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INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
I.C.T.P., P.O. BOX 586, 34100 TRIESTE, ITALY, CABLE CENTRATOM TRIESTE

UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION

INTERNATIONAL CENTRE FOR SCIENCE AND HIGH TECHNOLOGY
c/o INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS 34100 TRIESTE (ITALY) VIA GRIGNANO, 9 (ADRIATICO PALACE) P.O. BOX 586 TELEPHONE 040-224572 TELEFAX 040-224575 TELEX 460449 APH I

SMR. 628 - 12

Research Workshop in Condensed Matter, Atomic and Molecular Physics
(22 June - 11 September 1992)

Working Party on
"DISORDERED ALLOYS"
(24 August - 4 September 1992)

" ALLOYS PROBLEM "

R. PRASAD
Indian Institute of Technology
Department of Physics
Kanpur 208 016
India

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

Alloy Problem

No translational invariance

Bloch's theorem not applicable

Two ways

1. Take average over all configurations
2. Use some approximate scheme

Coherent Potential Approximation (CPA)

$\langle \bullet \; \bullet \; \bullet \; \bullet \rangle$ = 

$x\, G_A + y\, G_B = \langle G \rangle$

Single particle Green's function

Substitutional binary alloy $A_x B_{1-x}$

$$H = H_0 + V$$

$$V = \sum_n V_n$$

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

$$G(\vec{r}, \vec{r}'; E) = \sum_i \frac{\psi_i^*(\vec{r})\, \psi_i(\vec{r}')}{(E - E_i)}$$

$$\langle \rho(E) \rangle = -\frac{1}{\pi} \operatorname{Im} \int d^3r \, \langle G(\vec{r}, \vec{r}; E) \rangle$$

$$\langle \rho_{A(B)}(E) \rangle = -\frac{1}{\pi} \operatorname{Im} \int d^3r \, \langle G(\vec{r}, \vec{r}; E) \rangle_{0 = A(B)}$$

$$\langle \rho_{A(B)}(\vec{r}) \rangle = -\frac{1}{\pi} \operatorname{Im} \int_{-\infty}^{E_F} dE \, \langle G(\vec{r}, \vec{r}; E) \rangle_{0 = A(B)}$$

KKR - CPA

(Korringa - Kohn - Rostoker - coherent pot. Approx)

Consider a substitutional binary alloy $A_x B_{1-x}$

$$H = H_0 + V$$

↓ Free electron Hamiltonian

$$V = \sum_n v_n$$

↳ muffin-tin potentials

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

$$G_0(E) = (E - H_0)^{-1}$$

$$G = G_0 + G_0 V G$$

$$= G_0 + G_0 V G_0 + G_0 V G_0 V G_0 + \cdots$$

$$= G_0 + G_0 T G_0$$

where

$$T = V + V G_0 V + \cdots$$

$$= \sum_n v_n + \sum_n v_n G_0 \sum_n v_n + \cdots$$

$$= \sum_n t_n + \sum_n t_n G_0 \sum_{m \neq n} t_m + \cdots$$

where t_n = atomic scattering matrix

$$t_n = v_n + v_n G_0 v_n + \cdots$$

$$= v_n + v_n G_0 (v_n + v_n G_0 v_n + \cdots)$$

$$= v_n + v_n G_0 t_n$$

$$= v_n (1 - G_0 v_n)^{-1}$$

$$T = \sum_{nn'} T_{nn'}$$

↳ path operators

$$T_{nn'} = t_n \delta_{nn'} + t_n G_0 \sum_{m \neq n'} T_{mn'}$$

muffin-tin form of the potential simplifies the solution

$$\langle \vec{r} | t_n | \vec{r}' \rangle = t_n(\vec{r}, \vec{r}') = \sum_L Y_L(\vec{r})\, t_n^\ell(r, r')\, Y_L(\vec{r}')$$

$$t_n(\vec{k}, \vec{k}') = \iint e^{-i\vec{k}\cdot\vec{r}}\, t_n(\vec{r}, \vec{r}')\, e^{i\vec{k}\cdot\vec{r}}\, d^3r\, d^3r'$$

$$= (4\pi)^2 \sum_L Y_L(\vec{k})\, t_n^\ell(k, k')\, Y_L(\vec{k}')$$

$k = k' = \chi = \sqrt{E}$ matrix element of t_n^ℓ

$$t_n^\ell(\chi, \chi) = \tau_n^\ell(\chi) = -\frac{1}{\chi} e^{i\delta_n^\ell} \sin\delta_n^\ell$$

↓ energy shell matrix ↓ phase shifts

$T_{nn'}(x,x) = T_{nn'}(x)$

$$T_{nn'}^{LL'}(x) = \tau_n^l \delta_{nn'} \delta_{LL'} + \tau_n^l \sum_{m L_1} B_{nm}^{LL_1} T_{mn'}^{L_1 L'}(x)$$

$B_{nm}^{LL'}$ depend on structure only

= Fourier transform of the KKR structure constants

$$T_{nn'}^{LL'}(x) = \left\{ (\tau^{-1}(x) - B)^{-1} \right\}_{nn'}^{LL'}$$

Faulkner & Stocks, Phys. Rev. B 21, 3222 (80)

$$G(\vec{r}_n, \vec{r}_{n'}; E) = \sum_{LL'} Z_L^n(\vec{r}_n, E)\, T_{nn}^{LL'}\, Z_{L'}^{n}(\vec{r}_{n'}, E) - \sum_L Z_L^n(\vec{r}_n, E)\, J_L^n(\vec{r}_{n'}; E)$$

regular solution — irregular sol^n

KKR - CPA

$\langle$ ○ ○ ○ ○ $\rangle$ = ● ● ● ●

$x \langle G \rangle_{o=A} + (1-x) \langle G \rangle_{o=B} = \langle G \rangle$

x (● ● ○ ●) + y (● ● ○ ●) = ● ● ● ●

$$G = G_o + G_o T G_o$$

$$x\, T_{oo}^A + (1-x)\, T_{oo}^B = T_{oo}^c$$

$$T_{oo}^c = \frac{1}{N} \sum_{\vec{k}} \left[\tau_c^{-1} - B(k, E) \right]^{-1}$$

$$T_{oo}^{A(B)} = \left[1 + T_{oo}^c (\tau_c^{-1} - \tau_{A(B)}^{-1}) \right]^{-1} T_{oo}^c$$

CPA condition

$$\tau_c^{-1} = \langle \tau^{-1} \rangle + (\tau_c^{-1} - \tau_A^{-1})\, T_{oo}^c\, (\tau_c^{-1} - \tau_B^{-1})$$

$$\langle \tau^{-1} \rangle = x \tau_A^{-1} + (1-x) \tau_B^{-1}$$

KKR - CPA

1. Replace the disordered alloy by an effective medium characterized by τ_c

2. To determine τ_c, embed an A or B atom in the effective medium and impose the condition

$$x\, T_{00}^{A} + (1-x)\, T_{00}^{B} = T_{00}^{c}$$

$$T_{00}^{c} = \frac{1}{N_c} \sum_{\vec{k}} \left[\tau_c^{-1} - B(\vec{k}, E) \right]^{-1}$$

$$T_{00}^{A(B)} = \left[1 + T_{00}^{c} (\tau_c^{-1} - \tau_{A(B)}^{-1}) \right]^{-1} T_{00}^{c}$$

3 Find the average Green's function $\langle G(\vec{r}, \vec{r}'; E) \rangle$

4. Find density of states and the charge densities

$$\langle \rho(E) \rangle = -\frac{1}{\pi} \operatorname{Im} \int d^3r \, \langle G(\vec{r}, \vec{r}; E) \rangle$$

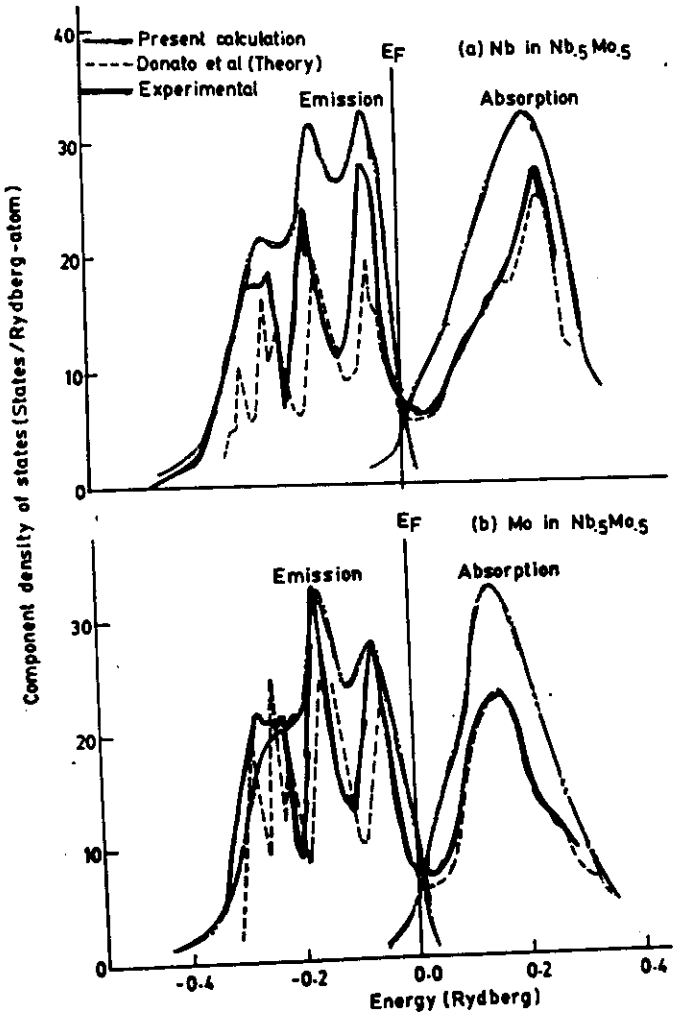
$$\langle \rho_{A(B)}(\vec{r}) \rangle = -\frac{1}{\pi} \operatorname{Im} \int_{-\infty}^{E_F} dE \, \langle G(\vec{r}, \vec{r}; E) \rangle_{a_{A(B)}}$$

5. From $\langle \rho_{A(B)}(\vec{r}) \rangle$ determine the potentials $v_{A(B)}$ using LDA and iterate the whole procedure till self-consistency.

6. At this level the KKR-CPA theory attains the same level as the band theory of pure metals.

7. In this formulation single impurity, pure metal and the disordered alloy are treated at the same footing.

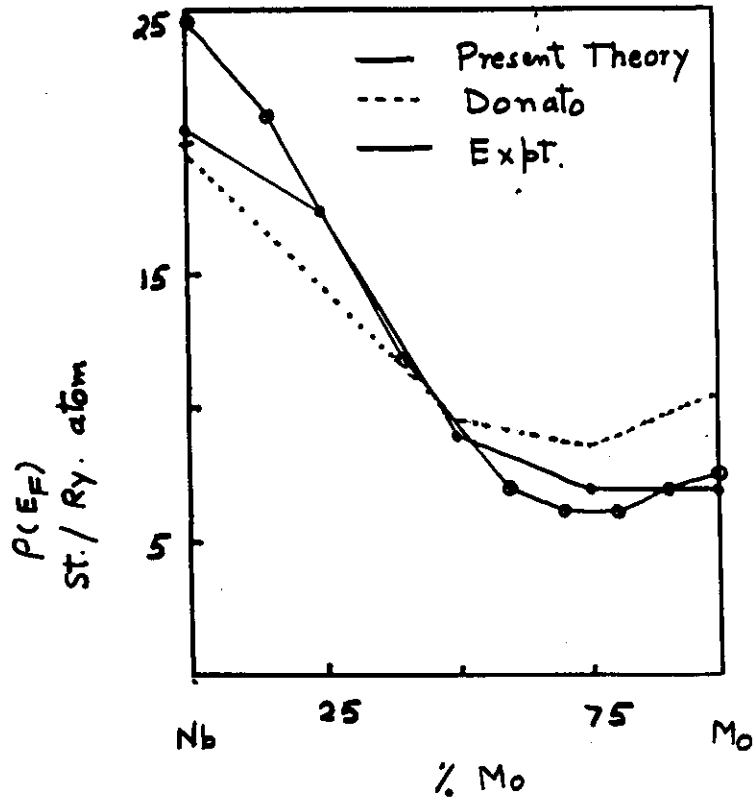
Component density of states



Rajput and Prasad

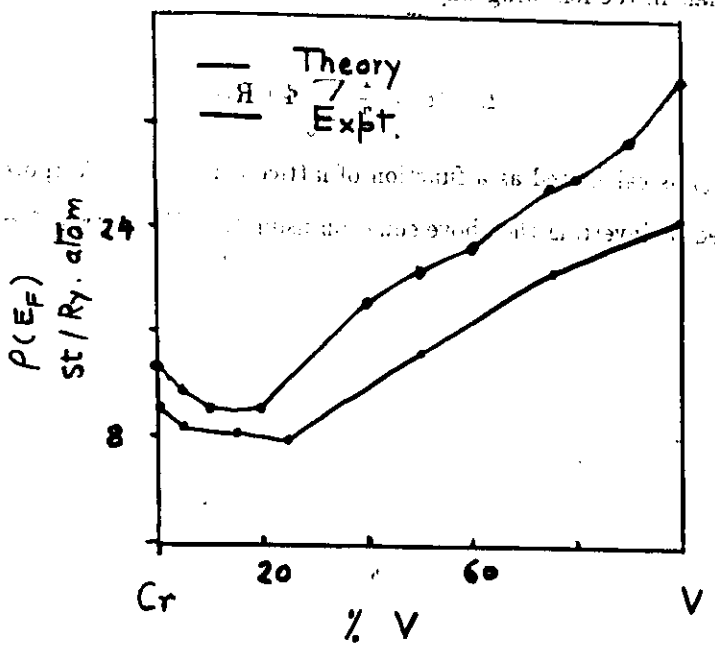
Density of states at E_F

$Nb_{100-x}\ Mo_x$



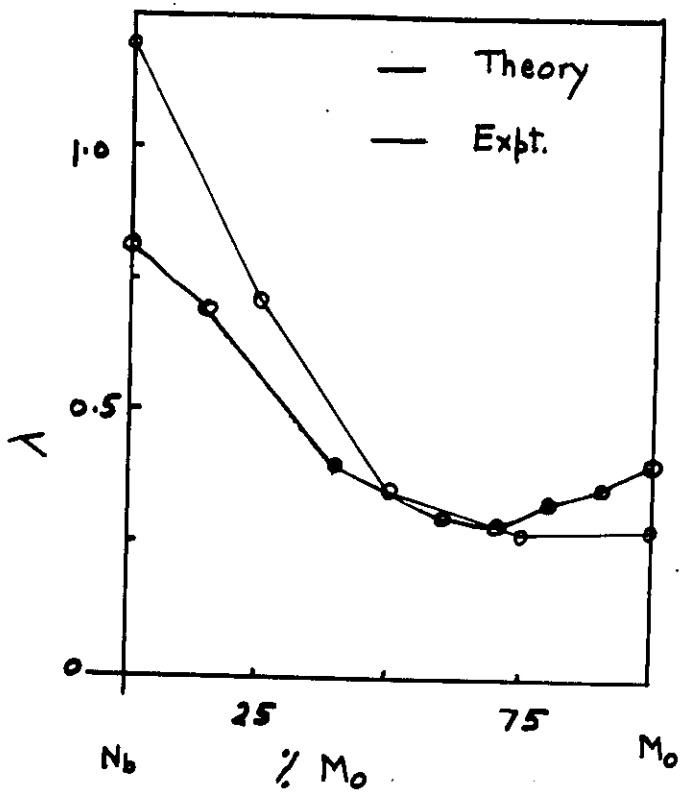
Density of States at E_F

$Cr_{100-x}\ V_x$



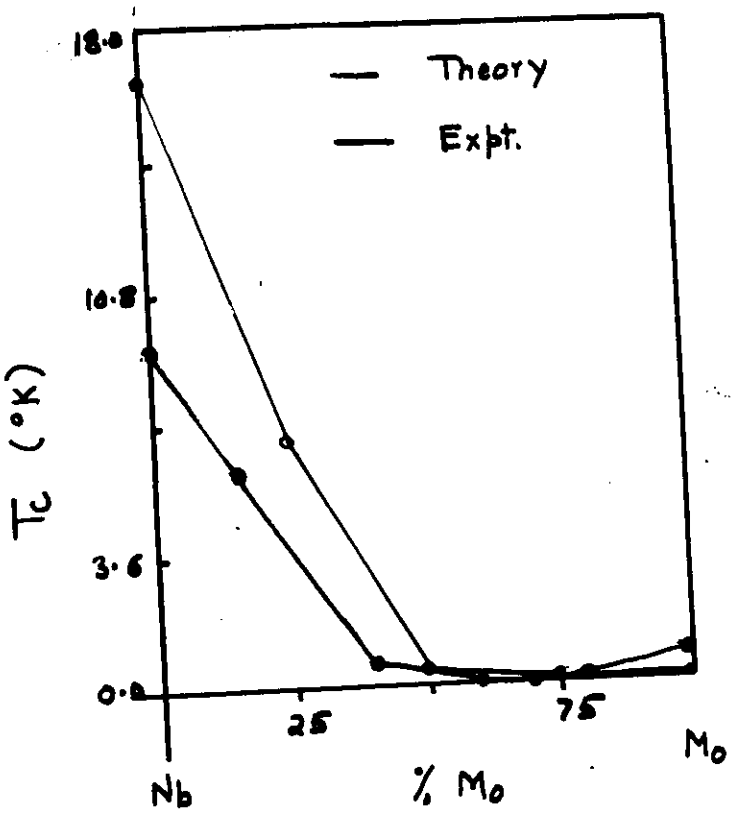
λ

$Nb_{100-x}\ Mo_x$

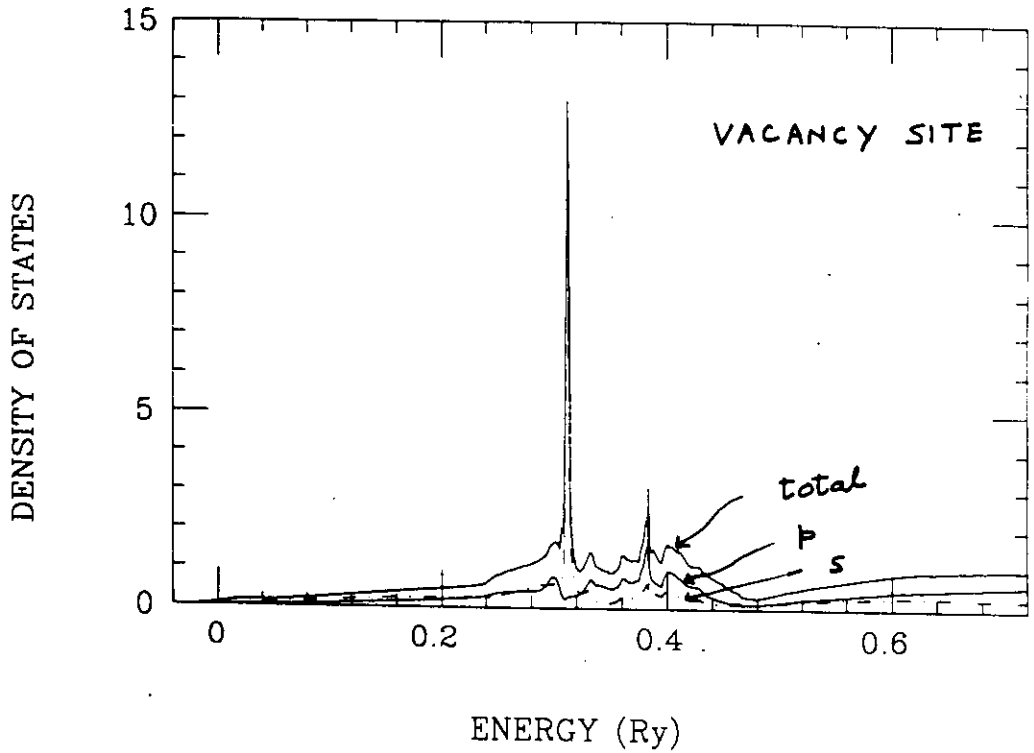


T_c

$Nb_{100-x}\ Mo_x$



VACANCY IN COPPER



Prasad et. al, Phys. Rev. B 40, 8620 (1989).

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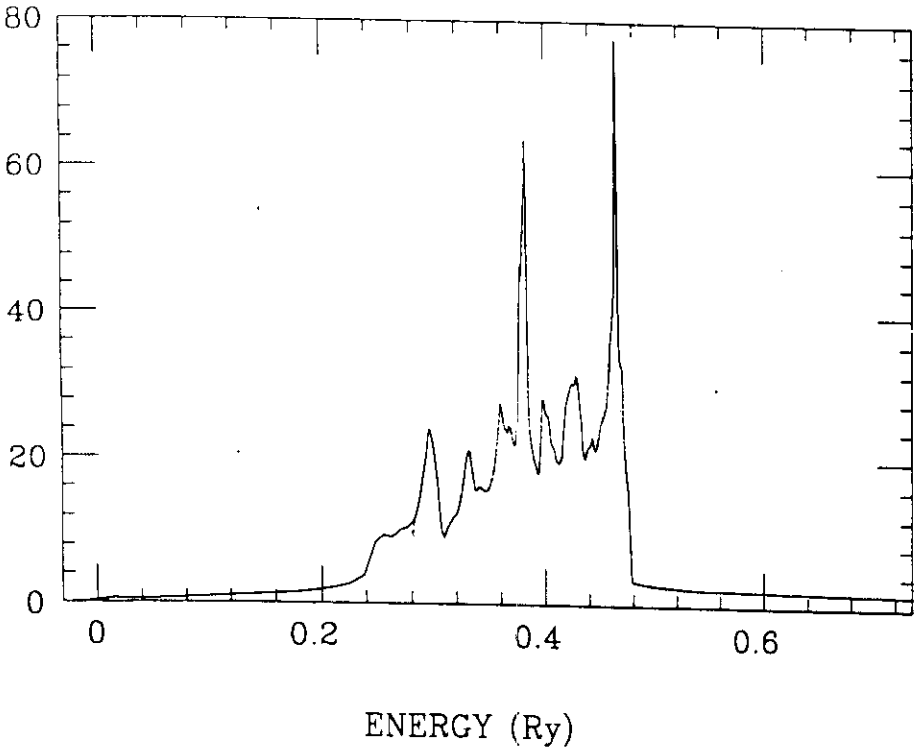


Prasad et. al., Phys. Rev. B40, 8620 (1989)

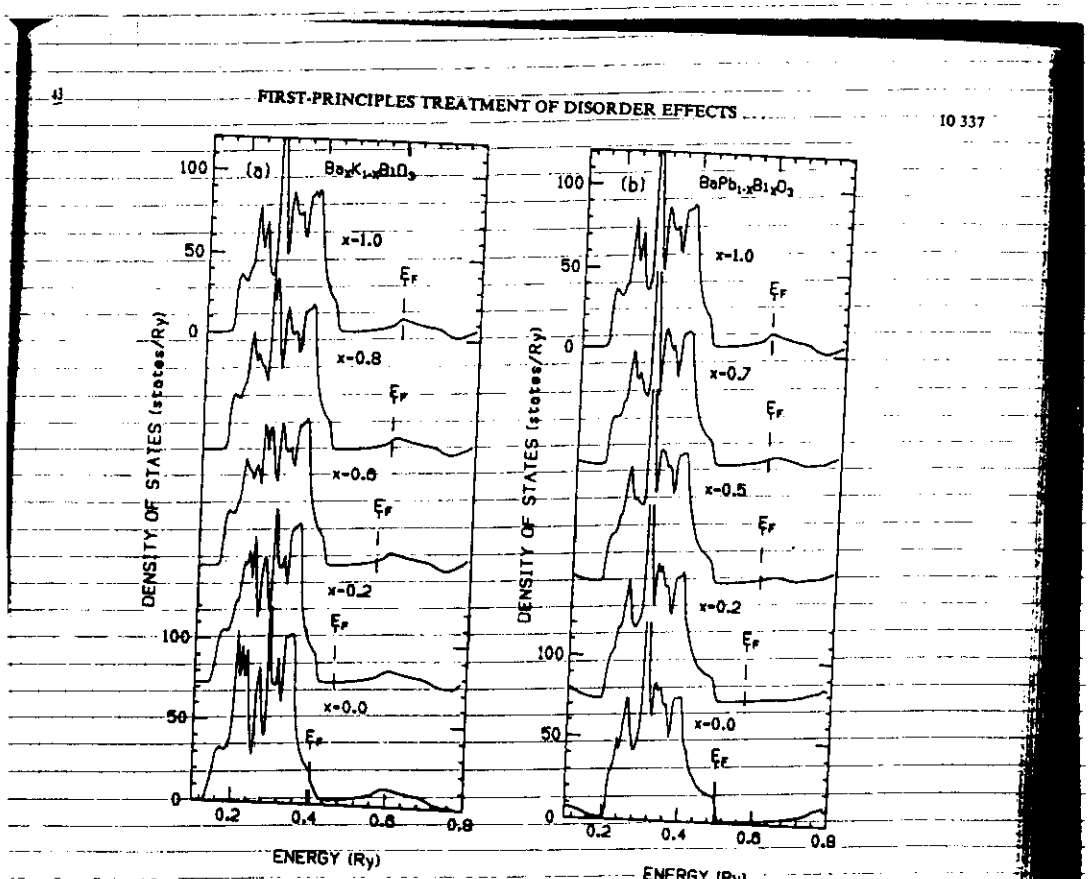


FIG. 2. Charge self-consistent KKR-CPA total densities of states in $Ba_xK_{1-x}BiO_3$ and $BaPb_{1-x}Bi_xO_3$. Fermi energies (E_F) are as marked.

$Cu_{75}Pd_{25}$

IGHT *et al.* 35

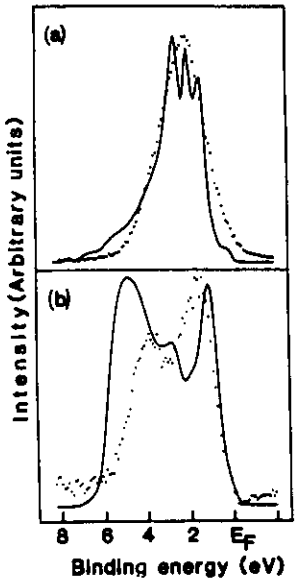


FIG. 5. The dots show $D_{Cu}(E)$ and $D_{Pd}(E)$ from Fig. 3. The curves are the results of Ref. 3 broadened by Gaussians of FWHM of 0.5 eV.

Wright et. al. Phys. Rev. B 35, 519 (87)

Complex Energy Bands

$$\| \tau_{cp}^{-1} - B_{\vec{k}}(E) \| = 0$$

potential — Structure

Perfect Crystal: $\tau_{cp} \rightarrow \tau_A$ or τ_B

KKR determinant

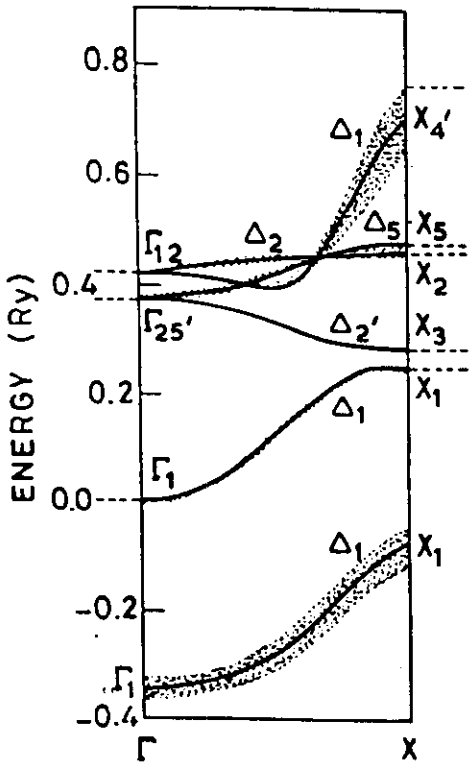
↓

Bloch Energy Bands

Alloy → Complex energy bands

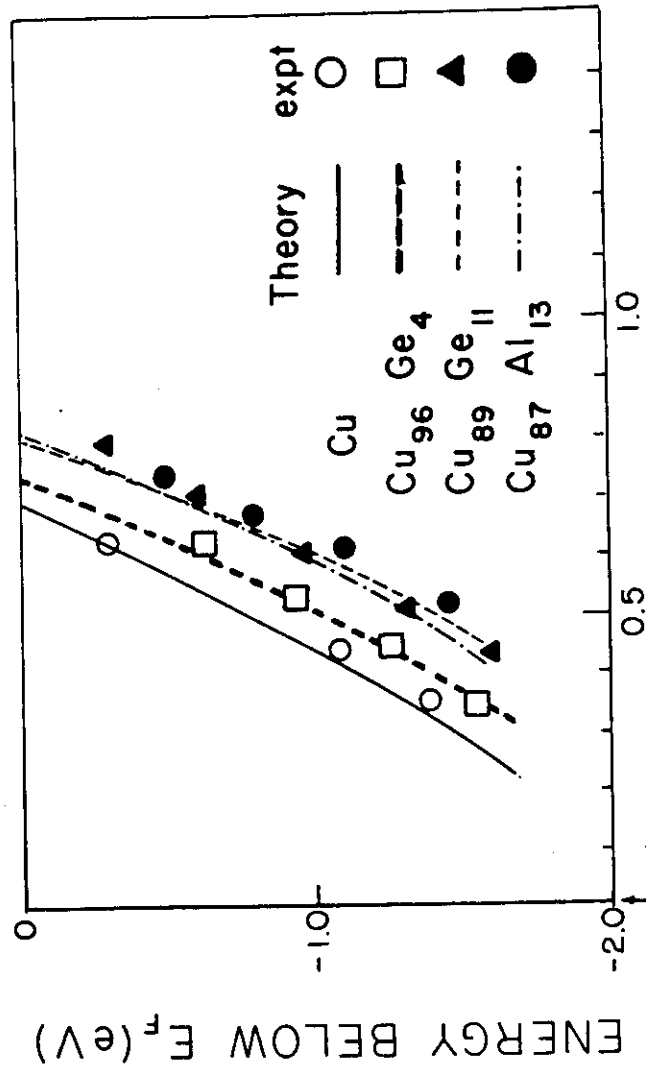
Energy Bands

$Cu_{90}Ge_{10}$



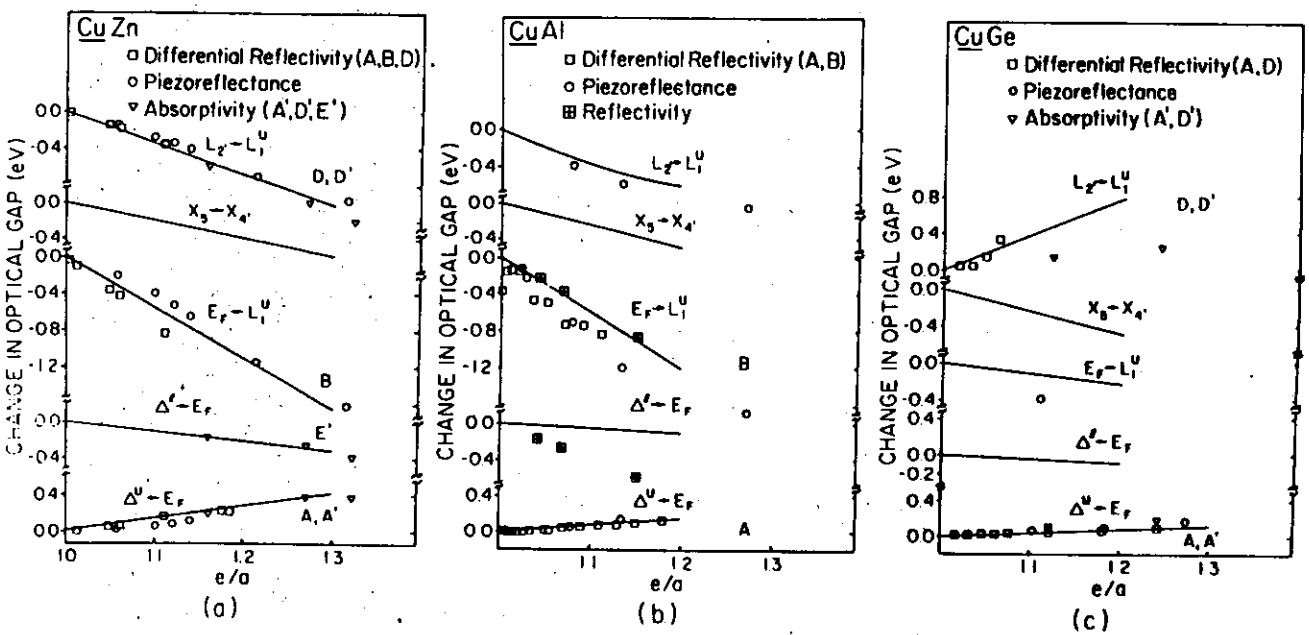
Prasad & Bansil, Phys. Rev. Lett. 48, 113 (1982).

Energy Bands

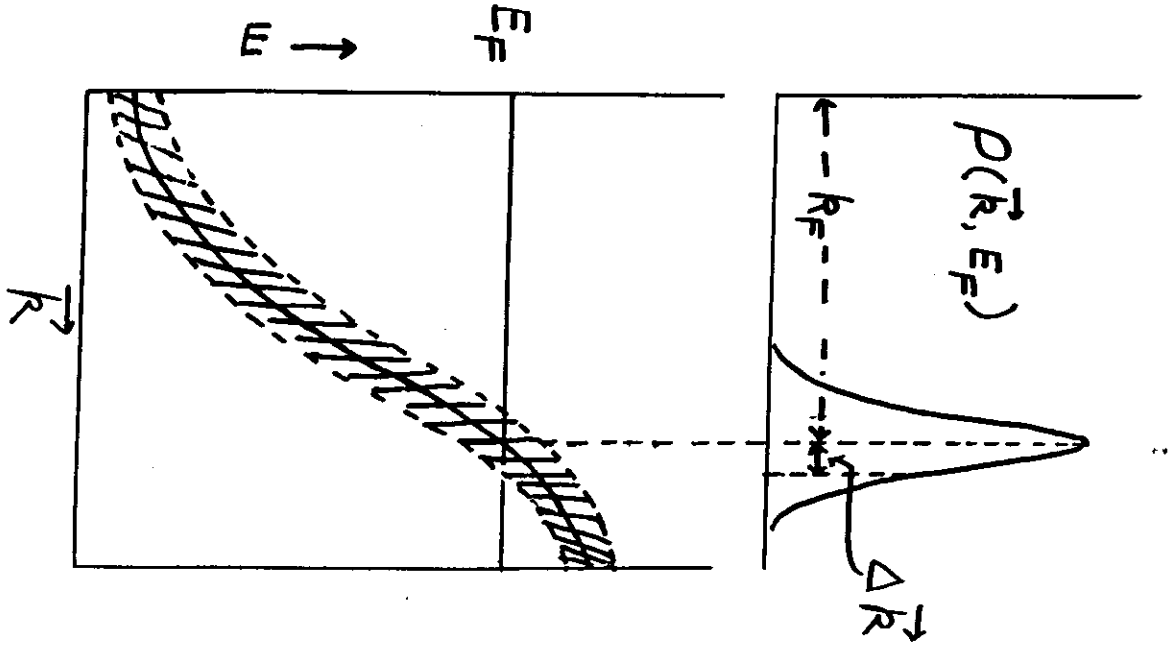


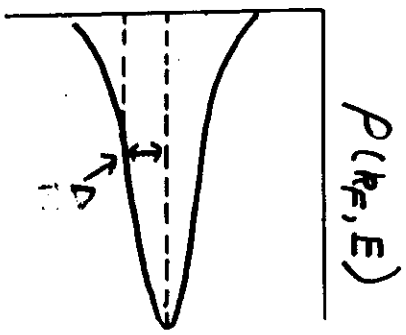
Bansil, Rao, Prasad and Peisa, Asonen, J. Phys. F 13, (1984)

Optical gaps



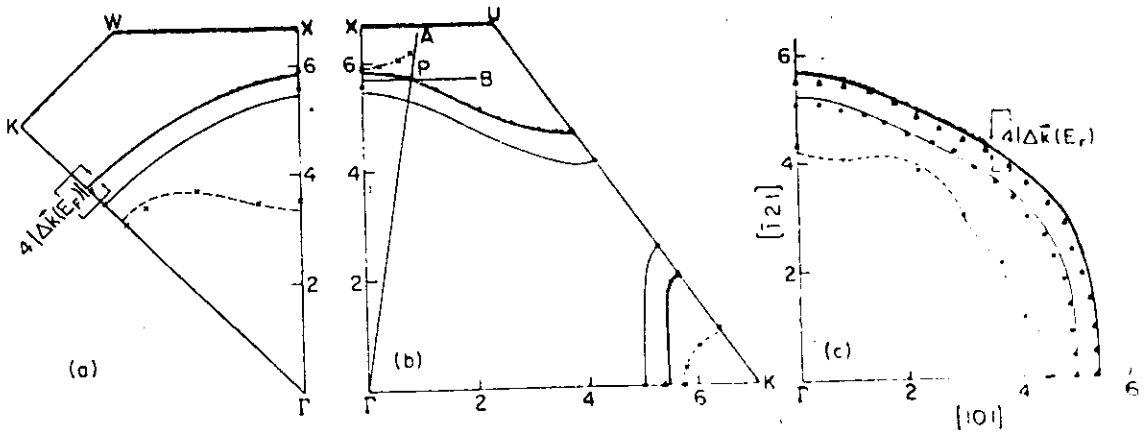
Rao, Prasad and Bansil, Phys. Rev. B 28, 5762 (1983)





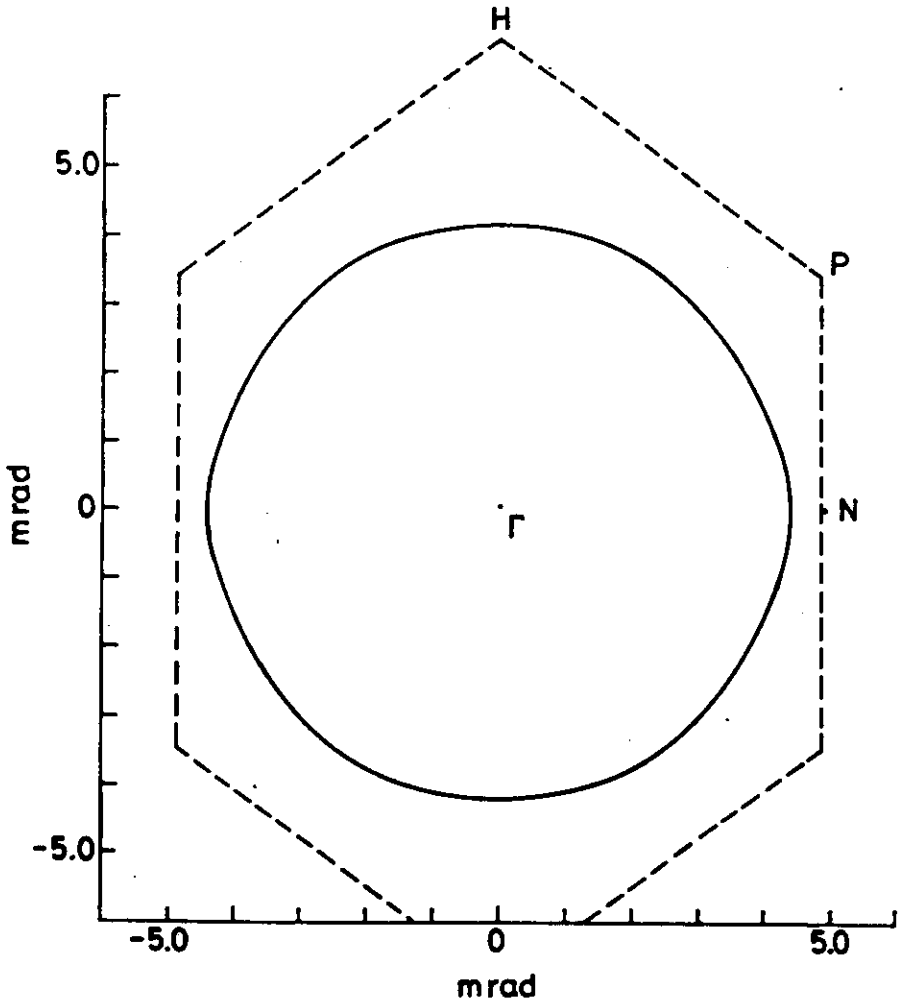
Fermi Surface

$Cu_{70}Zn_{30}$

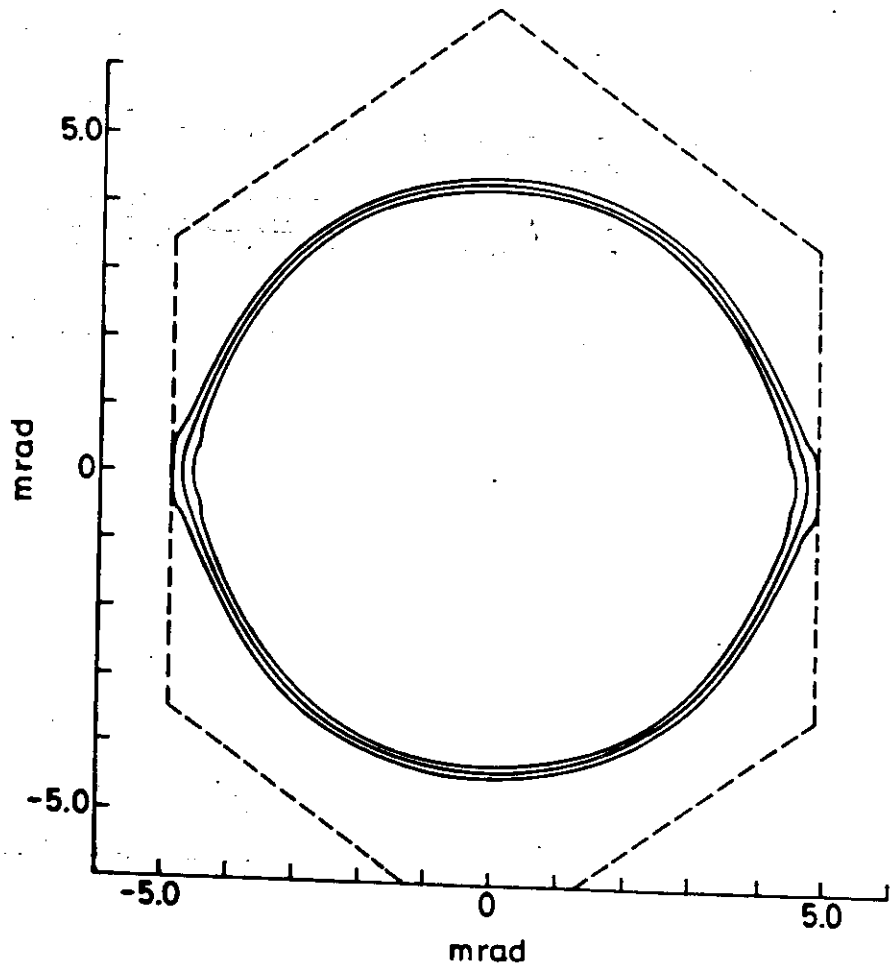


Prasad, Papadopoulos and Bansil, Phys. Rev B 23, 2607 (81)

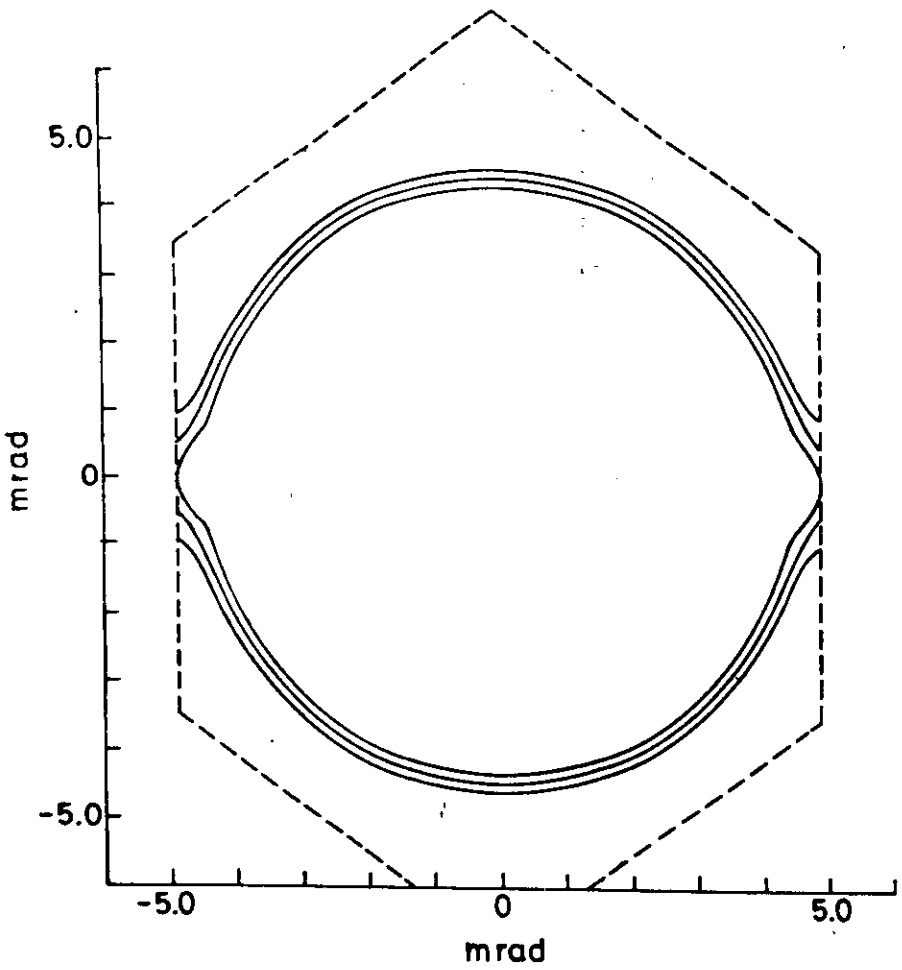
Fermi Surface : Li



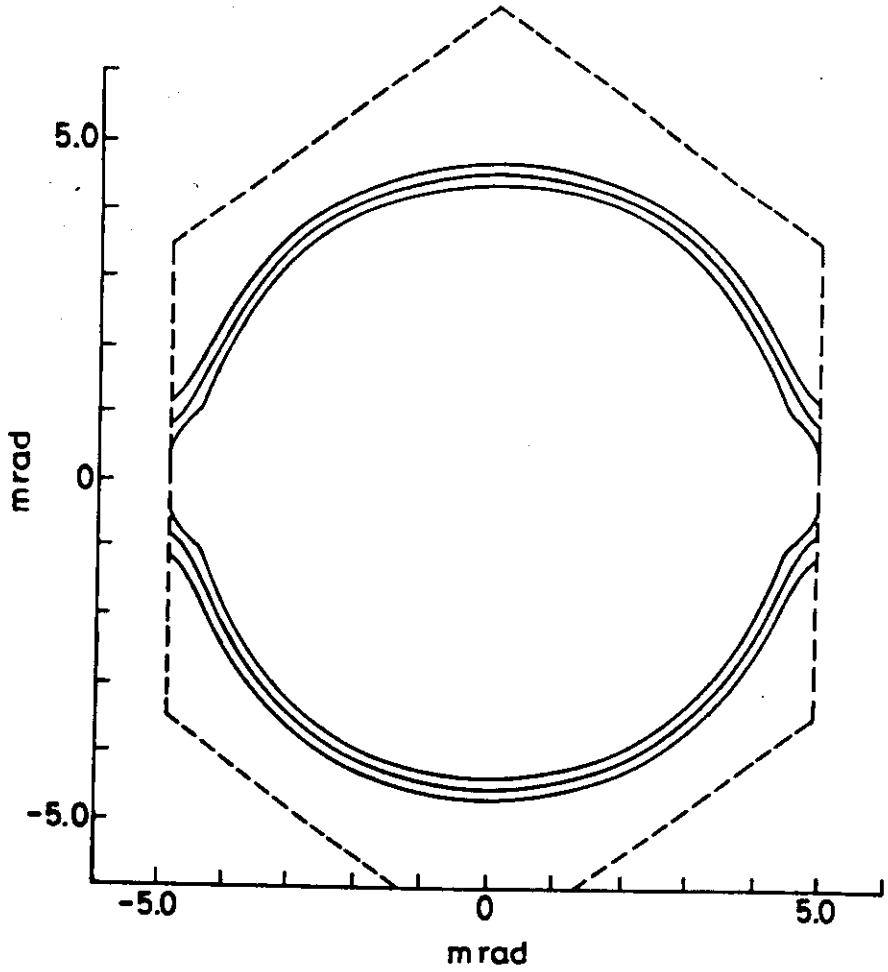
Fermi Surface : $Li_{86}Mg_{14}$

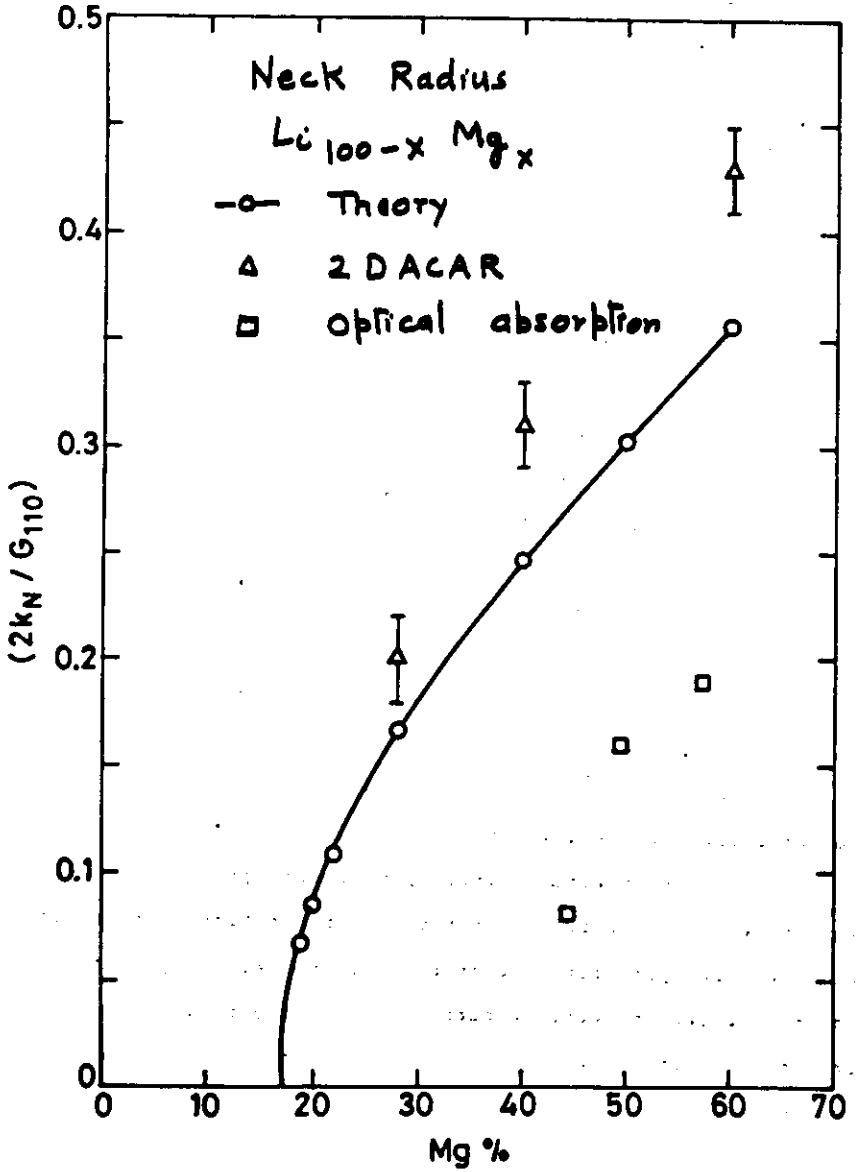


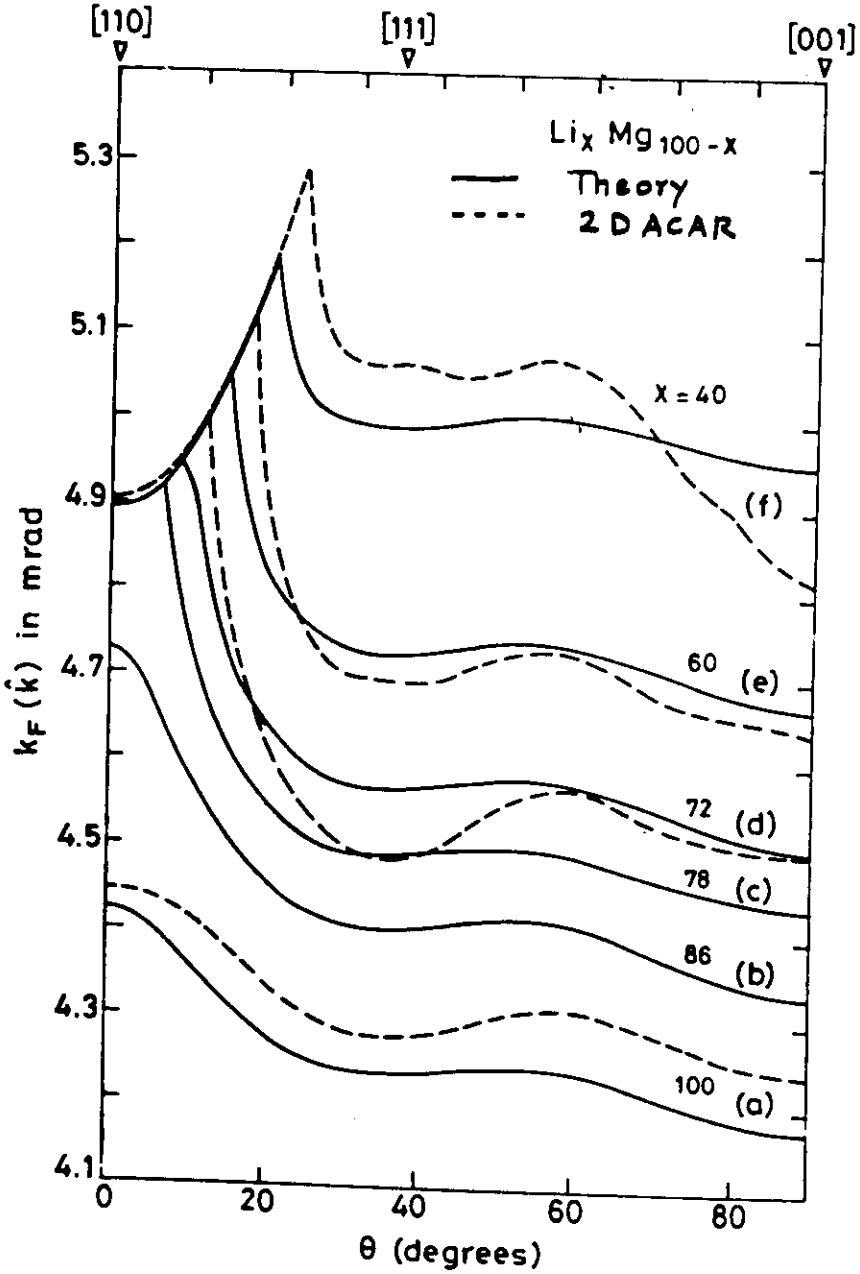
Fermi Surface: $Li_{78}Mg_{22}$



Fermi Surface: $Li_{72}Mg_{28}$

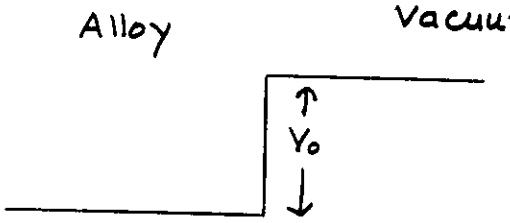



Neck Radius
$Li_{100-x}\ Mg_x$
Theory
2 D ACAR
optical absorption
$(2k_N / G_{110})$
Mg %
0.5
0.4
0.3
0.2
0.1
0
0
10
20
30
40
50
60
70


[110]
[111]
[001]
$Li_x\ Mg_{100-x}$
Theory
2 D ACAR
X = 40
(f)
60
(e)
72
(d)
78
(c)
86
(b)
100
(a)
$k_F(\hat{k})$ in mrad
θ (degrees)
5.3
5.1
4.9
4.7
4.5
4.3
4.1
0
20
40
60
80

Surface states in disordered alloys

Green's function matching method



Prasad, Serageldin & Bansil, J. Phys: Cond. Matter
3, 801 (1991)

Green's Function Matching Technique

I V_I G_I

Surface

II V_{II} G_{II}

$$(-\nabla^2 + V(\vec{r}) - E)\, G(\vec{r}, \vec{r}') = -\delta(\vec{r} - \vec{r}') \qquad (1)$$

$V(\vec{r}) = V_I(\vec{r})$ when $\vec{r}$ in I

$= V_{II}(\vec{r})$ when $\vec{r}$ in II

For $\vec{r} = \vec{r}_1$ in I

$$(-\nabla^2 + V_I(\vec{r}_1) - E)\, G(\vec{r}_1, \vec{r}') = -\delta(\vec{r}_1 - \vec{r}') \qquad (2)$$

$$(-\nabla^2 + V_I(\vec{r}_1) - E)\, G_I(\vec{r}, \vec{r}_1) = -\delta(\vec{r}_1 - \vec{r}) \qquad \cdots (3)$$

$G_I(\vec{r}, \vec{r}_1) \times (2)$ and integrate over $\vec{r}_1$

$$\int d^3\vec{r}_1\, G_I(\vec{r}, \vec{r}_1)\,[-\nabla^2 + V_I(\vec{r}_1) - E]\, G(\vec{r}_1, \vec{r}')$$

$$= -\int \delta(\vec{r}_1 - \vec{r}')\, G_I(\vec{r}, \vec{r}')\, d^3\vec{r}_1$$

$$= -G_I(\vec{r}, \vec{r}') \qquad \cdots (4)$$

($\vec{r}'$ in I)

• Similarly, $G(\vec{r}_1, \vec{r}')$ × ③ and integrate

$$\int d^3\vec{r}_1\, G(\vec{r}_1, \vec{r}')\left[-\nabla^2 + V_I(\vec{r}_1) - E\right] G_I(\vec{r}, \vec{r}_1)$$

$$= -G(\vec{r}, \vec{r}') \quad \cdots ⑤$$

for $\vec{r}$ in I

④ − ⑤ ⇒

$$G(\vec{r}, \vec{r}') = G_I(\vec{r}, \vec{r}') + \int d^3\vec{r}_1 \left\{ G_I(\vec{r}, \vec{r}_1)\left[-\nabla^2\right] G(\vec{r}_1, \vec{r}') - G(\vec{r}_1, \vec{r}')\left[-\nabla^2\right] G_I(\vec{r}, \vec{r}_1)\right\}$$

$$= G_I(\vec{r}, \vec{r}') - \int d^2\vec{r}_s \left[G_I(\vec{r}, \vec{r}_s) \frac{\partial G(\vec{r}_s, \vec{r}')}{\partial n_s} - \frac{\partial G_I(\vec{r}, \vec{r}_s)}{\partial n_s} G(\vec{r}_s, \vec{r}')\right] \quad ⑥$$

($\vec{r}, \vec{r}'$ in I)

Similarly by integrating over II

$$G(\vec{r}, \vec{r}') = \int d^2\vec{r}_s \left[G_{II}(\vec{r}, \vec{r}_s) \frac{\partial G}{\partial n_s}(\vec{r}_s, \vec{r}') - \frac{\partial G_{II}(\vec{r}, \vec{r}_s)}{\partial n_s} G(\vec{r}_s, \vec{r}')\right] \quad ⑦$$

for $\vec{r}$ in II and $\vec{r}'$ in I

$\frac{\partial}{\partial n_s}$ is normal derivative outward from I

(i) Put $\vec{r} = \vec{r}_s$ in Eqs ⑥ and ⑦

(ii) Expand surface values in terms of some complete set

$G(\vec{r}_s, \vec{r}') \longrightarrow g$

$G(\vec{r}_s, \vec{r}_s') \longrightarrow \mathcal{G}$

$$g = g_I - (\mathcal{G}_I g' - \mathcal{G}_I' g)$$

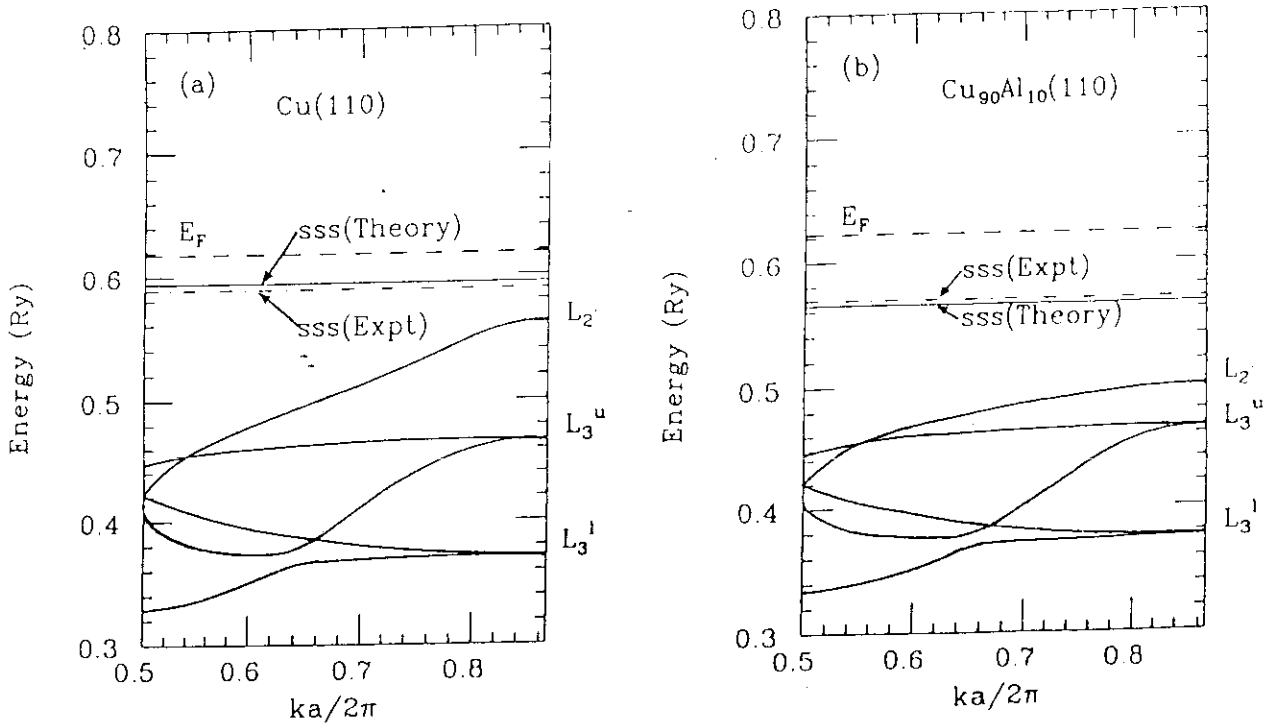
$$g = \mathcal{G}_{II} g' - \mathcal{G}_{II}' g$$

This gives

$$g' = \left[(1 - \mathcal{G}_I')(1 + \mathcal{G}_{II}')\mathcal{G}_{II} + \mathcal{G}_I\right]^{-1} g_I$$

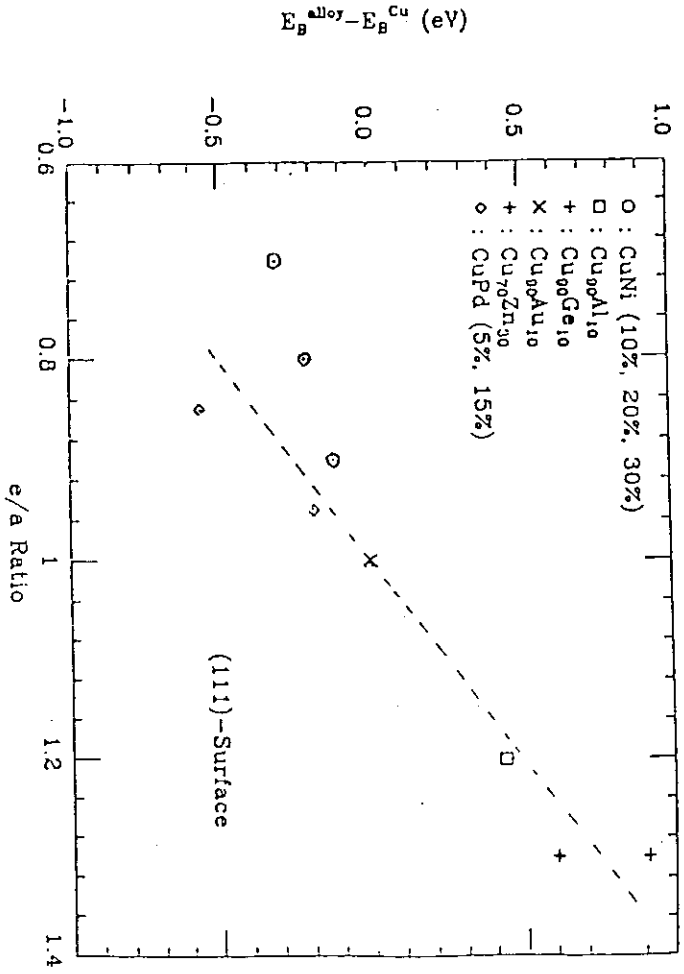
$$g = (1 + \mathcal{G}_I')^{-1} \mathcal{G}_{II}\, g'$$

Surface states in Cu(110) and $Cu_{.9}Al_{.1}$ (110)



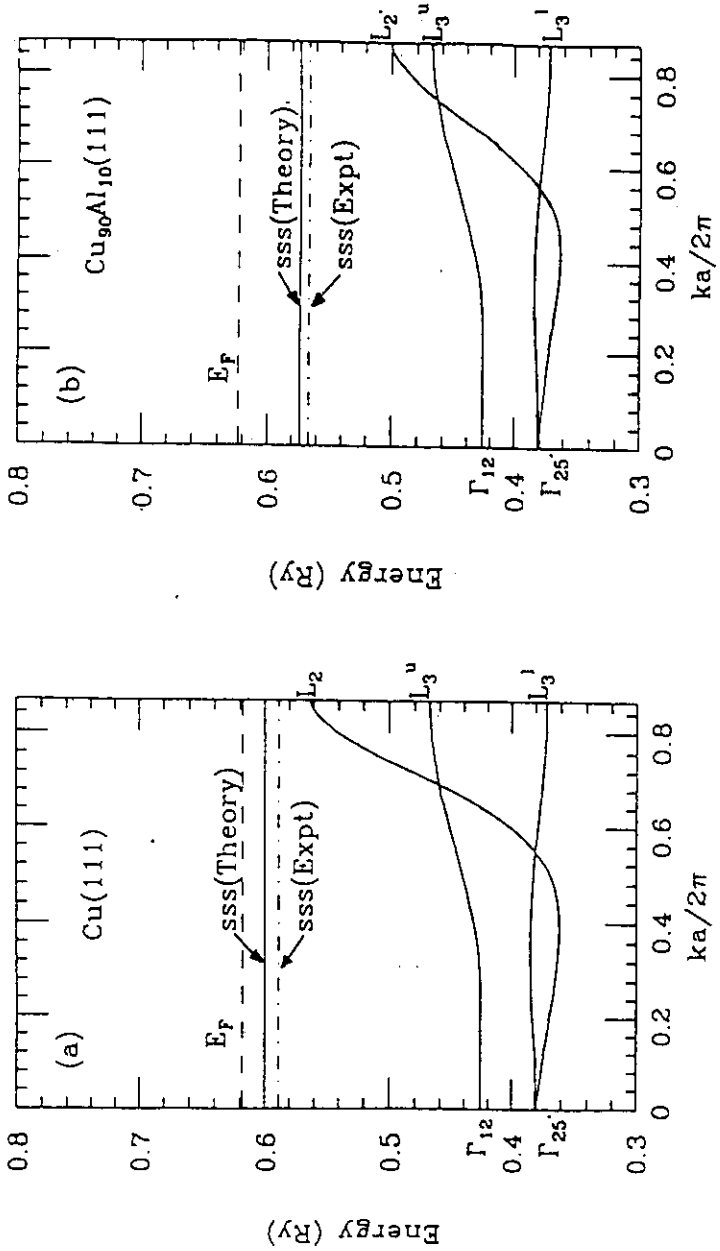
Figure(1)

Prasad, Serageldin and Bansil, J. Phys: Condensed Matter (91)



Change in binding energy $E_B^{alloy} - E_B^{Cu}$

($E_B = E_F - E_{ss}$)



Figure(2)

References

Bansil, Prasad, Gyorffy, Mookerjee — 'Band Theory and its Applications' edited by M. Yussouff (Springer-Verlag 1987).

2. Faulkner, Progress in Material Science ed. Massalski (Pergamon, 1982) Vol. 27.

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4. Raza, Rajput, Mookerjee & Prasad
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J. Phys. Cond. Matter 2, 2653 (1990)
" " 3, 3301 (1991)
Phys. Rev. B 45, 3265 (1992)