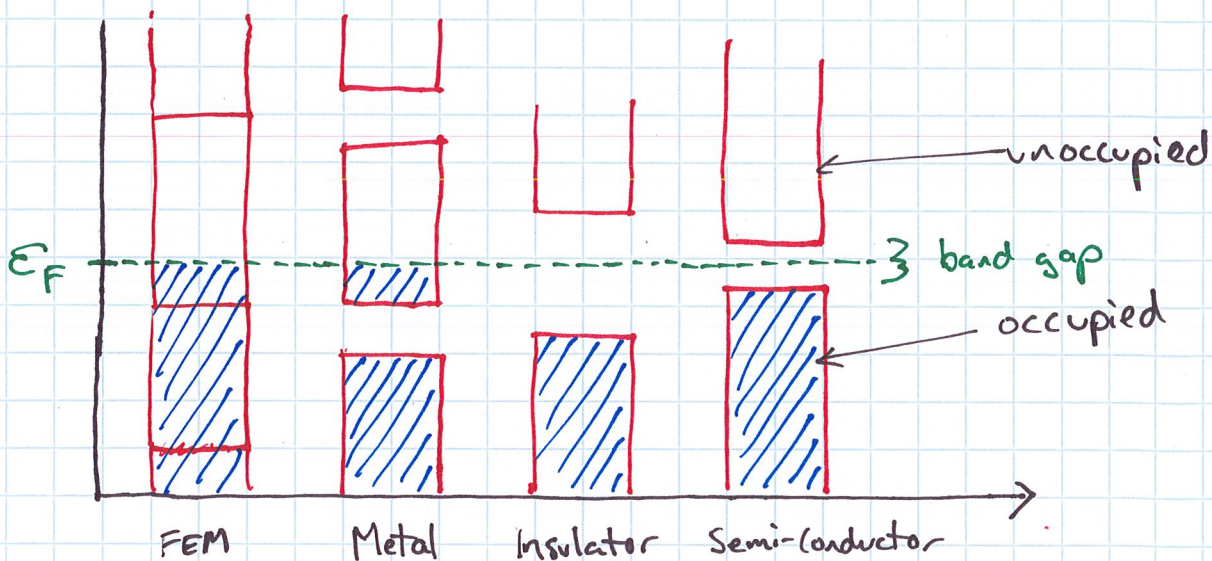## Band Gap

→ Free-e model predicts continuous dispersion curves or bands

→ periodic potential will lift the degeneracy @ some points

→ result is separated energy bands ⇒ band gap

→ fundamental properties of the material depend on the relation between the energy bands & the Fermi Energy:

Nearly Free Electron Model

For a periodic function $f(\bar{r}) = f(\bar{r} + \bar{R})$, $\bar{w}$ $\bar{R}$ defined as a Bravais Lattice vector, we can expand $f(\bar{r})$ as a Fourier series:

$$f(\bar{r}) = \sum_{\bar{K}} f(\bar{K}) e^{i\bar{K}\cdot\bar{r}}$$

$\bar{K}$ = recip. lattice vector

Fourier coefficient @ "frequency" $\bar{K}$

Bloch's Theorem:

For periodic potential: $V(\bar{r}) = V(\bar{r} + \bar{R})$

$\mathcal{H}$ eigenstates take form: $\psi(\bar{r}) = e^{i\bar{k}\cdot\bar{r}} u(\bar{r})$

where: $u(\bar{r}) = u(\bar{r} + \bar{R})$

$\therefore$ Can write in general:

$$V(\bar{r}) = \sum_{\bar{K}} V_{\bar{K}} e^{i\bar{K}\cdot\bar{r}}$$

By convention the notation is usually switched $\bar{K} \to \bar{G}$

$$u(\bar{r}) = \sum_{\bar{K}} u_{\bar{K}} e^{i\bar{K}\cdot\bar{r}}$$

$\bar{K}$ & $\bar{G}$ rep. the same thing: recip. lattice vector

where $V_{\bar{K}}$ & $u_{\bar{K}}$ are Fourier coefficients @ "frequency" $\bar{K}$.

What if our potential is weak?

if $V(\vec{r}) = 0 \implies$ Free particle

$V(\vec{r}) = V(\vec{r} + \vec{R}) \neq 0 \implies$ use perturbation theory!

$\rightarrow$ we can predict that the presence of weak, but periodic, potential will cause slight modifications to the free $\bar{e}$ states & energies.

Complete Hamiltonian: $\hat{\mathcal{H}} \Psi = \varepsilon \Psi$ $\hat{\mathcal{H}} = \dfrac{-\hbar^2}{2m} \vec{\nabla}^2 + V(\vec{r})$

Unperturbed Hamiltonian: $\hat{\mathcal{H}}^{(0)} \Psi^{(0)} = \varepsilon^{(0)} \Psi^{(0)}$

$\hspace{6cm} \searrow$ PT order index, not exp!

$$\hat{\mathcal{H}}^{(0)} = \dfrac{-\hbar^2}{2m} \nabla^2 \hspace{1cm} \rightarrow \text{Free } \bar{e}$$

$$\varepsilon^{(0)}(k) = \dfrac{\hbar^2 k^2}{2m} \hspace{0.5cm} = \hspace{0.3cm} \varepsilon_k^{(0)}$$

$$\Psi^{(0)}(\vec{k}) = \dfrac{1}{\sqrt{\Omega}} e^{i \vec{k} \cdot \vec{r}} = \Psi_{\vec{k}} \hspace{1cm} \rightarrow \text{plane wave soln's}$$

$\hspace{2.5cm} \searrow$ total crystal volume

Time-independent PT:

$$\varepsilon(\vec{k}) = \varepsilon^{(0)}(\vec{k}) + \varepsilon^{(1)}(\vec{k}) + \varepsilon^{(2)}(\vec{k}) + \cdots$$

Hot Notes on QM & notation

1. Eigenstates: $\psi_k^{(0)}(\bar{r}) = \psi^{(0)}(\bar{k}) = |\psi_k^{(0)}\rangle = |k\rangle$

   <u>All represent the same thing</u>

   $$\psi_k^{(0)}(\bar{r}) = \frac{1}{\sqrt{\Omega}} e^{i\bar{k}\cdot\bar{r}}$$

2. Eigenstates of Hermitian operators are orthogonal
   (as long as they are degenerate)

   $$\langle k | k' \rangle = \delta_{k,k'}$$

   Also: $\langle k | k' \rangle = \int_\Omega \psi_k^{(0)*} \psi_{k'}^{(0)} \, d^3r$

   $\longrightarrow$ integral over entire crystal.

   $$= \frac{1}{\Omega} \int_\Omega e^{-i(\bar{k}-\bar{k}')\cdot\bar{r}} \, d^3r \qquad = \delta_{k,k'}$$

3. Operators: e.g. $\hat{A}$

   $$\langle k | \hat{A} | k \rangle = \int_\Omega \psi_k^{(0)*} \hat{A} \psi_k^{(0)} \, d^3r$$

From PT, the first order energy correction is:

$$\varepsilon^{(1)}(k) = \langle k | V(\bar{r}) | k \rangle$$

$\hookrightarrow$ $V(\bar{r})$ is the perturbation to $\hat{\mathcal{H}}$

$$= \frac{1}{\Omega} \int_{\Omega} e^{-ik\cdot\bar{r}} V(\bar{r}) e^{ik\cdot\bar{r}} d^3\bar{r}$$

$$= \frac{1}{\Omega} \int_{\Omega} V(\bar{r}) d^3\bar{r} \quad = \quad V_0 \quad = \overline{V(\bar{r})}$$

$\rightarrow$ this is the avg. of $V(\bar{r})$ over the crystal....

Note: due to the periodicity of $V(\bar{r})$, the avg. of $V(\bar{r})$ over the entire crystal is equal to the avg. over a unit cell.

V_0 is independent of k & is a constant.

$\therefore$ First order correction: $\varepsilon^{(1)} = V_0$ $\rightarrow$ constant energy shift

NBD

Second order energy correction:

$$\varepsilon^{(2)}(k) = \sum_{k'} \frac{\left| \langle k' | V(\bar{r}) | k \rangle \right|^2}{\varepsilon_k^{(0)} - \varepsilon_{k'}^{(0)}}$$

What is $\langle k' | V(\bar{r}) | k \rangle$?

Recall: $V(\bar{r}) = \sum_{\bar{G}} V_{\bar{G}} \, e^{i\bar{G}\cdot\bar{r}}$

$\bar{G}$ = recip. lattice vector (same as $\bar{K}$)

$\therefore \langle k' | V(\bar{r}) | k \rangle = \langle k' | \sum_{\bar{G}} V_{\bar{G}} \, e^{i\bar{G}\cdot\bar{r}} | k \rangle$

$= \frac{1}{\Omega} \int_{\Omega} e^{-ik'\cdot\bar{r}} \left(\sum_{\bar{G}} V_{\bar{G}} \, e^{i\bar{G}\cdot\bar{r}} \right) e^{ik\cdot r} \, d^3\bar{r}$

$= \frac{1}{\Omega} \sum_{\bar{G}} V_{\bar{G}} \int_{\Omega} e^{-i(k'-k)\cdot\bar{r}} \, e^{i\bar{G}\cdot\bar{r}} \, d^3\bar{r}$

$= \sum_{\bar{G}} V_{\bar{G}} \underbrace{\langle k'-k | \bar{G} \rangle}_{= \delta_{k'-k, \bar{G}}}$

$\langle k' | V(\bar{r}) | k \rangle = V_{\bar{G}} \, \delta_{k'-k, \bar{G}}$ for any $\bar{G}$

if $k'-k = \bar{G}$; $\langle k' | V(\bar{r}) | k \rangle = V_{\bar{G}}$

else ; $\langle k' | V(\bar{r}) | k \rangle = 0$

Where have we seen this before?

$$\not{k}' - \not{k} = \bar{G}$$

$$\hookrightarrow \not{k}' - \not{k} = \bar{K} \quad \cdots\rightarrow \text{ oh my! Diffraction !!?!}$$

$$\underbrace{\phantom{\not{k}' - \not{k} = \bar{K}}}$$

Von Laue condition for diffraction

And where does this occur? Brillouin zone boundaries!

$\Rightarrow$ Back to $\mathcal{E}^{(2)}$

$$\mathcal{E}^{(2)}(\not{k}) = \sum_{\bar{G}} \frac{|V_{\bar{G}}|^2}{\mathcal{E}^{(0)}_{\not{k}} - \mathcal{E}^{(0)}_{\not{k}'}} = \frac{2m}{\hbar^2} \sum_{\bar{G}} \frac{|V_{\bar{G}}|^2}{k^2 - (\bar{G}+\not{k})^2}$$

Problem: blows up when $\mathcal{E}^{(0)}_{\not{k}} = \mathcal{E}^{(0)}_{\not{k}+\bar{G}}$ $\Rightarrow$ degenerate

$$\rightarrow |\not{k}|^2 = |\bar{G}+\not{k}|^2 \Rightarrow \text{B.Z. boundary}$$

$\rightarrow$ At B.Z. boundaries, energy states are degenerate $\Rightarrow$ need degerate P.T.

Degenerate Perturbation Theory

For N degenerate states $\psi_i^{(0)}$ in energy $\mathcal{E}^{(0)}$
(or near)

define N new wavefunctions as L.C. of $\psi_i^{(0)}$

$$\psi_n^{(0)} = \sum_i^N \alpha_i \psi_i^{(0)}$$

First order correction:

$$\mathcal{E} \, \alpha_j = \sum_i \langle \psi_j^{(0)} | \hat{\mathcal{H}} | \psi_i^{(0)} \rangle \alpha_i$$

$$\hookrightarrow \hat{\mathcal{H}} = \hat{\mathcal{H}}^{(0)} + V(\vec{r})$$

Diagonal elements: $\mathcal{E}_i^{(0)} + \mathcal{E}_i^{(1)} - \mathcal{E}$

Off-diagonal: $\langle \psi_j^{(0)} | V(\vec{r}) | \psi_i^{(0)} \rangle$

Recall: 1) $\mathcal{E}_i^{(1)} = \mathcal{E}^{(1)} = V_0 \implies$ constant.

2) $\langle \psi_j^{(0)} | V(\vec{r}) | \psi_i^{(0)} \rangle = \langle \vec{k} | V(\vec{r}) | \vec{k}' \rangle = V_{\vec{G}}$

$$(\vec{k}' = \vec{k} + \vec{G})$$

Form: $\hat{M} \alpha = \mathcal{E} \alpha$

Solve: $|\hat{M} - \mathcal{E}| = 0$ to get eigenvalues (energies)

e.g. 2 - state degeneracy $\Rightarrow$ k & $k' = k + \bar{G}$

$$\begin{vmatrix} \mathcal{E}_k^{(0)} + V_0 - \mathcal{E} & V_{\bar{G}} \\ V_{\bar{G}}^* & \mathcal{E}_{k'}^{(0)} + V_0 - \mathcal{E} \end{vmatrix} = 0$$

$$\mathcal{E} = V_0 + \frac{1}{2}\left(\mathcal{E}_k^{(0)} + \mathcal{E}_{k'}^{(0)}\right) \pm \sqrt{\frac{1}{4}\left(\mathcal{E}_k^{(0)} - \mathcal{E}_{k'}^{(0)}\right)^2 + |V_{\bar{G}}|^2}$$

I: $|V_{\bar{G}}| \ll \frac{1}{2}\left(\mathcal{E}_k^{(0)} - \mathcal{E}_{k'}^{(0)}\right)$

$\hookrightarrow$ Reverts to non-degen. case.

II: $|V_G| \gg \frac{1}{2}\left(\mathcal{E}_k^{(0)} - \mathcal{E}_{k'}^{(0)}\right)$

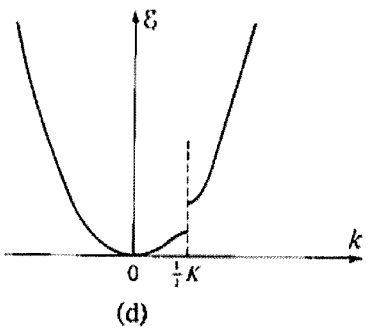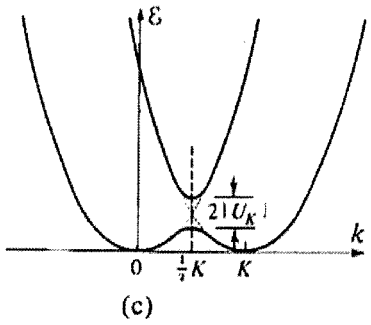$$\boxed{\mathcal{E}^{\pm} = V_0 + \frac{1}{2}\left(\mathcal{E}_k^{(0)} + \mathcal{E}_{k'}^{(0)}\right) \pm |V_{\bar{G}}|}$$

At B.Z. boundary, energy band split by:

$$\mathcal{E}^+ - \mathcal{E}^- = 2|V_{\bar{G}}|$$

$\Downarrow$ Band gap

$$-\pi/a \qquad 0 \qquad \pi/a$$

$$2|V_{\bar{G}}|$$

(a)

(b)

(c)

(e)

(f)

(d)

(g)

Energy (eV)

$L_{4,5}$ L_6 Γ_8 Γ_7 L_6 Γ_6 Γ_8 GaAs Γ_8 Γ_7 X_7 X_6 Γ_5 Γ_8 $L_{4,5}$ L_6 Γ_7 X_7 X_6 Γ_7 L_6 X_6 (a) L_6 X_6 Γ_6 Γ_6

L   Λ   Γ   Δ   X   K   Σ   Γ

Wavevector **k**

(eV)

W   L   G   X   W   K

Si(diamond,LDA) a=10.25a.u.
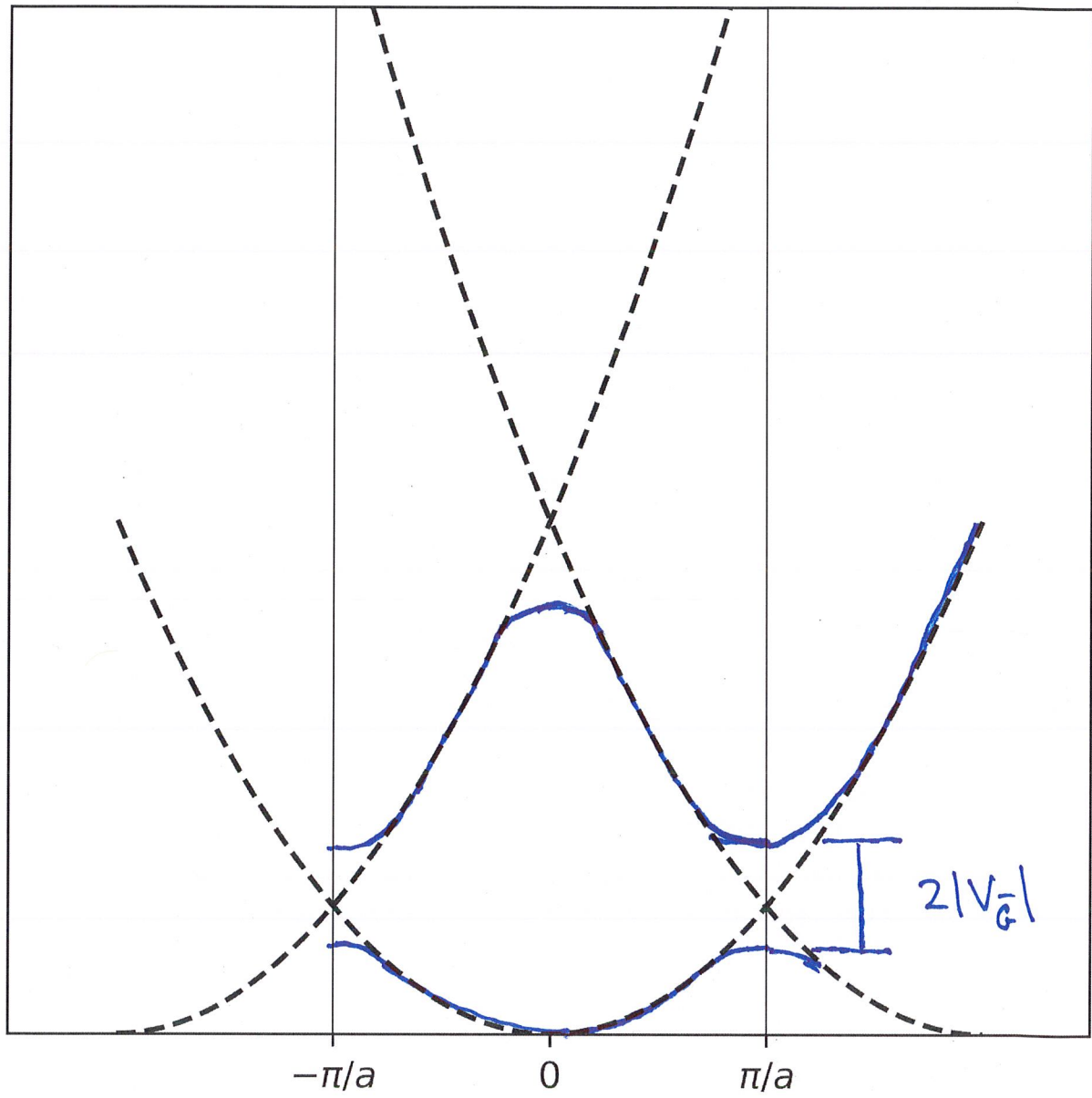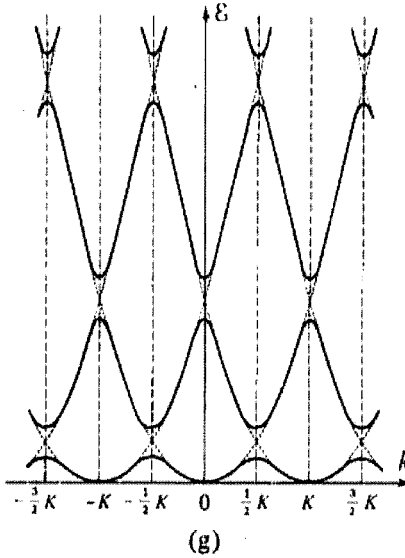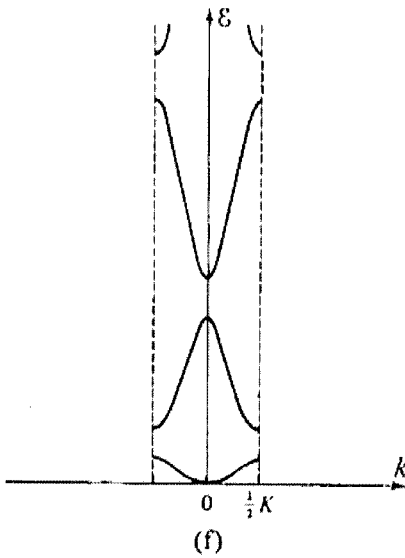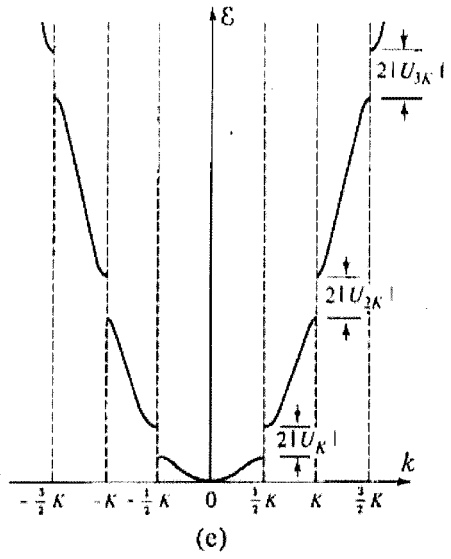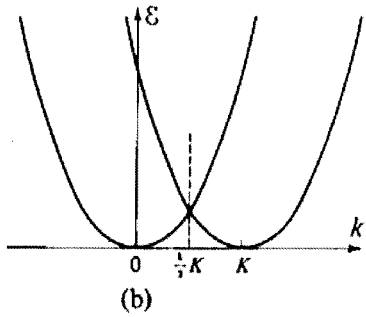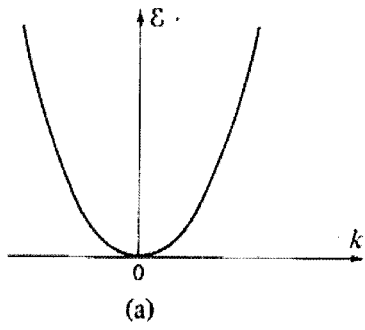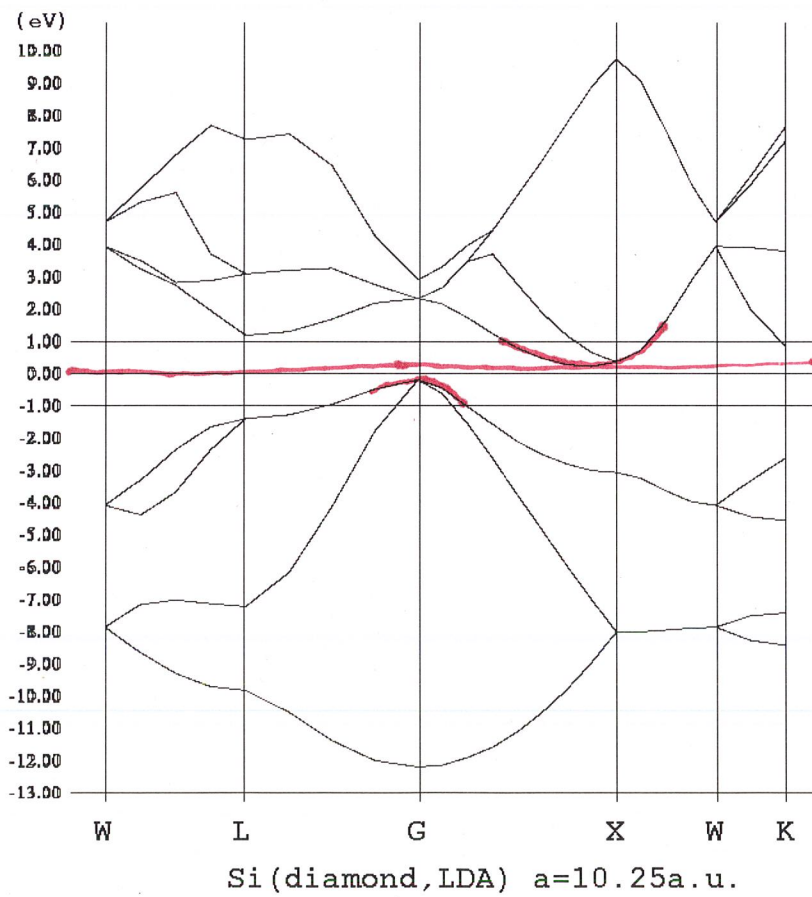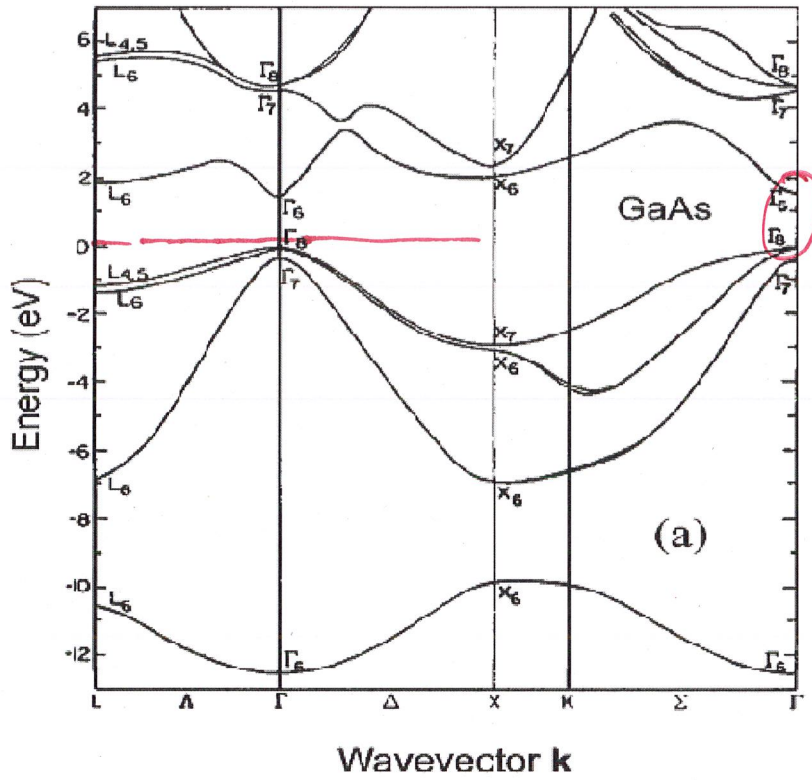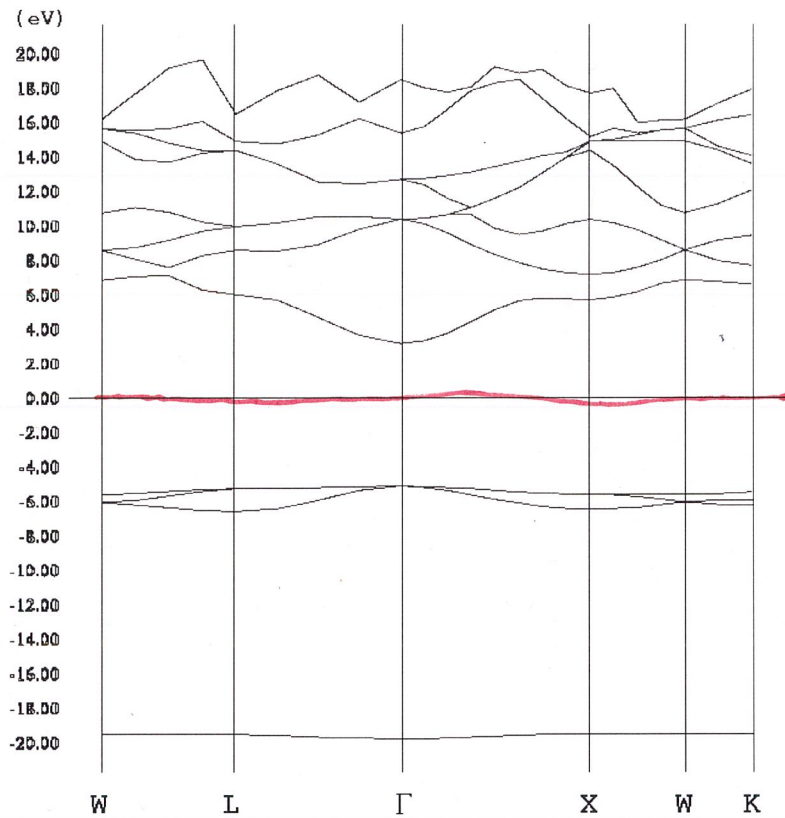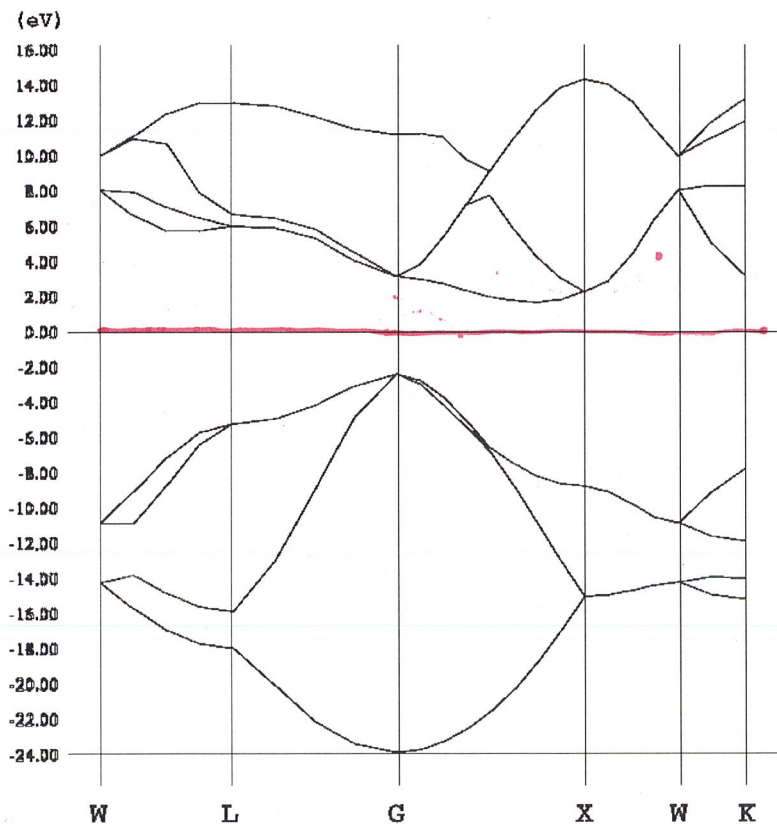
Ar(fcc,pcc) a = 9.9 a.u.

C(diamond) a=6.72a.u.

Cu(fcc) a=6.76a.u.

Au(fcc) a=8.2a.u

Na(bcc,pcc)

Ca(fcc, pcc, 100Ry) a = 10.0 a.u.