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"Selfconsistent Green's Function Method for Disordered Bulk and Surfaces"

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

SELFCONSISTENT GREEN's FUNCTION METHOD FOR DISORDERED BULK & SURFACES

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We develope a scheme which allows to treat electronic properties of ordered and disordered alloys, their surfaces, interfaces and overlayers from a unified point of view on the ab-initio level. This scheme:

(i) describes electronic states within first-principles TB-LMTO

(ii) includes electron correlations within LSDA

(iii) takes into account a true semiinfinite geometry, for description of surfaces, interfaces and overlayers

(iv) uses spherical potentials, but the non-spherical part of charge density is taken into account to describe behaviour of electrons close to the surface (surface barrier)

(v) employes the CPA, and its generalization to inhomogeneous systems like surfaces, to describe disorder

(vi) relativistic effects can be included via r-TB-LMTO method

Unifying feature is the use of GF formalism, inevitable for treatment of disorder and surfaces.

Development of computer codes to solve eqeations for realistic systems in unseparable part of theory.

TB-LMTO METHOD FOR SOLIDS: features

1. Fixed basis set : minimal basis possible as in empirical LCAO method

2. ASA : WS cells $\Rightarrow$ WS spheres (no interstitial space)

   Potential: inside AS - spherical LDA-potential

   outside AS - constant ($E=0$) potential

   common for all elements (transferability)

3. Separation of structural (lattice) and atom-dependent parts of any operator (e.g. H)

4. Infinite number of LMTO basis sets (representations): alloys, open structures, surfaces

5. Reliable description of metals, semiconductors and insulators for energies ± 0.5 Ry around chosen energy of interest (center of occupied bands, E_F, middle of gap region, etc).

DEFINITION OF MTO : α-REPRESENTATION

$L = lm$ $\qquad$ $r_R = r - R$

$$\chi^{\alpha}_{RL}(r_R) = \Phi_{RL}(r_R) + \sum_{R'L'} \dot{\Phi}^{\alpha}_{R'L'}(r_{R'})\, h^{\alpha}_{R'L',RL} + \chi^{\alpha,i}_{RL}(r_R) \quad \Big\} \text{ full space}$$

$$\dot{\Phi}^{\alpha}_{RL}(r_R) = \dot{\Phi}_{RL}(r_R) + \sigma^{\alpha}_{RL}\, \Phi_{RL}(r_R) \leftarrow (\text{nonzero in own AS})$$

Φ_{RL}, $\dot{\Phi}_{RL} = \dfrac{\partial \Phi_{RL}}{\partial E}$ $\rightarrow$ solution of SE in atomic sphere at R evaluated for $E = E_{\nu L}$

$\sigma^{\alpha}_{RL} \rightarrow$ such that $\partial \ln \dot{\Phi}^{\alpha}_{RL} / \partial \ln r$ has correct value at sphere boundary

$$h^{\alpha}_{RL,R'L'} = (C^{\alpha}_{RL} - E_{\nu RL})\,\delta_{RR'}\,\delta_{LL'} + (\Delta^{\alpha})^{1/2}_{RL}\, S^{\alpha}_{RL,R'L'}\, (\Delta^{\alpha})^{1/2}_{R'L'},$$

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

$S^{0}_{RL,R'L'}$ - canonical structure constant: depends only on the lattice type, not on atoms on it and lattice constant

$\alpha \rightarrow \alpha_{RL}$ - specifies given MTO-representation

$\chi^{\alpha,i}_{RL}$ - interstitial part of χ^{α}_{RL} (vanishes in ASA)

$c^\alpha - E_\nu$, Δ^α, σ^α – potential parameters which characterize scattering properties of individual atoms; they depend on lattice constant

$$c^\alpha - E_\nu = -P^\alpha/\dot{P}^\alpha \,, \quad \Delta^\alpha = 1/\dot{P}^\alpha \,, \quad \sigma^\alpha = \ddot{P}^\alpha/2\dot{P}^\alpha \quad \left(\dot{X} = \frac{dX}{dE}\Big|_{E_\nu}\right)$$

$$P^\alpha \equiv \frac{P^\circ(E)}{1-\alpha P^\circ(E)}\Big|_{E_\nu} \,, \quad P^\circ_{RL}(E) = \frac{D_{RL}(E)+l+1}{D_{RL}(E)-l} \,,$$

$$D_{RL}(E) = \frac{\partial \ln \Phi_{RL}(r,E)}{\partial \ln r}\Big| \; r = \text{AS radius}$$

Potential parameters are determined from first-principles {not fitted like in empirical TB method} in scf manner (LSDA)

Physical meaning of $P^\circ_{RL}(E)$:

$P^\circ_{RL}(E) \propto \operatorname{cotg} \eta_{RL}(E)$, $\eta_{RL}(E)$ – phase shift

SUMMARY OF BASIC PROPERTIES OF LMTO BASIS SETS

(i) $|\chi^{\alpha}_{RL}\rangle$ depend on lattice type – via $S^{\alpha}(S^0)$

(ii) $|\chi^{\alpha}_{RL}\rangle$ depend on properties of atom sitting at site R – via potential parameters

(iii) localization of $\langle r|\chi^{\alpha}_{RL}\rangle$ in real space and overlap $\langle\chi^{\alpha}_{R'L'}|\chi^{\alpha}_{RL}\rangle$ vary with LMTO representation α (surfaces !.)

(iv) evaluation of $\langle\chi^{\alpha}_{RL}|\,X^{op}\,|\chi^{\alpha}_{R'L'}\rangle$ is straightforward : product of structure constants and radial integrals (advantage over LCAO!)

(v) variational principle : perturbations added easily!

LMTO set can be 'tailored' to lattice, material and physical problem of interest

HAMILTONIAN & OVERLAP MATRICES IN ASA

$$O^{\alpha}_{RL,R'L'} = \langle \chi^{\alpha}_{RL} | \chi^{\alpha}_{R'L'} \rangle \quad , \quad H^{\alpha}_{RL,R'L'} = \langle \chi^{\alpha}_{RL} | -\Delta + V^{LDA} | \chi^{\alpha}_{R'L'} \rangle$$

$$O^{\alpha} = (1 + h^{\alpha} o^{\alpha})(o^{\alpha} h^{\alpha} + 1) \quad , \quad H^{\alpha} = (1 + h^{\alpha} o^{\alpha})(h^{\alpha} + E_{\nu}(1 + o^{\alpha} h^{\alpha}))$$

Orthogonal MTO-representation: $\alpha_{RL} = \gamma_{RL}$, $o^{\gamma}_{RL} \equiv 0$!

$O_{RL,R'L'} = \delta_{RR'} \delta_{LL'}$ (no overlap) $\quad S^{\gamma}$

$$H_{RL,R'L'} = C_{RL} \delta_{RR'} \delta_{LL'} + \Delta^{1/2}_{RL} \{ \overbrace{S^{0}(1 - \gamma S^{0})^{-1}}^{S^{\gamma}} \}_{RL,R'L'} \Delta^{1/2}_{R'L'}$$

C_{RL} ↓ levels; $\Delta^{1/2}_{RL}$ ↓ widths; S^{γ} → distortions

(i) Structural (S^0) & atomic (C, Δ, γ) features separated.

(ii) Factor $(1 - \gamma S^0)^{-1}$ important for s,p-states

RANDOM ALLOY $A_x B_{1-x}$

$X = C, \Delta, \gamma$ are random: $X_{RL} = \begin{cases} X^{A}_{L} \ \ldots\ X \\ X^{B}_{L} \ \ldots\ 1-X \end{cases}$

S^0 is non-random for substitutional alloys

CPA averaging of $G(z) = (z \cdot 1 - H)^{-1}$ impossible in orthogonal MTO repres (off-site disorder)
[S^{γ} is random]

COHERENT POTENTIAL APPROXIMATION

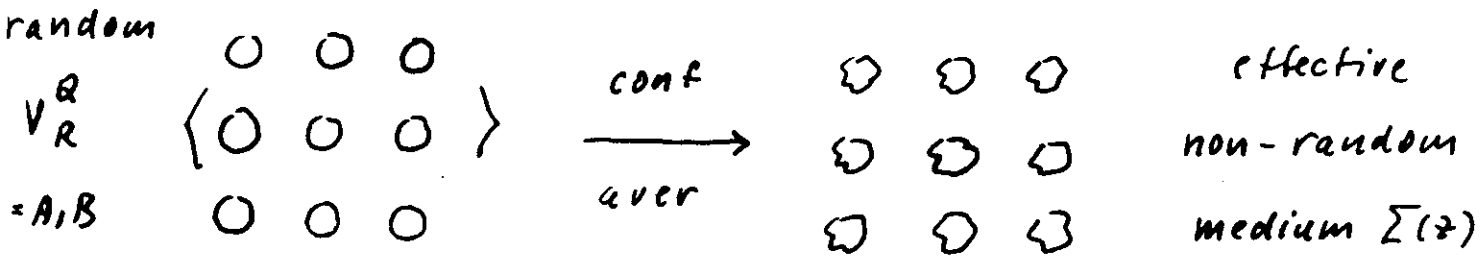
Soven: PR 156 (1967) 809 Velický et al: PR 175 (1968) 747

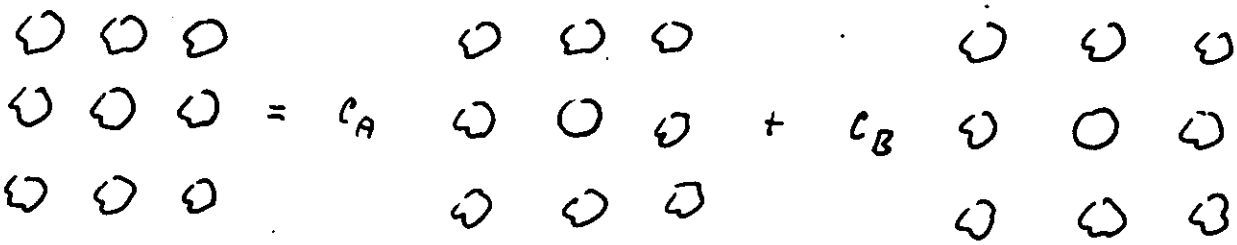
Kaplan & Gray; Mookerjee and coworkers

Multiple scattering formalism

Embedded cluster method, Augmented space formalism,

Recursion method (cluster effect $\propto Z^{-1}$, dimensionality)





$$0 = c_A T_R^A(z) + c_B T_R^B(z) \quad \ldots \text{ no scattering}$$

$$T_R^Q(z) = (V_R^Q - \Sigma_R(z)) \{1 + \bar{G}_{RR}(z, \Sigma(z)) (V_R^Q - \Sigma_R(z))\}^{-1}$$

CPA equation for $\Sigma(z)$

COMMENTS:

(i) Equation is related to a single site R
(no multisite scatterings)

(ii) Non-linear equation for unknown $\Sigma_R(z)$

(iii) $\Sigma_R(z)$ is complex, energy-dependent

$\mathrm{Re}\,\Sigma_R(z)$ .... level shift due to disorder

$\mathrm{Im}\,\Sigma_R(z)$ ..... damping of states due to disorder

(iv) CPA is exact in

1. low concentration limit (c_A or $c_B \to 0$)
2. weak scattering limit
3. split-band limit (separated bands)

First-principles alloy theory (LDA)

KKR CPA: Gyorffy & Stocks, Winter & Stocks (rcf)
Livermore & Oak Ridge, Staunton (magnetic state)
Staunton, Weinberger (relativity)

LMTO CPA: present approach

CPA FOR TB-LMTO HAMILTONIAN: 3 steps

1st: Transform exactly to non-random MTO repres β

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

$$g^{\beta}_{RL,R'L'}(z) = \left\{\left(P^{\beta}(z) - S^{\beta}\right)^{-1}\right\}_{RL,R'L'};\quad \lambda^{\beta}_{RL},\ \mu^{\beta}_{RL} \equiv f\left(C_{RL}, \Delta_{RL}, \gamma_{RL}\right)$$

$$P^{\beta}_{RL}(z) = \frac{z - C_{RL}}{\Delta_{RL} + (\gamma_{RL} - \beta_{RL})(z - C_{RL})} \rightarrow \text{random, site-diagonal}$$

$$S^{\beta}_{RL,R'L'} = \left\{S^{0}(1 - \beta S^{0})^{-1}\right\}_{RL,R'L'};\quad \beta \rightarrow \beta_{RL} \equiv \beta_{L} \rightarrow \text{non random}$$

Non random β (examples) $\Rightarrow$

- $\beta_{RL} \equiv 0$ – canonical: $S^{0}(k)$ – Ewald summ
- $\beta_{RL} \equiv (\beta_s, \beta_p, \beta_d)$ – most localized: $S^{\beta}(k)$ – 2 NN Bloch

2nd: CPA averaging of $g^{\beta}(z)$ → only site-diagonal disorder (like KKR CPA)

$$\langle g^{\beta}(z)\rangle = \left(\mathcal{P}^{\beta}(z) - S^{\beta}\right)^{-1},\quad \mathcal{P}^{\beta}_{RL}(z) \equiv \mathcal{P}^{\beta}_{L}(z) \rightarrow \text{coherent potential function}$$

Set of CPA-equations to be solved:

$$\mathcal{P}^{\beta}_{L}(z) = \Omega^{\beta}_{L}(z) + \left[\Phi^{\beta}_{L}(z)\right]^{-1},\quad \Phi^{\beta}_{L}(z) = \frac{1}{N}\sum_{k}\left\{\left(\mathcal{P}^{\beta}(z) - S^{\beta}(k)\right)^{-1}\right\}_{LL} =$$

$$= x\left(P^{\beta,A}_{L}(z) - \Omega^{\beta}_{L}(z)\right)^{-1} + (1-x)\left(P^{\beta,B}_{L}(z) - \Omega^{\beta}_{L}(z)\right)^{-1}$$

[$L = s, p, t_{2g}, e_g$ for cubic lattices]

3rd: Transform back to orthogonal MTO repres.

$$\langle G(z)\rangle_{RL,R'L'} = \Lambda^{\beta}_{L}(z)\,\delta_{RR'}\delta_{LL'} + M^{\beta}_{L}(z)\,\langle q^{\beta}(z)\rangle_{RL,R'L'}\,M^{\beta}_{L'}(z)\,, \quad \text{where}$$

$$\Lambda^{\beta}_{L}(z),\ M^{\beta}_{L}(z) \equiv f(P^{\beta,A}_{L},\ P^{\beta,B}_{L},\ \mathcal{P}^{\beta}_{L}) \quad - \text{details: PRB 41 (1990) p. 7515}$$

EFFECTIVE HAMILTONIAN

$$\langle G(z)\rangle_{RL,R'L'} = \left\{\left(z.1 - H^{\text{eff}}(z)\right)^{-1}\right\}_{RL,R'L'}\,, \quad \text{where}$$

$$H^{\text{eff}}_{RL,R'L'}(z) = \tilde{C}_{L}(z)\,\delta_{RR'}\delta_{LL'} + \tilde{\Delta}^{1/2}_{L}(z)\left\{S^{0}\left(1-\tilde{\mathcal{P}}(z)\,S^{0}\right)^{-1}\right\}_{RL,R'L'}\tilde{\Delta}^{1/2}_{L'}(z)$$

$\tilde{C}(z),\ \tilde{\Delta}(z),\ \tilde{\mathcal{P}}(z)$ – non random coherent potential parameters renormalizing random potential parameters $C_{RL},\ \Delta_{RL},\ \mathcal{P}_{RL}$

Empirical TB-CPA: only $\tilde{C}(z) \to \Sigma(z)$ determined within CPA, $\tilde{\mathcal{P}}(z)$ and $\tilde{\Delta}(z) \to \mathcal{P}^{VCA}$, Δ^{VCA}

SELFENERGY with respect to H^{ref}

J. Phys. Chem. Sol. 49 (1988) 349

$$\langle G(z)\rangle_{RL,R'L'} = \left\{\left(z.1 - H^{ref} - \Sigma(z)\right)^{-1}\right\}_{RL,R'L'}\,; \quad H^{ref} = H^{VCA}, H^{host}, \ldots$$

$$\Sigma_{RL,R'L'}(z) = z\,\delta_{RR'}\delta_{LL'} - H^{ref}_{RL,R'L'} - \left\{\langle G(z)\rangle^{-1}\right\}_{RL,R'L'} \quad \text{or}$$

$$\Sigma_{LL'}(k) = z\,\delta_{LL'} - H^{ref}_{LL'}(k) - \left\{\langle G(k,z)\rangle^{-1}\right\}_{LL'}$$

closed expression for $\langle G(k,z)\rangle^{-1}$

$\Sigma(z)$ is k-dependent (not site-diagonal) although $\mathcal{P}^{\beta}_{L}(z)$ is site-diagonal {k-independent in ETB-CPA}

CHARGE SELFCONSISTENCY

Charge density in random alloy $A_x B_{1-x}$ (CPA)

$$n^Q(r) = \frac{1}{4\pi} \sum_L 2 \int^{E_F} |\varphi_L^Q(E,r)|^2 g_L^Q(E)\, dE \qquad (Q = A, B)$$

and (cubic symmetry)

$$g_L^Q(E) = -\frac{1}{\pi} \frac{d P_L^{\beta,Q}(E)}{dE} \operatorname{Im}\left(P_L^{\beta,Q}(E) - \Omega_L^{\beta}(E+i0) \right)^{-1} \equiv -\frac{1}{\pi} \operatorname{Im} \langle G(E+i0) \rangle_{RL,RL}$$

$$\Phi_L^{\beta}(z) = \frac{1}{N} \sum_k \left\{ \left(\mathcal{T}^{\beta}(z) - S^{\beta}(k) \right)^{-1} \right\}_{LL}, \quad \Omega_L^{\beta}(z) = \mathcal{T}_L^{\beta}(z) - \left\{ \Phi_L^{\beta}(z) \right\}^{-1}$$

and $\varphi_L^Q(E,r)$ is the solution of radial SE in AS with the LDA potential $V^Q(r)$

$$V^Q(r) = -\frac{2Z^Q}{r} + 2 \int_0^{s^Q} \frac{n^Q(r')}{|\bar{r} - \bar{r}'|} 4\pi r'^2 dr' + \mu_{xc}(n^Q(r))$$

scf LDA - CPA LOOP

i-th $\Longrightarrow$ $i+1$-th

$\varphi_L^{Q(i)}(E,r)$ $P_L^{Q(i)}(z)$ $\mathcal{T}_L^{(i)}(z)$ $\Rightarrow$ **CPA solver** $\Rightarrow$ $\mathcal{T}_L^{(i+1)}(z)$ $g_L^{Q(i+1)}(E)$ $n^{Q(i+1)}(r)$ $V^{Q(i+1)}(r)$ $\Longrightarrow$

LDA solver $\Rightarrow$ $\dfrac{\partial \ln \varphi^{Q(i+1)}(r,E)}{\partial \ln r}\Big|_{r=s^Q}$ $P_L^{\beta,Q(i+1)}(z)$ $\Longrightarrow$ next loop

Details of scf LDA-CPA loop:

(i) Zig-Zag CPA-LDA iterations

{ neither CPA – $g(z)$ nor LDA – $V^Q(r)$ are solved till scf in a given loop }

(ii) Mixing of old/new $V^Q(r)$ necessary to prevent oscillations (divergency): $\alpha_{mix}^{LDA} \sim$ few % of new

{ espeeially delicate: alloys close to ferro instab }

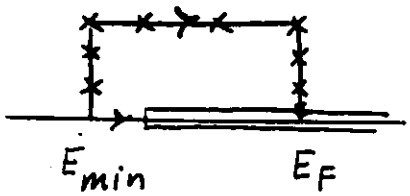
(iii) LDA loop can be terminated if:

$\delta \| r V(r) \| < \varepsilon$ for each $r \in (0, s^Q)$

$\delta \| P^Q(E) \| < \varepsilon$ for each E and $Q = A, B$

$\delta \| n^Q(r) \| < \varepsilon$ for each $r \in (0, s^Q)$ etc ...

(iv) E-integration for $n^Q(r)$:



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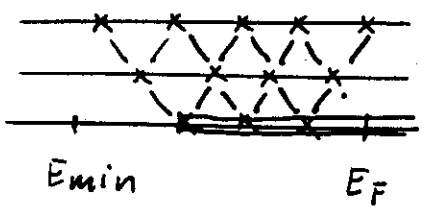
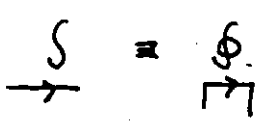




complex contour integrations

analytic deconvolution back to real axis

(v) Brillouin-zone integration:

1. Standard (regular mesh, rays, tetrahedrons...)
2. Surface-like:

3. Weyl-type (fast LMTO CPA)

(vi) CPA equation:

We solve CPA equation for coherent interactor $\hat{\Omega}^{\beta}(z)$ rather than for coherent potential function $\hat{\mathcal{P}}^{\beta}(z)$:

$$\hat{\phi}_L^{\beta}(z) = \frac{1}{N}\sum_k \left\{ \left(\hat{\mathcal{P}}^{\beta}(z) - S^{\beta}(k) \right)^{-1} \right\}_{LL} \qquad \text{(cubic lattices, } l \le 2\text{)}$$

$$\hat{\Omega}_L^{\beta}(z) = \hat{\mathcal{P}}_L^{\beta}(z) - \left\{ \hat{\phi}_L^{\beta}(z) \right\}^{-1} \qquad \text{(interactor)}$$

$$\tilde{\hat{\phi}}_L^{\beta}(z) = \sum_Q^{A,B} c^Q \left(\mathcal{P}_L^{\beta,Q}(z) - \hat{\Omega}_L^{\beta}(z) \right)^{-1} \qquad \text{(CPA equation)}$$

$$\mathcal{P}_L^{\beta,\text{new}}(z) = \hat{\Omega}_L^{\beta}(z) + \left\{ \tilde{\hat{\phi}}_L^{\beta}(z) \right\}^{-1}$$

This form of CPA converges in each case with $\alpha_{mix}^{CPA} = 1$

CPA selfconsistency is reached if $\delta \| \hat{\Omega}^{\beta}(z) \| < \varepsilon$ for each z simultaneously with LDA

(vii) Possibility for selfconsistency with respect to the choice of WS-radii s^Q (charge neutrality in AS)

FAST LMTO-CPA METHOD : Weyl k-integration

Akai (1989) : KKR CPA , Abrikosov et al (1991) : LMTO CPA

Repeated IBZ integration in each LSDA-CPA loop is the most numerically demanding part of calculations

$\hat{\Phi}_{LL'}(z) = \frac{1}{V} \int \{ (\hat{\mathcal{P}}(z) - \hat{S}(k))^{-1} \}_{LL'} d^3k$ – central quantity for LSDA & CPA

Consider a set of k-points $\{k_n\}$ distributed uniformly in IBZ

$$I^N = \lim_{N\to\infty} \frac{1}{N} \sum_{n=1}^{N} f(k_n) \longrightarrow I = \frac{1}{V} \int f(k)\, d^3k$$

Monte Carlo : convergence rate to I is $1/\sqrt{N}$

Weyl : $k_n^\alpha = n k_0^\alpha - [n k_0^\alpha]$ $(\alpha = x,y,z;\ k_n^\alpha \in IBZ)$

k_0^α – irrational

convergence rate to I is $1/N$

Basic trick :

I^N is continuously improved by adding additional k-points without recalculating previous one

$$\Phi_{LL'}^{(n)}(z) = (1-r_n)\, \Phi_{LL'}^{(n-1)}(z) + r_n \{ \mathcal{P}(z) - S(k_n) \}^{-1}_{LL'}$$

Simplest choices:

(i) $r_n = 1/n$

(ii) $r_n = \frac{w_n}{s_n}$, $s_n = s_{n-1} + w_n$, $s_0 = 0$

$w_n = 1 - \alpha^n$ $(\alpha \approx 0.99)$. If $w_n = 1$, $r_n = 1/n$

{weighting factor to get rid of bad history of early steps}

Practical procedure:

(i) start from some guess for $\phi(z)$, say summing up first 50 k-points without CPA & LDA

(ii) perform LDA & CPA loop

(iii) add few additional k-points (1-5) and perform LDA & CPA loop etc

Advantages / disadvantages

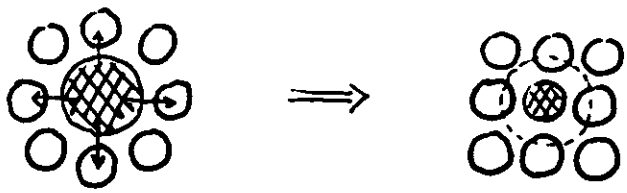
(i) numerical requirements comparable to those for nsc crystal

(ii) large number of LSDA & CPA loops can be done (alloys close to magnetic instability)

(iii) uniform distribution; oscillatory convergence of k-points

ALLOY OF ATOMS WITH DIFFERENT SIZES

- Single MT-impurity model



real case single MT-model

(i) Charge sc is performed in smaller sphere ⇒ overscreening (shift Pd/Au d-band downwards of host Cu d-band)

(ii) Distances (hoppings) Cu-Pd (Cu-Au) become underestimated (overestimated) → Pd/Au -widths overestimated

- Cu-rich random alloy

(i) overscreening slightly suppressed → Pd/Au MT-impurity in effective, Cu-dominated medium

Cure: charge sc also on Inn (beyond CPA) or in enlarged Pd/Au -spheres (possible in ASA – neutral AS.)

(ii) lattice distortions stronger → finite probability for Inn Pd-Pd / Au-Au pair

We account approximately for both effects in TB-LMTO-CPA

ALLOY $Cu_{75}Au_{25}$: ordered, disordered, with LRO

The problem requires the solution of coupled CPA eqs on four interpenetrating sc lattices $\Rightarrow$ Cu_3Au lattice

$S^{B,fcc}_{Rl,R'l'}$ decomposed into four $S^{B,sc}_{R_\alpha L, R'_{\alpha'} L'}$ $\left(\begin{matrix}\alpha,\alpha' = 1,2,3,4 \text{ or} \\ Cu, Cu, Cu, Au\end{matrix}\right)$

We solve 36×36 CPA problem with sublattice component concentrations $c_Q(\alpha)$: $Q = Cu, Au$; $\alpha = Cu, Cu, Cu, Au$

$$c_{Cu}(Cu) = \frac{3+S}{4} \qquad c_{Au}(Cu) = \frac{1-S}{4}$$

$$c_{Cu}(Au) = \frac{3}{4}(1-S) \qquad c_{Au}(Au) = \frac{1+3S}{4}$$

$\Rightarrow$ $S \in (0,1)$ is the LRO parameter

$S = 0 \equiv$ disordered $Cu_{75}Au_{25}$; $S = 1 \equiv$ ordered Cu_3Au

ALLOY $Cu_{75}Au_{25}$: ordered, disordered, with LRO

(i) Ordered Cu_3Au alloy (no lattice relaxations)

Crystal Cu/Au potential parameters transferable:
just scale them to account for difference w^{Cu}/w^{Au} and w^{Cu_3Au} (w - WS radii) - Andersen

(ii) Disordered $Cu_{75}Au_{25}$ alloy (9x9 CPA problem for spd-LMTO's)

We perform calculations for model without and with lattice relaxations

(iii) $Cu_{75}Au_{25}$ alloy with LRO

$X^{LRO} = S\,X^{Cu_3Au} + (1-S)\,X^{Cu_{75}Au_{25}}$; $X = C, \Delta, f$; S - LRO param

The problem requires the solution of coupled CPA eqs on four interpenetrating sc lattices $\Rightarrow$ Cu_3Au lattice

$S^{B,fcc}_{Rl,R'l'}$ decomposed into four $S^{B,sc}_{R_\alpha L, R'_{\alpha'} L'}$ ($\alpha, \alpha' = 1,2,3,4$ or Cu, Cu, Cu, Au)

We solve 36x36 CPA problem with sublattice component concentrations $c_Q(\alpha)$: $Q = Cu, Au$; $\alpha = Cu, Cu, Cu, Au$

$c_{Cu}(Cu) = \frac{3+S}{4}$ $\quad c_{Au}(Cu) = \frac{1-S}{4}$

$c_{Cu}(Au) = \frac{3}{4}(1-S)$ $\quad c_{Au}(Au) = \frac{1+3S}{4}$

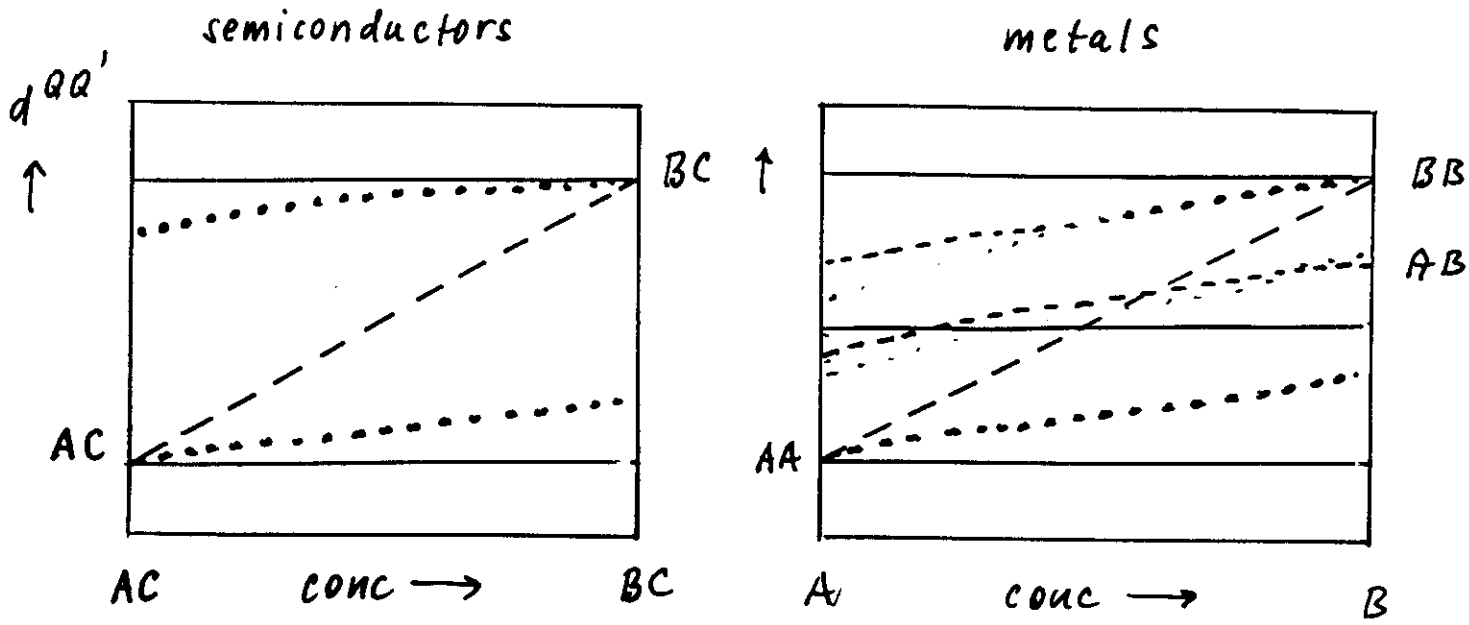
$\Rightarrow$ $S \in (0,1)$ is the LRO parameter

$S=0 \equiv$ disordered $Cu_{75}Au_{25}$; $S=1 \equiv$ ordered Cu_3Au

LATTICE RELAXATIONS

Mismatch in sizes of atoms → local distortions, different bond-lengths in random alloys

Models – experiments



—— full relaxation (conc. indept., pure QQ'-values preserved)

---- no relaxation (linear conc variation, all bonds same)

···· experiment (EXAFS – real situation: in between)

Remarks

(i) in metallic alloys $d^{AB} \approx (d^{AA} d^{BB})^{1/2} \approx \left(\frac{d^{AA} + d^{BB}}{2}\right)$

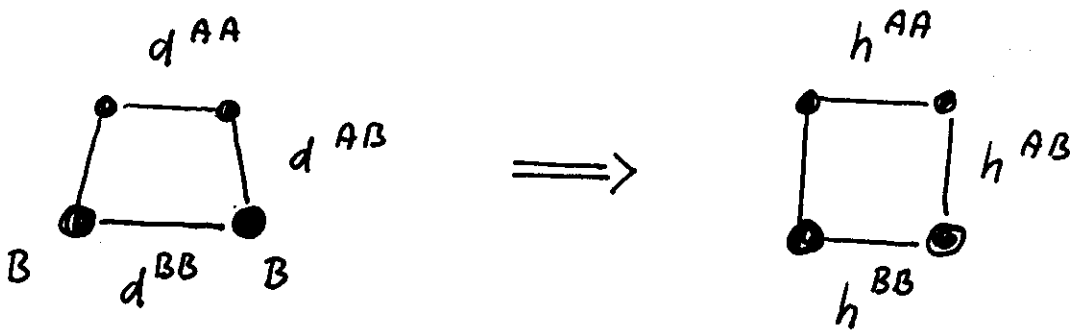
both for exp and fully relaxed model

(ii) lr are most relevant in Q-rich cases, so that for $Q = A$ are d^{AA} and especially d^{AB} important

(error in model for d^{BB} has less importance)

$N^{AA} \propto c_A^2$, $N^{AB} \propto 2 c_A c_B \gg N^{BB} \propto c_B^2$ for $c^A \gg c^B$

Modelling of lattice relaxations (TB, TB LMTO):



off-diagonal disorder

$S^{\alpha}_{RR'}$ is now random, configuration dependent and approximations are inevitable:

(i) terminal-point approximation

$$S^{\alpha}_{RR'} \Rightarrow S^{\alpha, QQ'}_{RR'}$$

depends only on occupation of R, R' → not on all alloy!

(ii) neglect of any angle distortions — close packed

$$S^{\alpha, QQ'}_{RR'} \propto \lambda^{Q}_{R}\, S^{\alpha(0)}_{RR'}\, \lambda^{Q'}_{R'}$$

non-random ideal lattice

Remarks: (i) simple choice: $\lambda^{Q}_{RL} \propto (W^{alloy}_{..} / S^{2}_{R})^{l+1/2}$

(ii) such mapping is valid only approximately but represents a reasonable first step

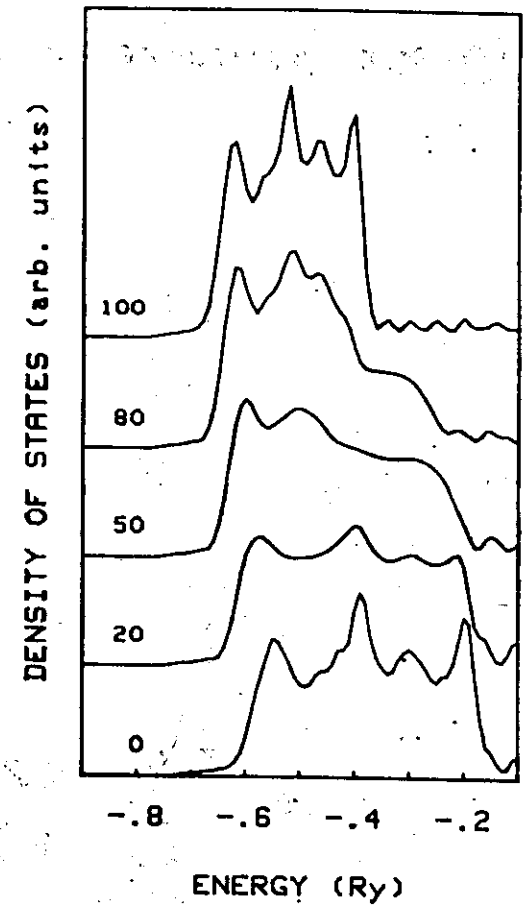
(iii) λ^{Q}_{R} are absorbed by $\Delta^{Q}_{R}, \mathcal{J}^{Q}_{R}$ and give rise to a modified $\tilde{\Delta}^{Q}_{R}, \tilde{\mathcal{J}}^{Q}_{R}$ as expected

(iv) transformation of spherical functions under shift

(v) real-space description (recursion method)

[illegible] not resolved problem [illegible] 21

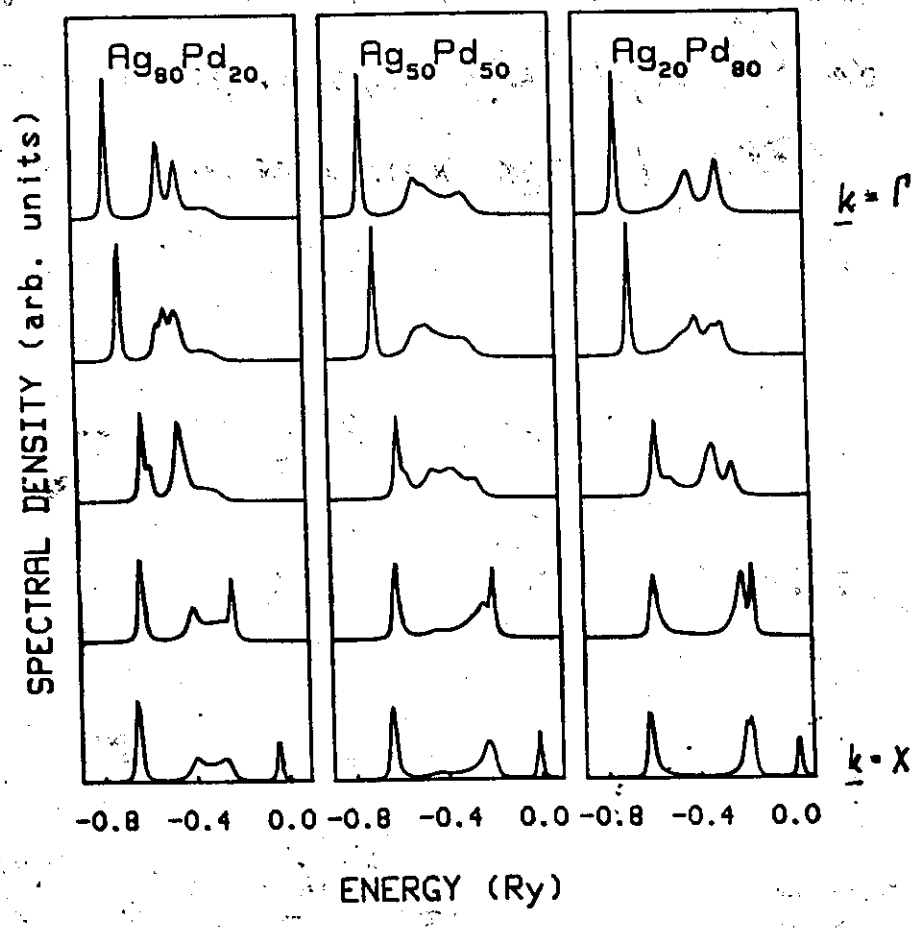
Total DOS



Dominating 'level' disorder,
non-negligible 'width' disorder

DOS: $Ag_x Pd_{1-x}$ random alloys

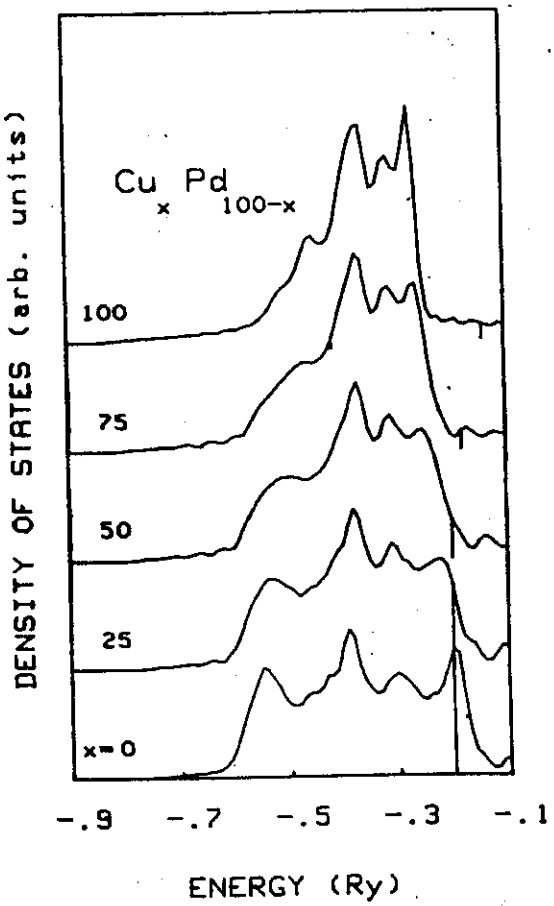
k-resolved spectral density $A(k, E)$



$$A(k, E) = -\frac{1}{\pi} \operatorname{Im} \operatorname{tr} \bar{G}(k, \bar{E} + i0), \quad k \in \text{1BZ}$$

$$A^{\circ}(k, \bar{E}) = \sum_n \delta(E - E_n(k)) \quad \text{— pure crystal}$$

Total DOS

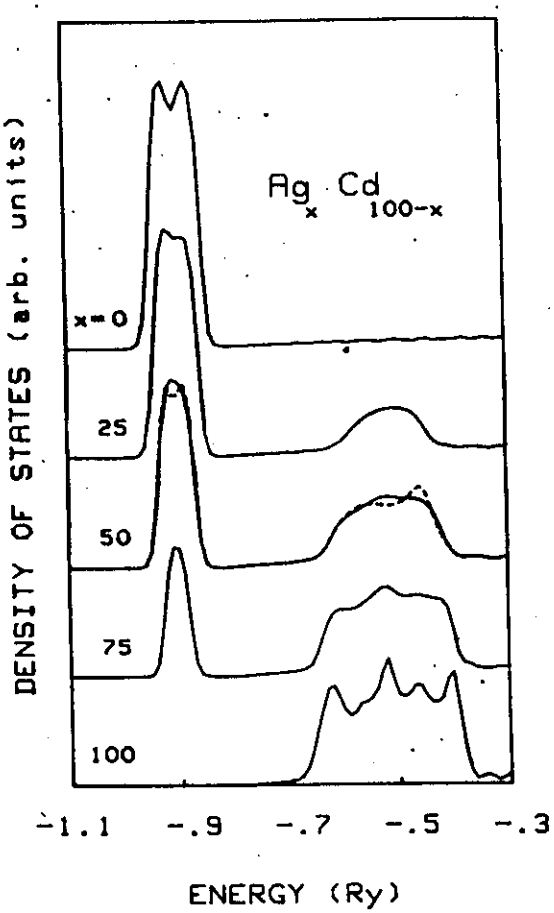


common alloy band

dominating 'band-width' disorder,

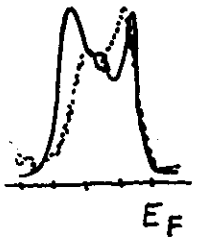
negligible 'level' disorder

Total DOS



split-band limit alloy

— KKRCPA ..... experiment: PES / Cooper minimum $\Rightarrow$ Pd LDOS

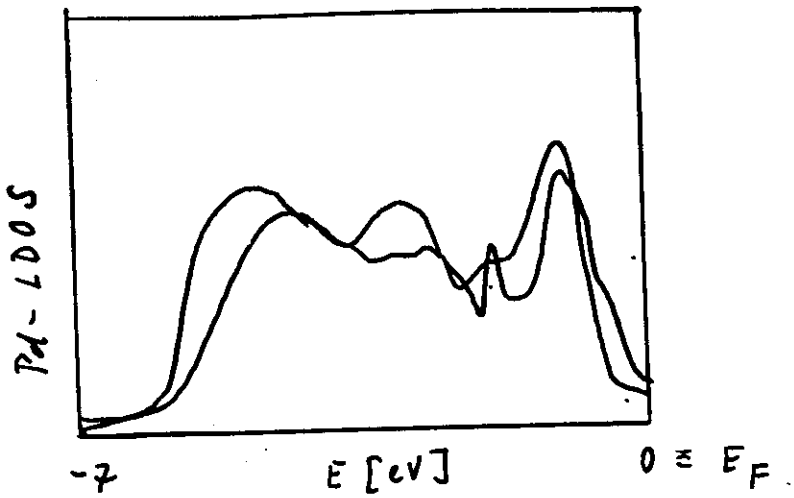


$Cu_{75}Pd_{25}$ alloy

— TB-LMTO-CPA (Ir incl)

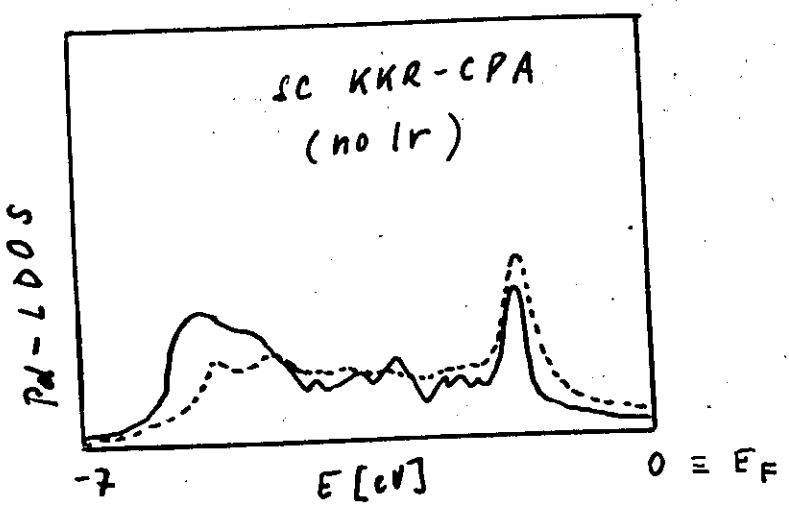
— KKR-CPA (sc in equal-size MT's)

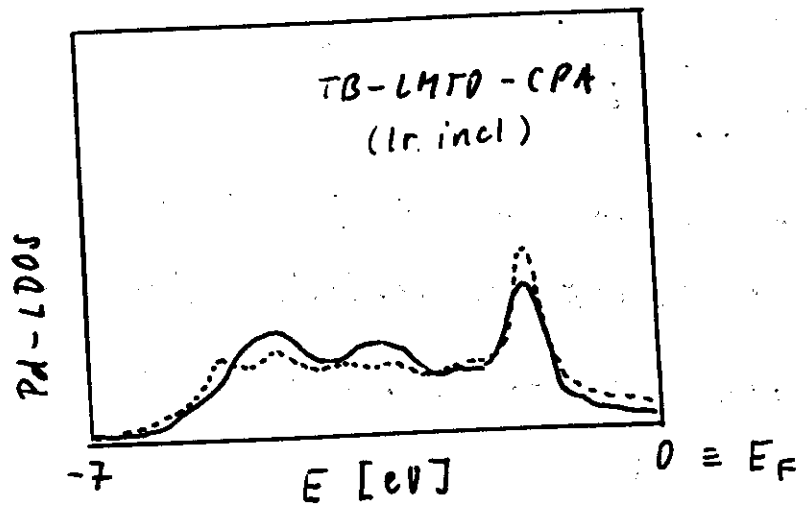
FWHM narrowing of TB-LMTO-CPA



$Cu_{95}Pd_5$ alloy

---- single impurity calc (broadened) : Dederichs et al SSC 62 (1987) 735





Experiment

Krummacher, Sen, Gudat, Johnson, Grey, Ghijsen:

Z. Phys. B 75 (1989) 235

Ref. 17 (Calculations)

Ginatempo, Staunton:

J. Phys. 18 (1988) 9985

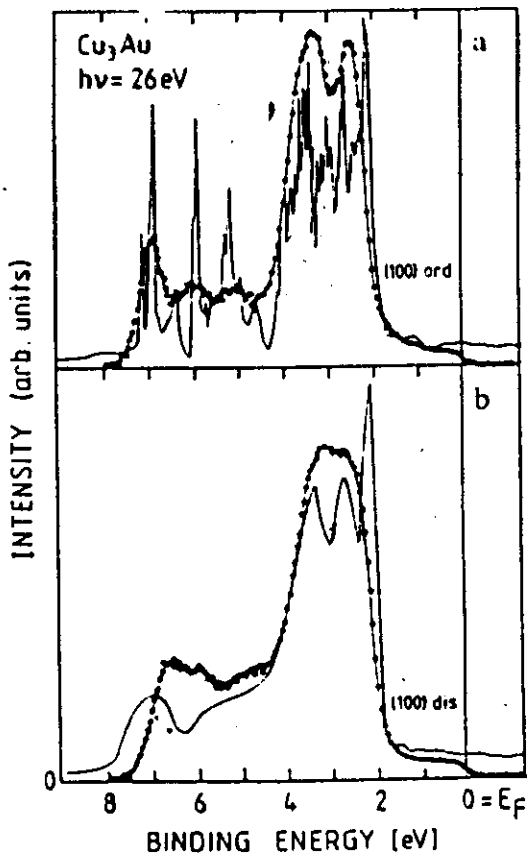


Fig. 4a and b. Comparison of the experimental valence band spectrum of $Cu_3Au(100)$ with relativistic density of states calculations: a self-consistent KKR calculation for the ordered state. b KKR CPA calculation for the random alloy, using the same potential function as in a). Calculations from Ref. 17

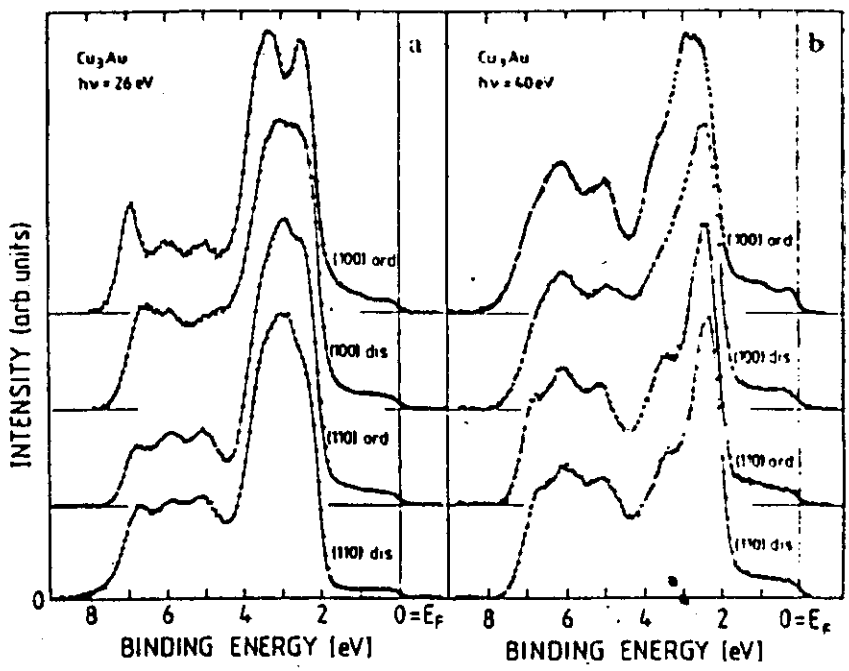
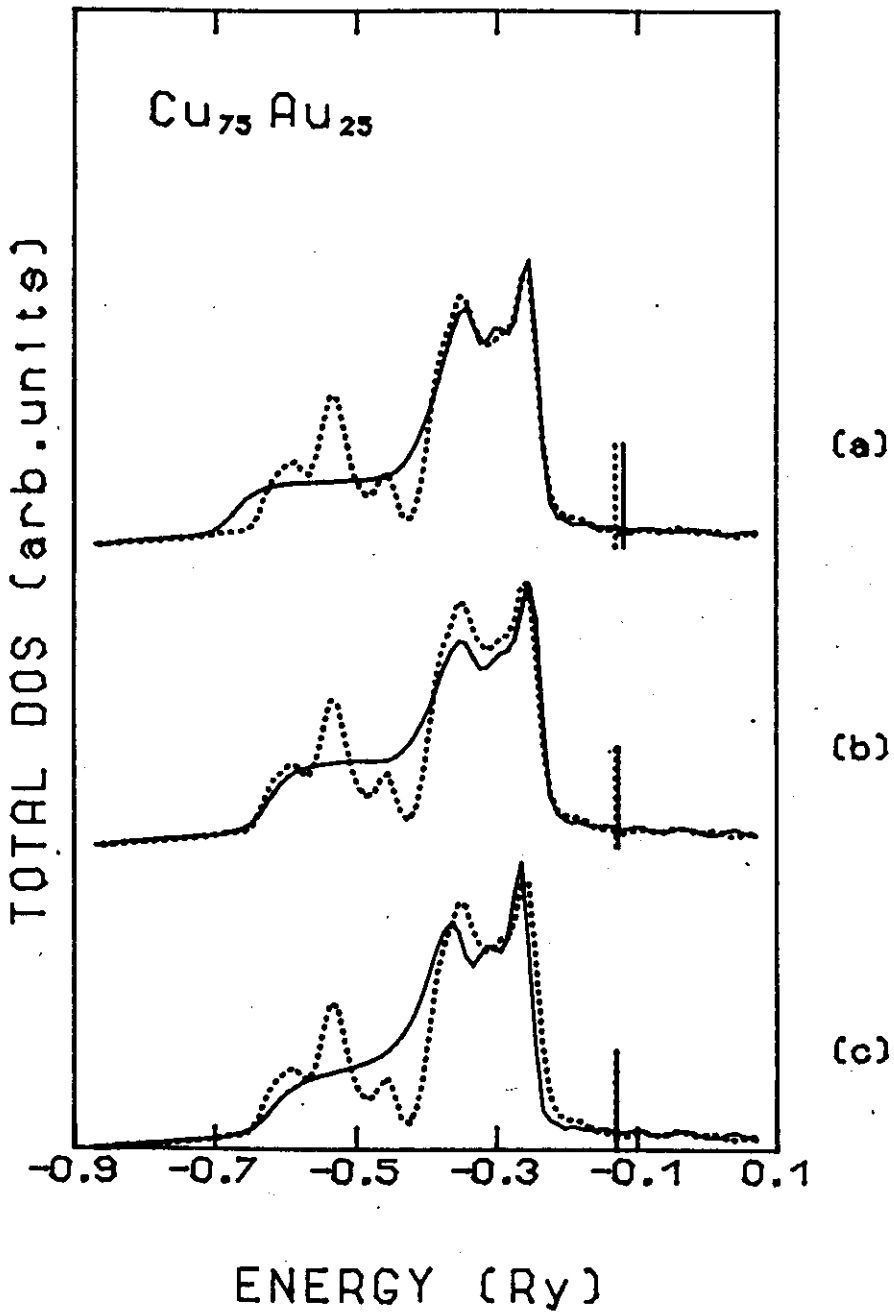
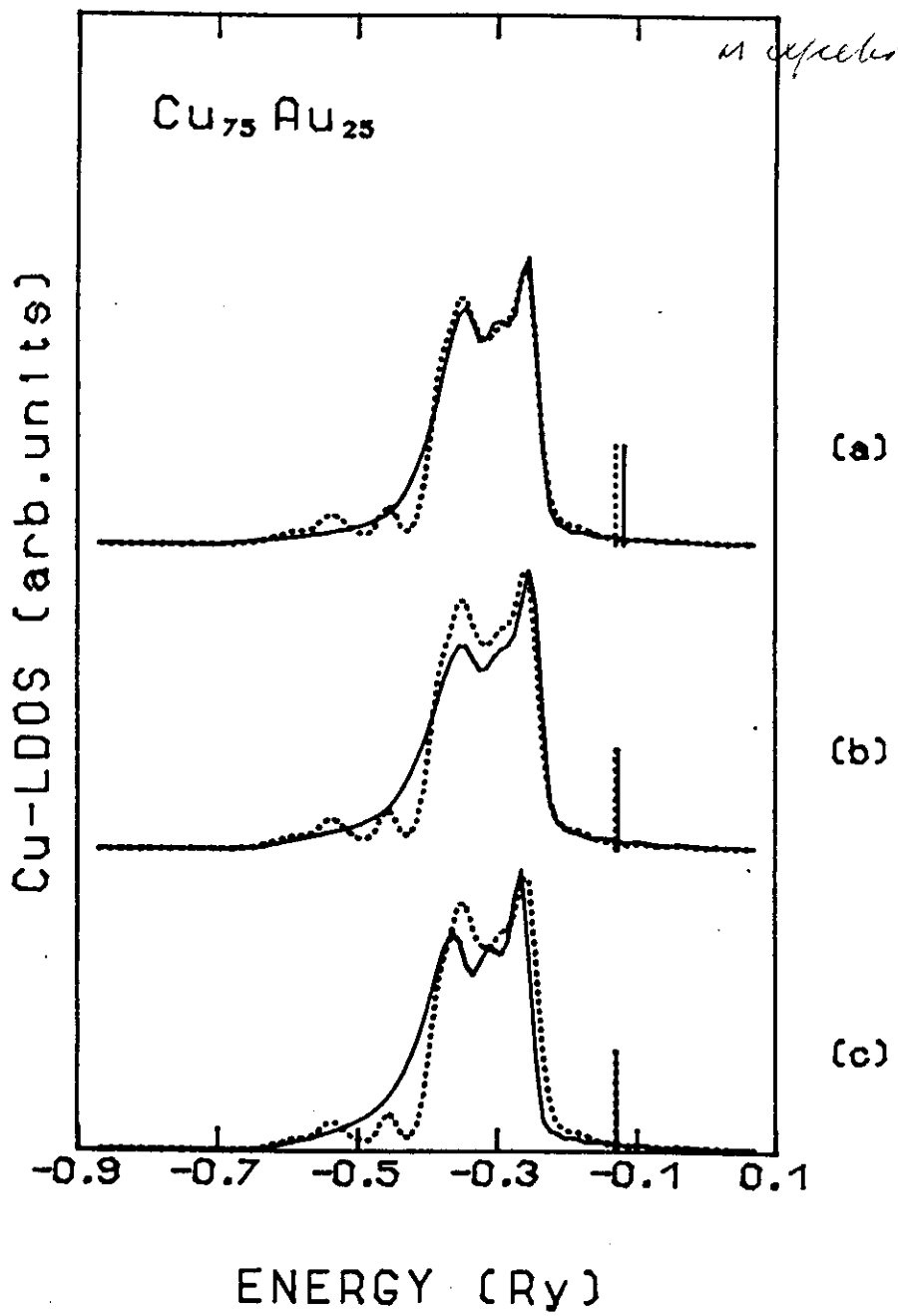
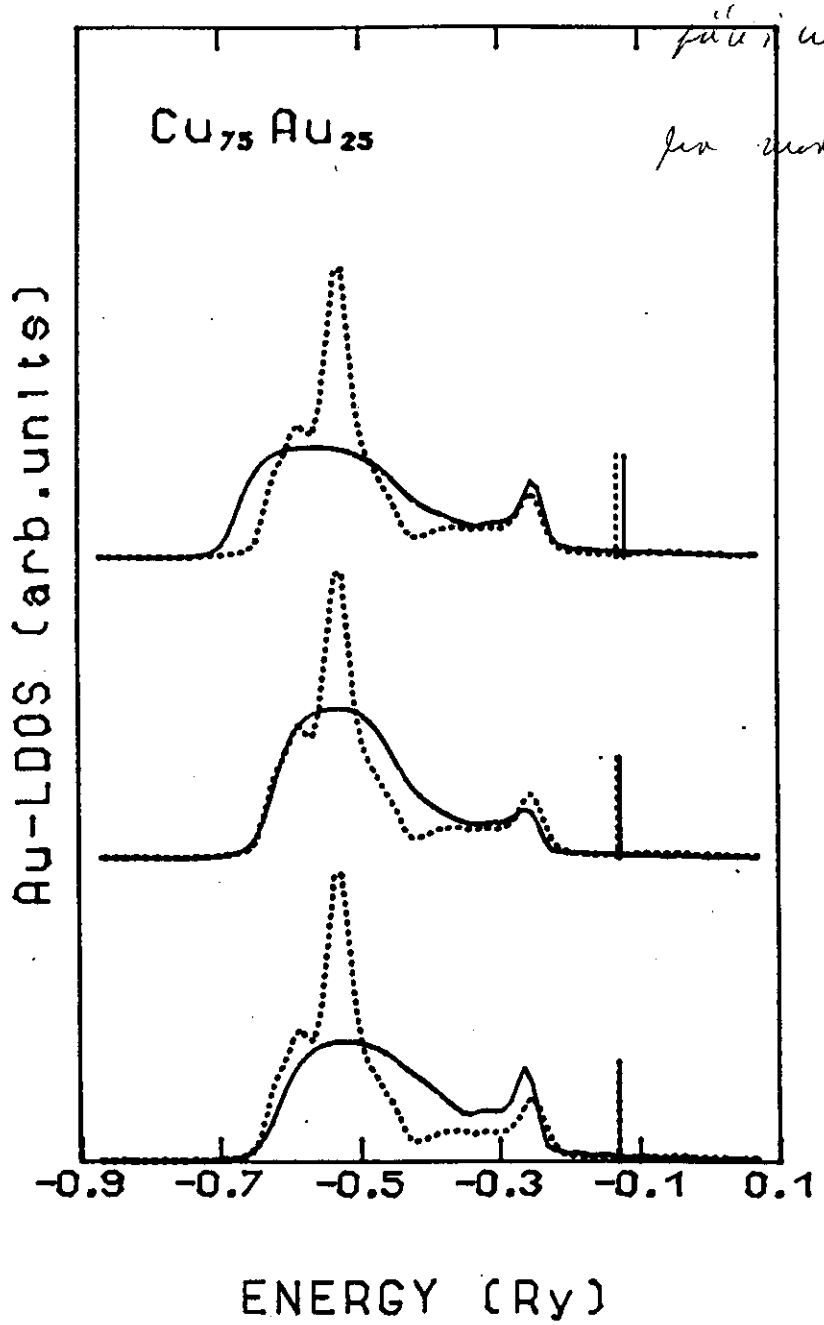


Fig. 8a and b. Comparison of valence band spectra of ordered and disordered $Cu_3Au(100)$ and $Cu_3Au(110)$ surfaces from Figs. 3 and 5 to 7 at a 26 eV photon energy and b 40 eV photon energy

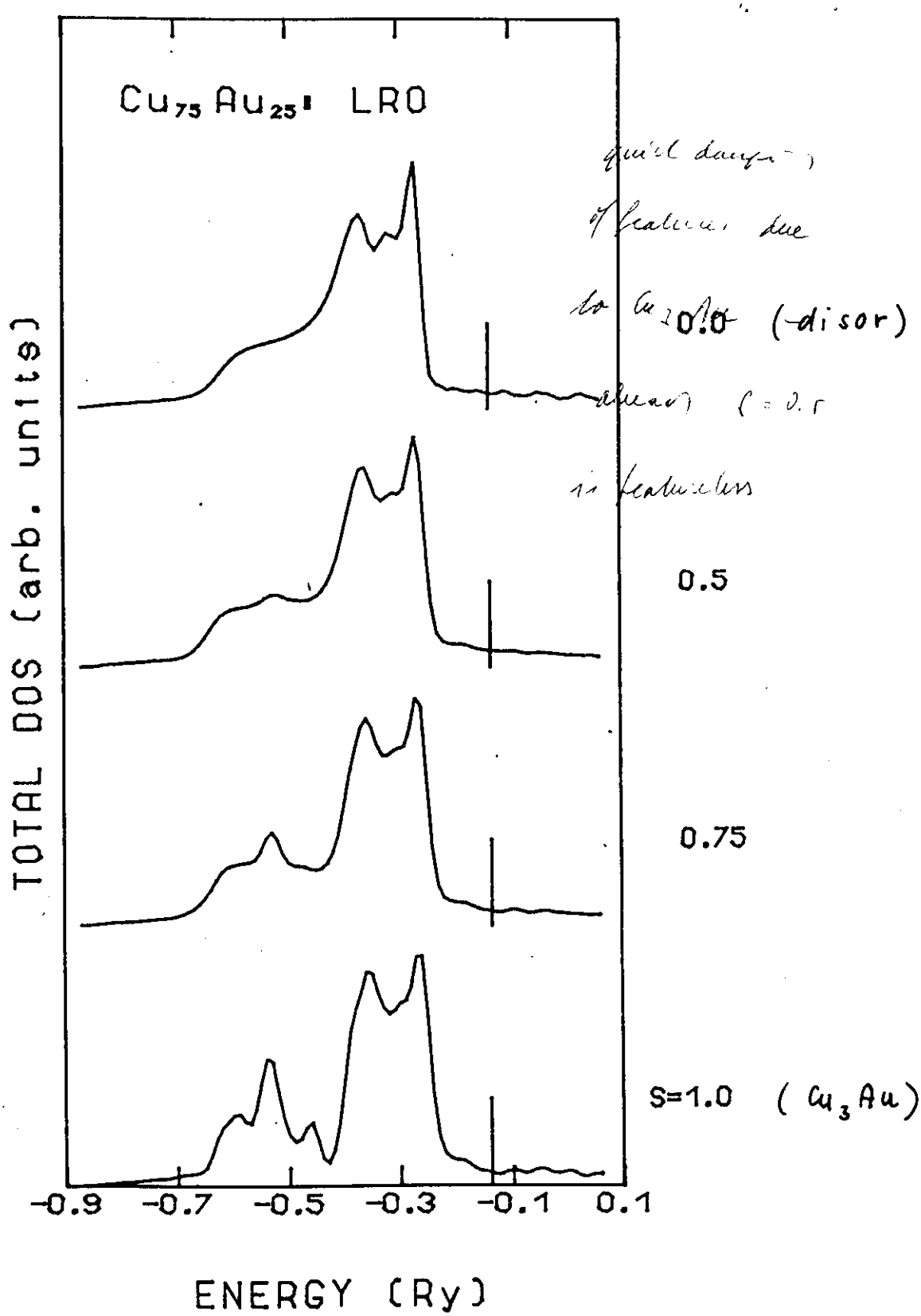
(a) - no lr (b) - lr incl (c) - lr incl + neutr




Cu75 Au25
(a)
(b)
(c)
Cu-LDOS (arb.units)
-0.9
-0.7
-0.5
-0.3
-0.1
0.1
ENERGY (Ry)


Cu75 Au25
(a)
(b)
(c)
Au-LDOS (arb.units)
-0.9
-0.7
-0.5
-0.3
-0.1
0.1
ENERGY (Ry)

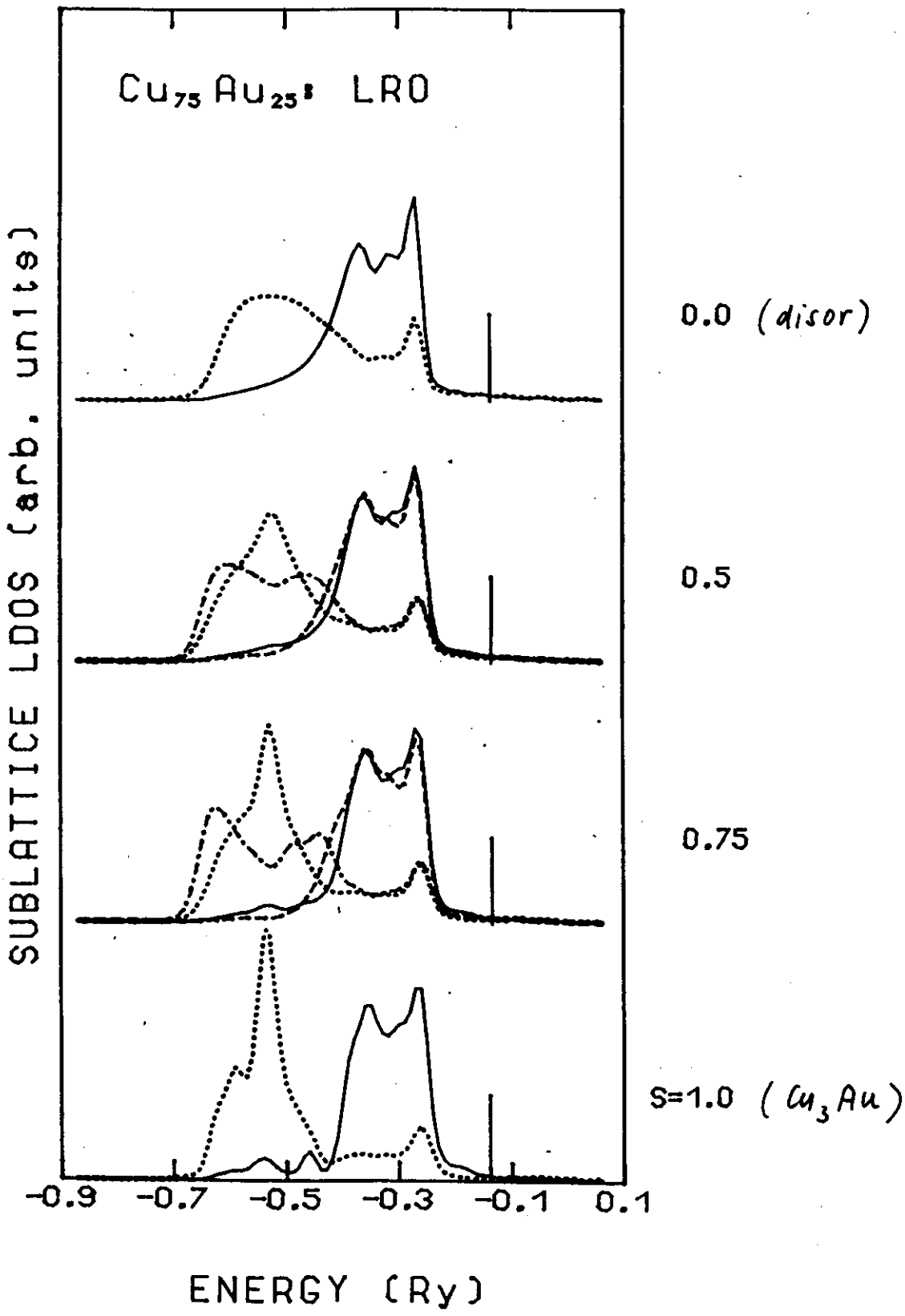
S ≡ LRO parameter

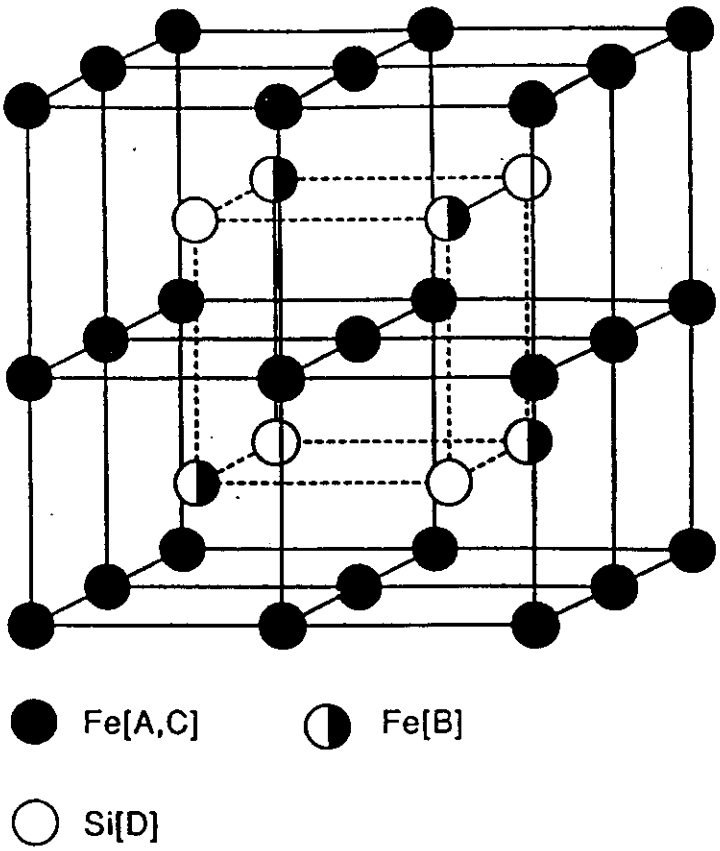


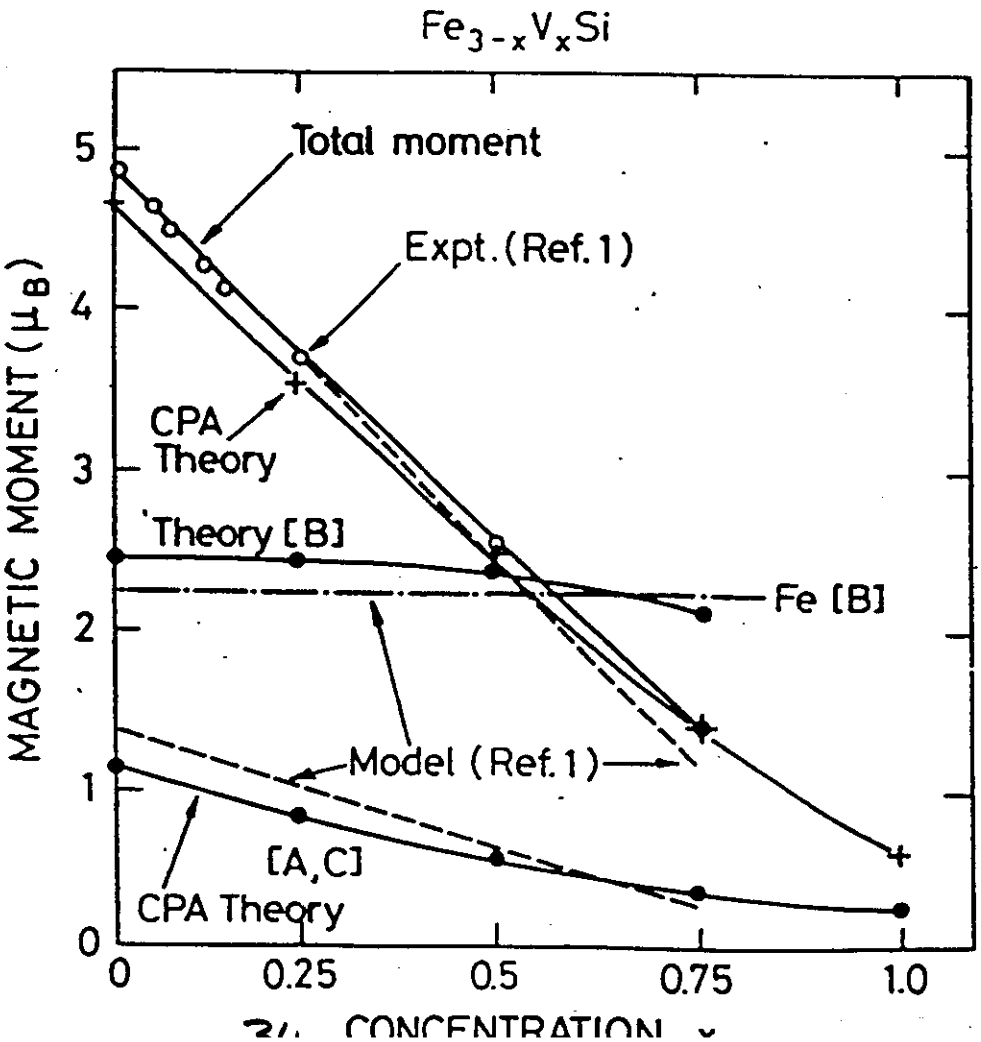
..... Au - LDOS on Au - sublattice

---- Cu - LDOS on Au - sublattice

-.-.-.- Au - LDOS on Cu - sublattices




Fe[A,C]
Fe[B]
Si[D]


Fe3-xVxSi
Total moment
Expt. (Ref. 1)
CPA Theory
Theory [B]
Fe [B]
Model (Ref. 1)
[A,C]
CPA Theory
MAGNETIC MOMENT (μB)
0
1
2
3
4
5
0
0.25
0.5
0.75
1.0

— total —— minority —— majority

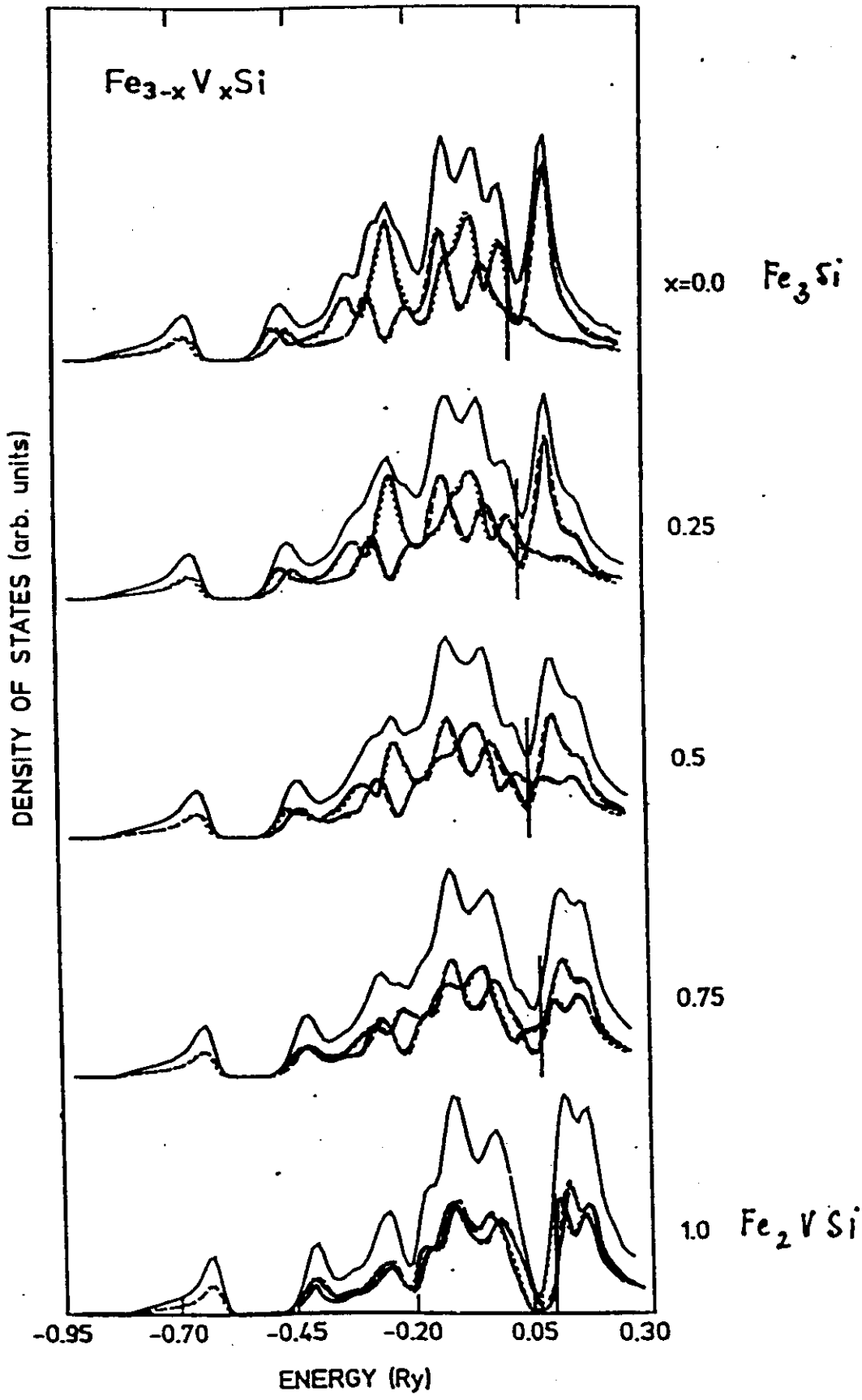


FIG. 8. $Fe_{3-x}V_xSi$. Total (solid lines) minority-spin (dashed) and majority-spin (dotted) DOS functions. The Fermi-level positions are indicated by vertical lines.

— Fe [B] ---- Fe [A, C] .... V [B] -.-.- Si [D]