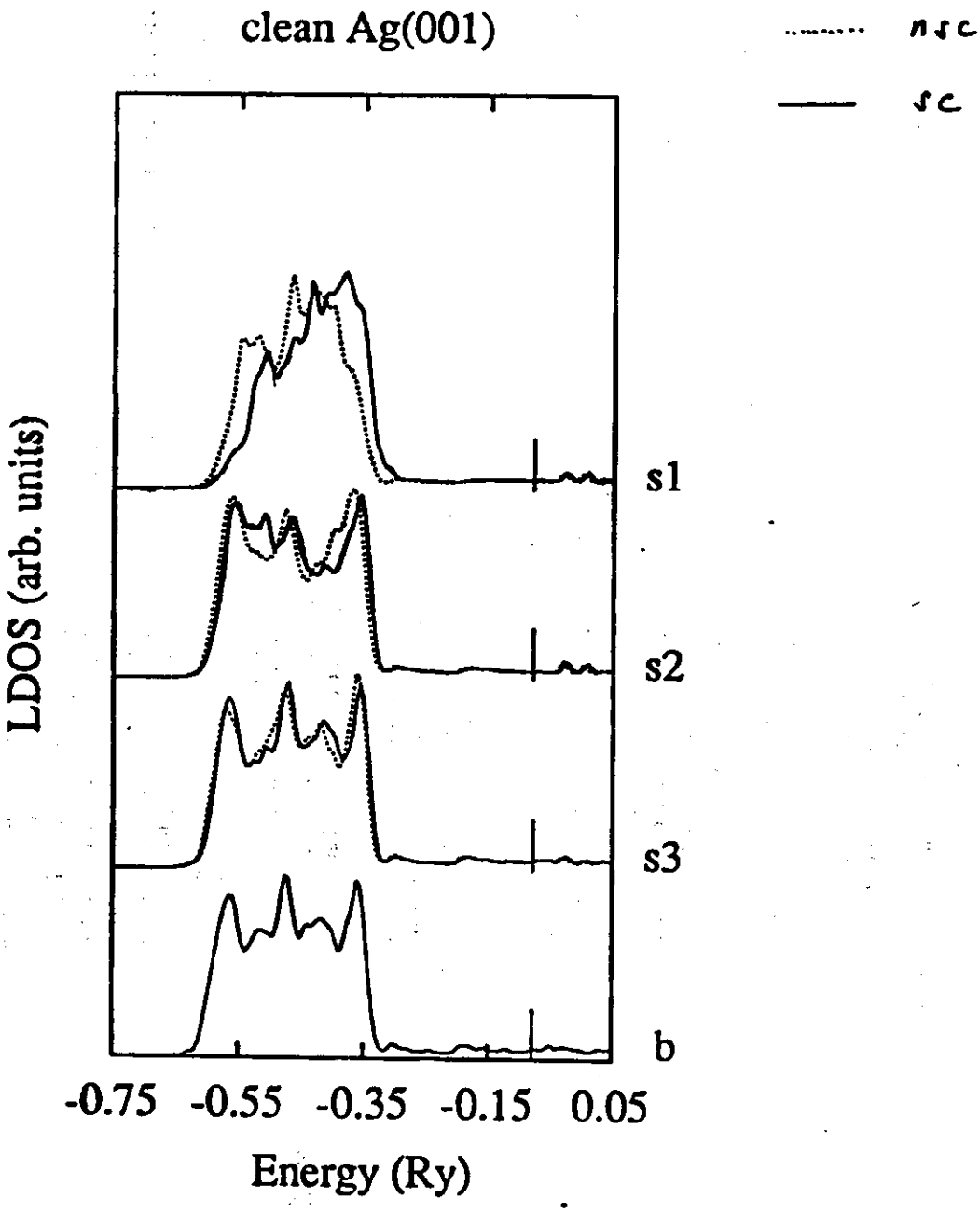
..... Pd LDOS

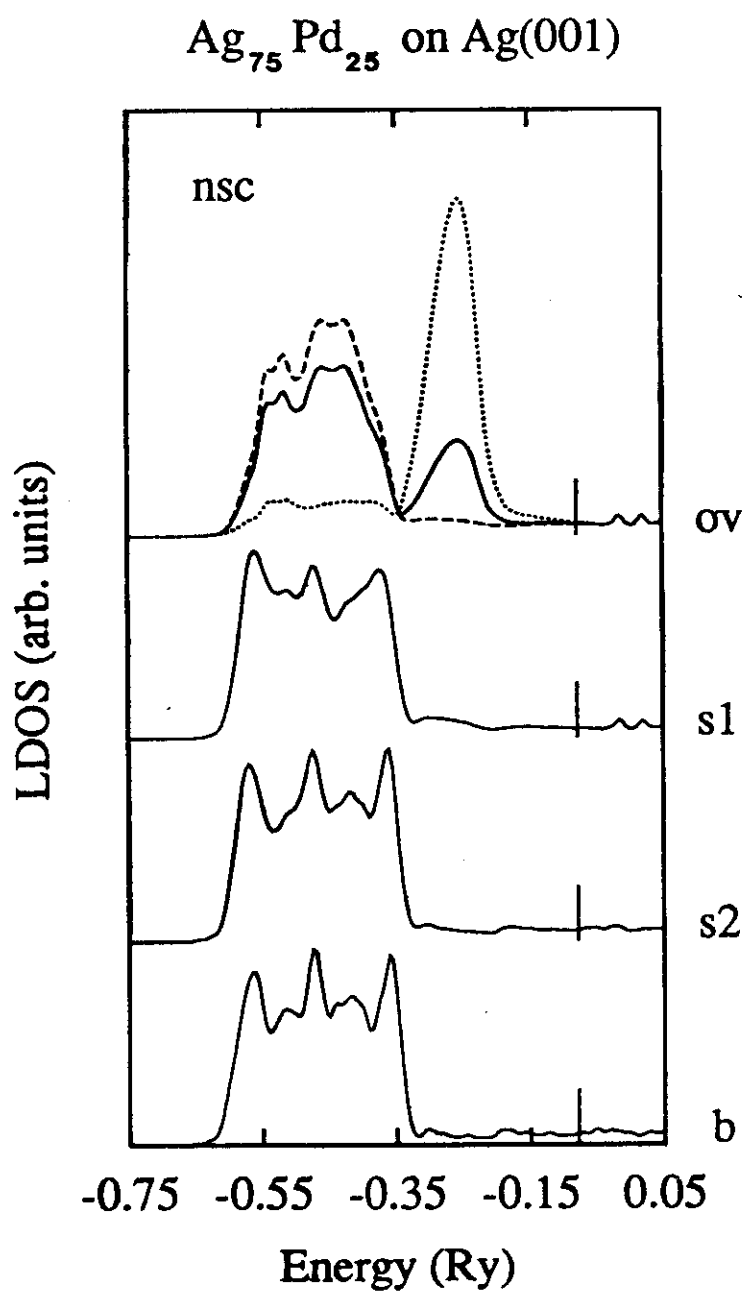


Intermediate region : 2 ES + 3 substrate layers

SBZ integration : 21 special $k_{\parallel}$ - points

Layer-resolved DOS




$Ag_{75}Pd_{25}$ on Ag(001)
nsc
ov
s1
s2
b
LDOS (arb. units)
-0.75
-0.55
-0.35
-0.15
0.05
Energy (Ry)

ORDERING ON SURFACES: Cu(001) c(2×2)-Pd

LEED exp: ≈ 50% Pd coverage, c(2×2) pattern found

Two possibilities:

(i) CuPd surface alloy (ii) Pd overlayer
(limited to top sample layer)

Remark: similar case is Au coverage on Cu(001)

Dynamical LEED calculation → surface alloy

ARPES → surface alloy (Pd-induced features similar as bulk CuPd)

New approach: PRL 69 (1992) 308

- we study the stability of disordered phases – $Cu_{50}Pd_{50}$ and $Pd_{50}Vac_{50}$ overlayers on Cu(001) towards the formation of ordered phase

(analogy to magnetic instabilities of $\chi(k)$ – e.g. bcc paramagnetic Cr → antiferromagnetic Cr).

- ordering is studied in the frame of effective 2D Ising model constructed from corresponding ab-initio electronic structure within the GPM

$$H = \sum_{R \neq R'} V_{RR'} \eta_R \eta_{R'}, \qquad V_{RR'} = V_{RR'}^{AA} + V_{RR'}^{BB} - V_{RR'}^{AB} - V_{RR'}^{BA}$$

$$V_{RR'}^{\alpha\alpha'} = -\frac{1}{\pi} \mathrm{Im}\, \mathrm{tr} \int_{z=E+i\delta}^{E_F} \{ t_R^{\alpha}(z)\, \bar{G}_{RR'}(z)\, t_{R'}^{\alpha'}(z)\, \bar{G}_{R'R}(z) \}\, dE \qquad \alpha,\alpha' = A,B$$

$t_R^{\alpha}(z)$ – overlayer CPA t-matrix

$$\bar{G}_{RR'}(z) = \frac{1}{N_{\parallel}} \sum_{k_{\parallel}}^{SBZ} \bar{G}(k_{\parallel}, z)\, e^{i k_{\parallel}(R-R')} \qquad (R, R' \in \text{overlayer})$$

– we look for extrema of $V(k_{\parallel}) = \sum_R{}' V_{0R}\, e^{i k_{\parallel} R}$

(i) $\max\{-V(k_{\parallel})\} = 0 \rightarrow$ no ordering

(ii) $\max\{-V(k_{\parallel})\}$ at $k_{\parallel}^{0} = (0,1) \rightarrow c(2\times 2)$ ordering

($k_{\parallel}^{0}$ – 2D analogy of Lifshitz special points)

Remark: V_{0R} up to 11-th shell were determined

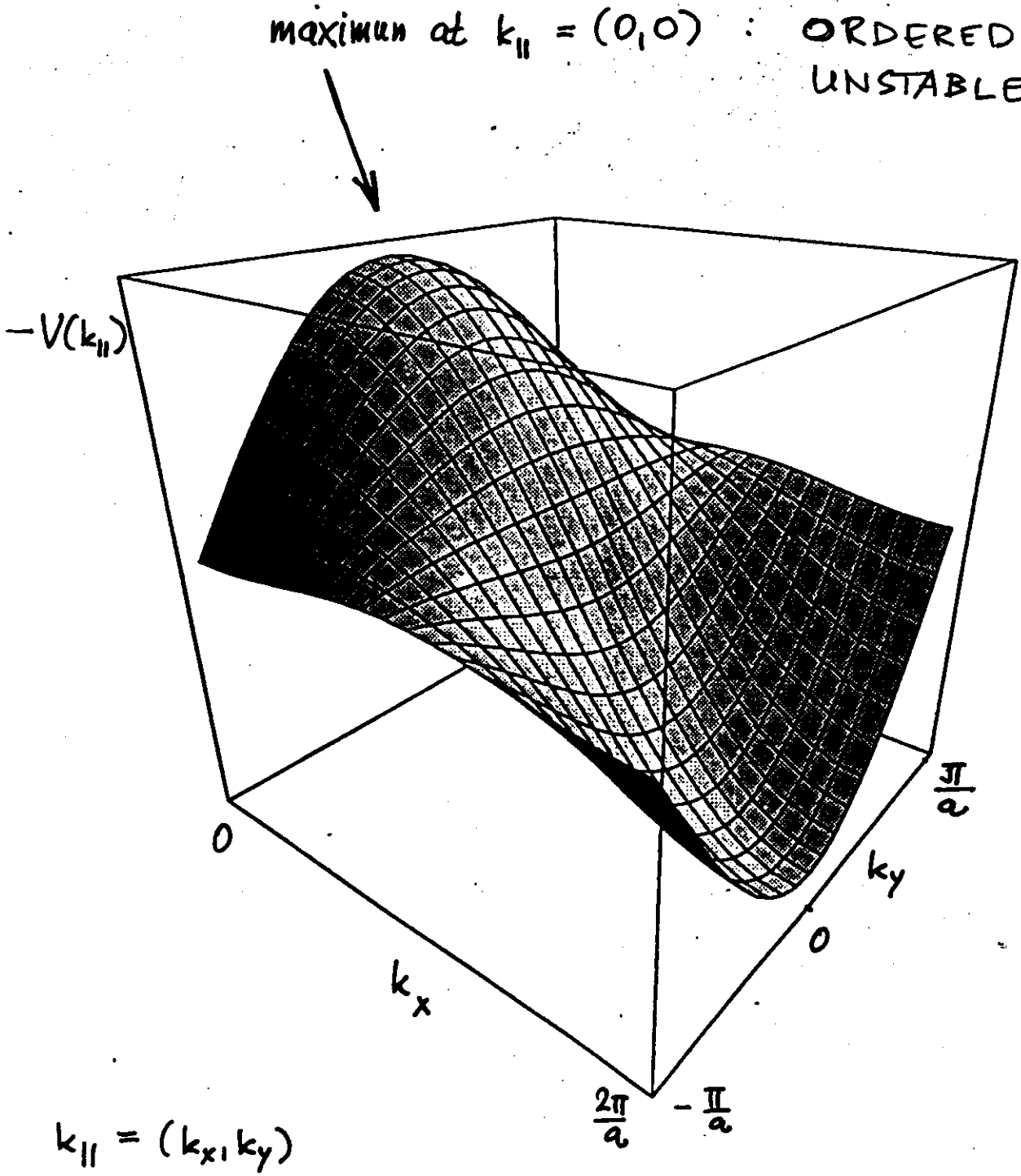
Values of V_{0R} for first few shells:

$V_{0R} = 6.51, -0.59, -0.36, -0.18$ [mRy] ... CuPd

$V_{0R} = -19.79, 1.38, -0.39, -0.03$ [mRy] ... PaVac

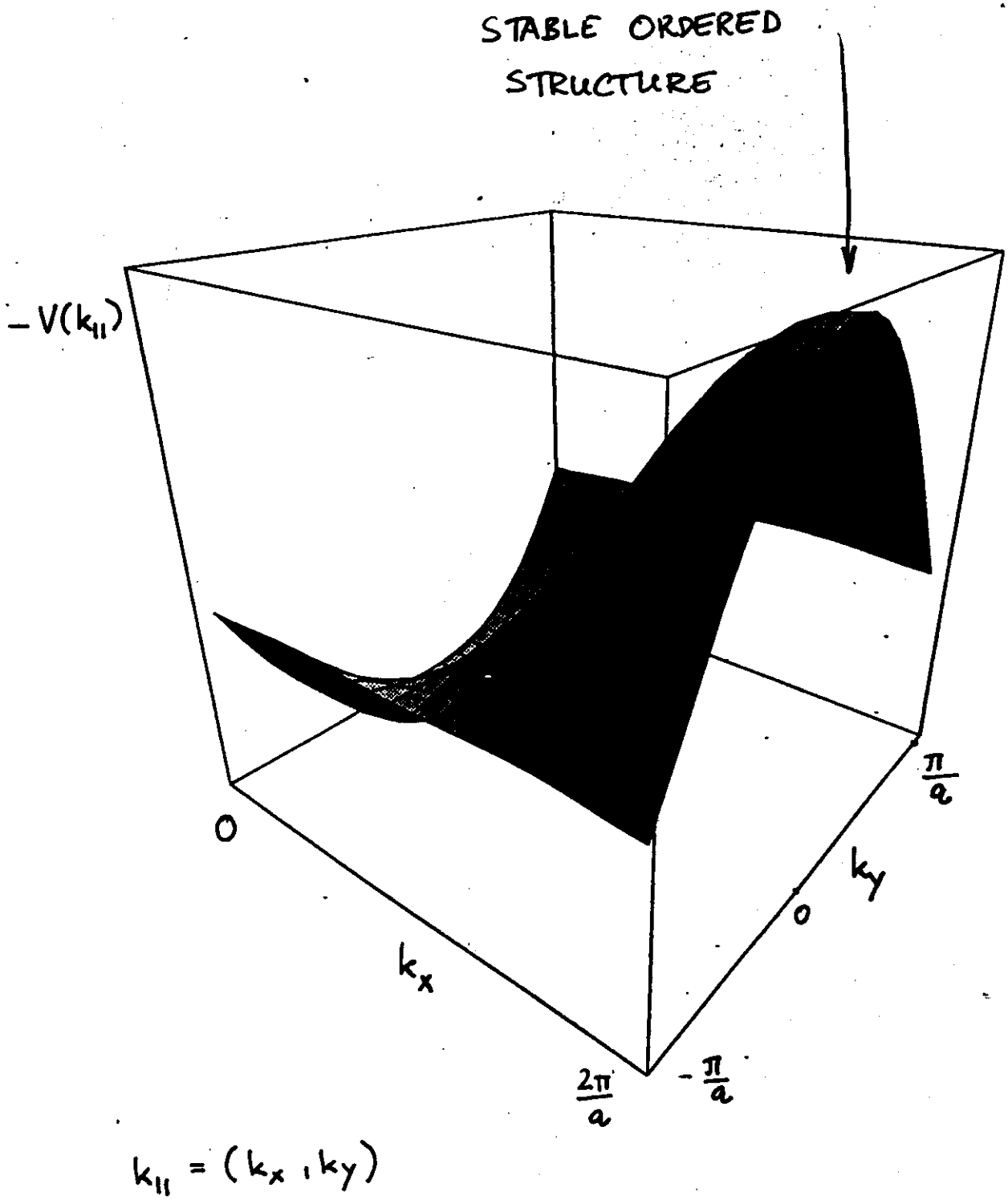
Remark: the same tendency to ordering (1st NN dominating); not the type of superstructure

- $Pd_{50}\ Vac_{50}$ overlayer on fcc (001) Cu



$Cu_{50}Pd_{50}$ overlayer on fcc (001) Cu

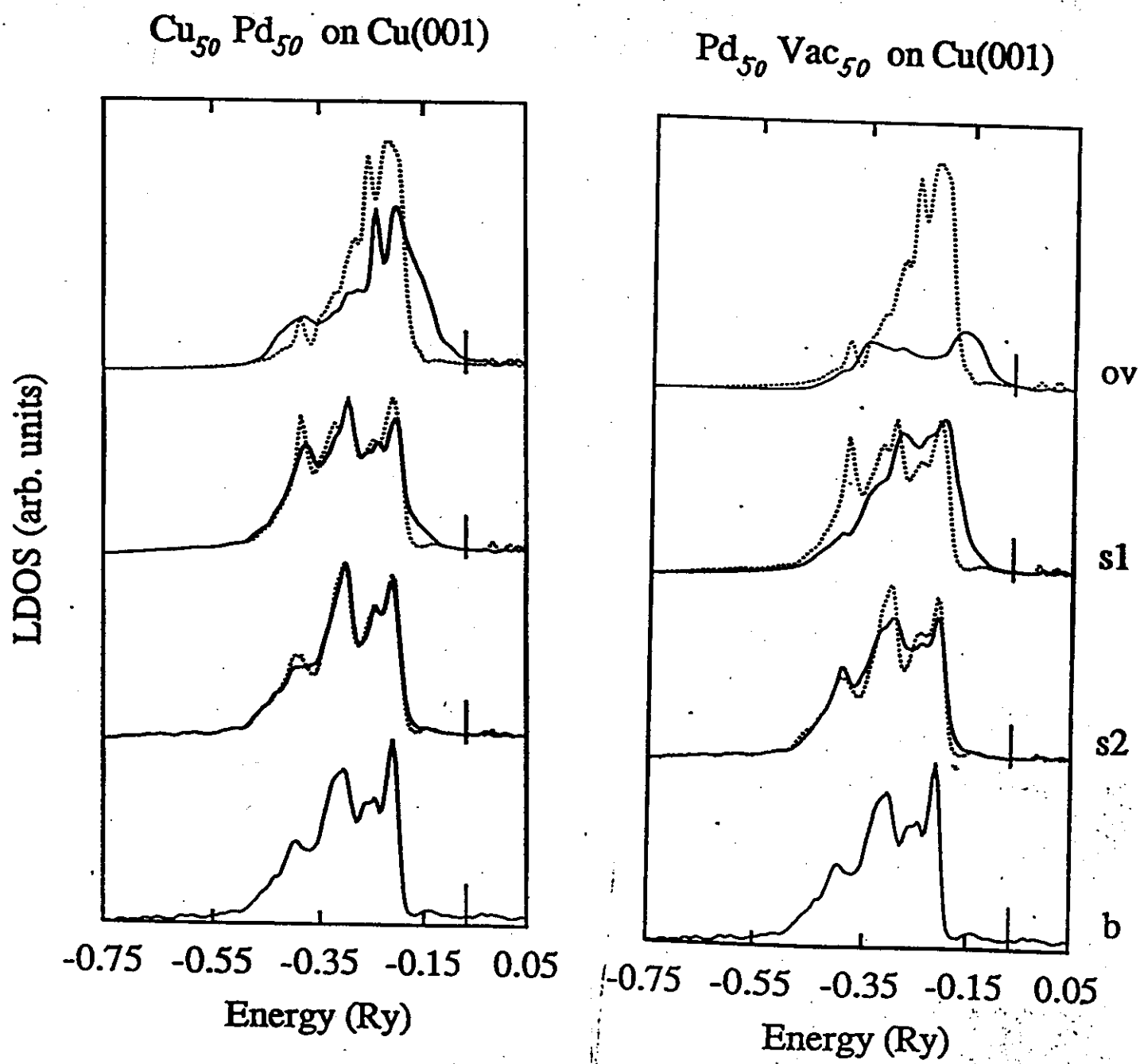
maximum at $k_{11} = \frac{2\pi}{a}(1,0)$



$k_{11} = (k_x, k_y)$

— Total DOS for Cu(001) coveraged by overlayer

..... Total DOS for clean Cu(001)



MONTE-CARLO SIMULATIONS OF SEGREGATION

We study segregation in $Cu_{1-x}Ni_x(001)$ alloys based on ab-initio Ising model derived for $\bar{a}$: homogeneous reference medium — scf bulk alloy

Details:

- computational cell consists of 8 fcc(001) alloy planes each containing 15x17 atoms with periodic boundary condition in layers // surface

- we start from a random configuration and interchange randomly two atoms. Their energy difference ΔE:

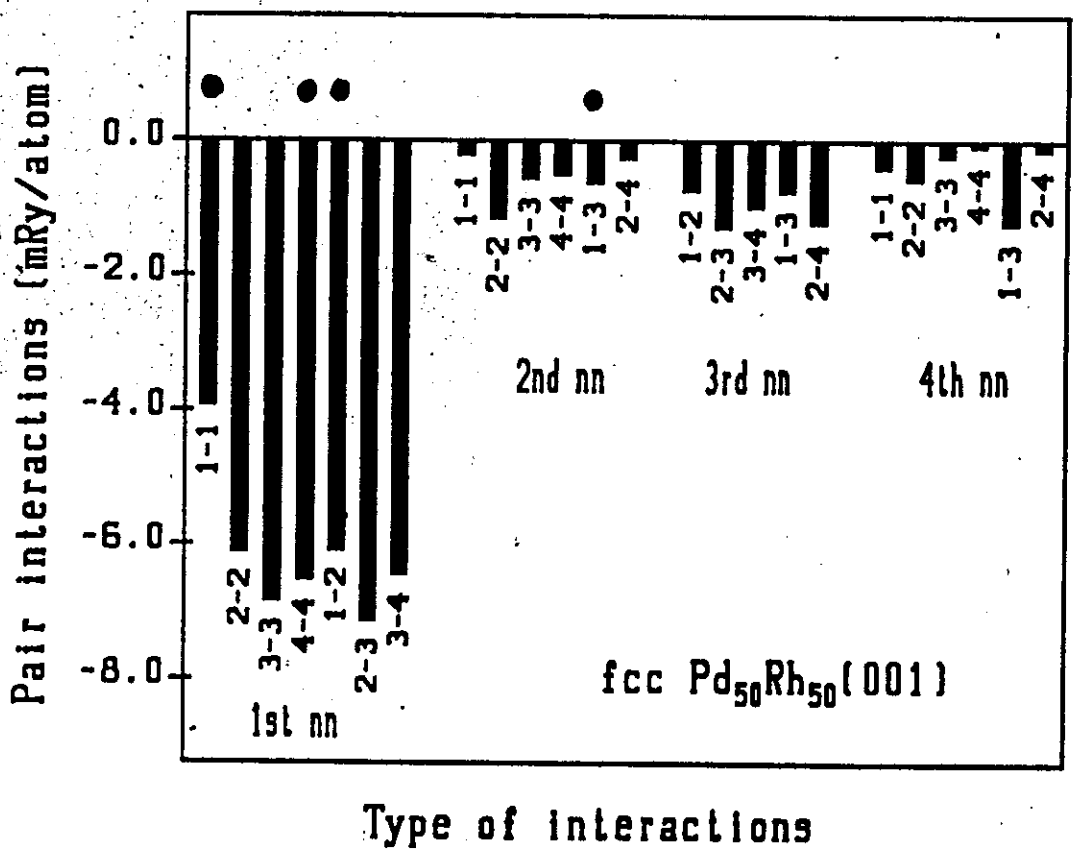
  (i) $\Delta E < 0$ — favorable, represents a new configuration

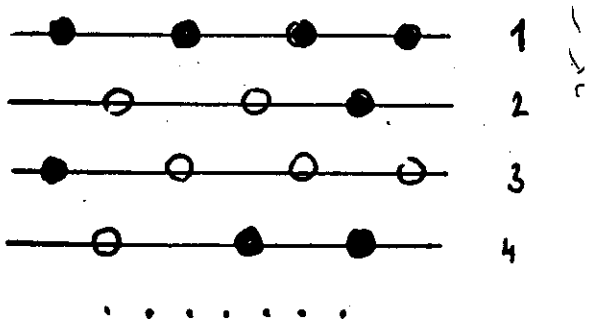
  (ii) $\Delta E > 0$ — represents a new configuration only if $\exp\{-\Delta E/kT\} > \tilde{a}$, $\tilde{a}$ - random number $\in (0,1)$

- this step is repeated and the system approaches the thermodynamical equilibrium if the number of interchanges is sufficiently large

- during MC steps, two bottom layers of slab have fixed bulk concentration

homogeneous profile

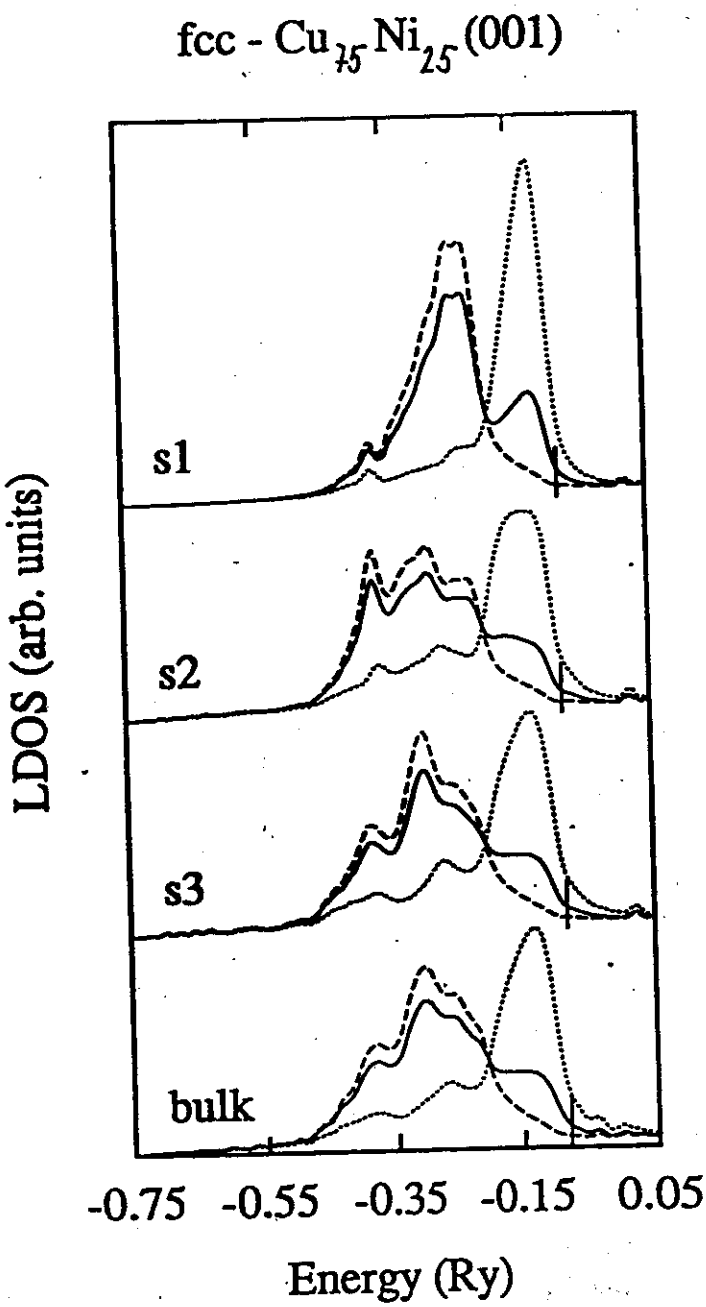




— total DOS

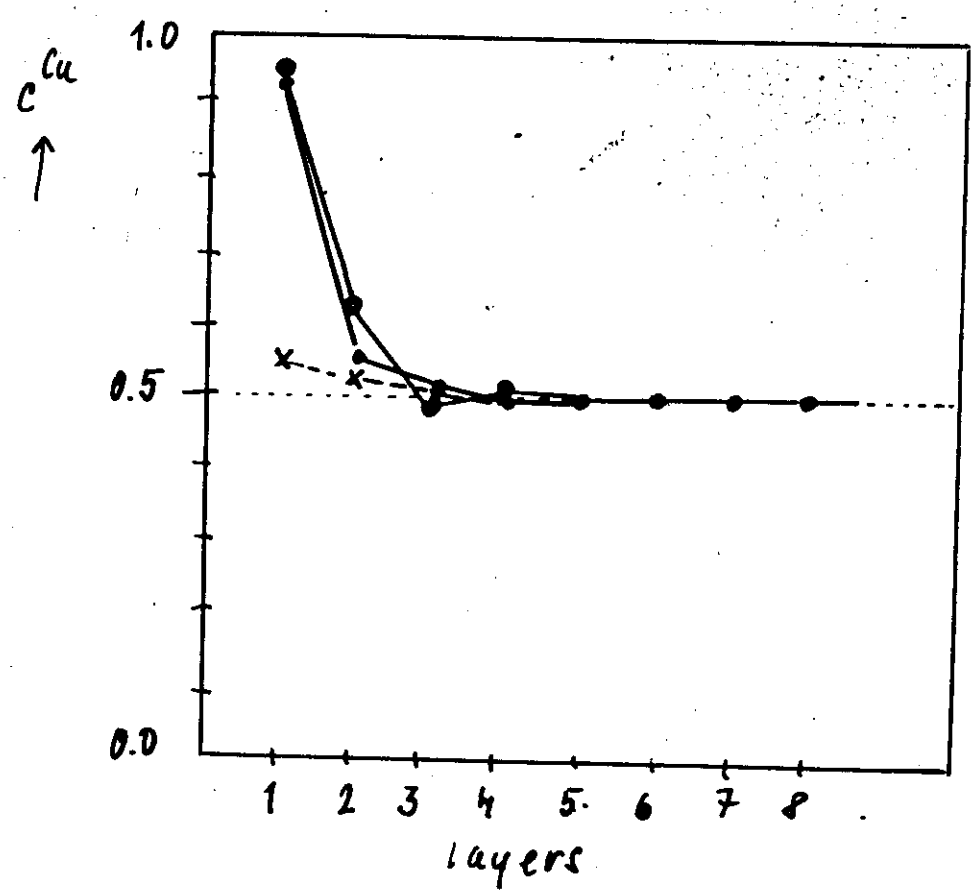
---- Cu - LDOS

..... Ni - LDOS



Results of MC simulations : fcc - $Cu_{50}Ni_{50}$ (001)

$T = 800\ K$



——— V_{OR} and $\mathcal{D}_R$ incl

——— $V_{OR} \equiv 0$ only $\mathcal{D}_R$ incl

- - - - - $\mathcal{D}_R = 0$ only V_{OR} incl

Remarks :

(i) Values of on-site terms of Ising Hamiltonian are decisive for segregation

(ii) Good agreement with experiment over all concentration range

SUMMARY

We have developed scf theory of electronic states of disordered surfaces within the LDA

- use of screened structure constants allows to include semiinfinite geometry simply and effectively
- use of inhomogeneous CPA allows a unified treatment of clean surfaces, various stages of adsorption (low coverage → films) and surface segregation
- use of multipole expansion of charge density at the surface gives proper description of dipole barrier
- in conjunction with GPM forms a theoretical background for study of ordering and segregation phenomena at surfaces from first principles

OUTLOOK

- surface magnetism: magnetic overlayes, surfaces of mag. allo
- relativistic effects: 4d and 5d metals, Dirac equation
- magnetic GPM: interplay of chemical & magnetic interactio