3.320: Lecture 20 (Apr 21 2005)

MODEL HAMILTONIANS

from alchemy to tight-binding

Images removed for copyright reasons.
Cover of "Harry Potter and the Philosopher's Stone."
Diagram of different types of knots.

New jobs for the 21st century

- The virtual alchemist (linear-response theory)
- The nanotechnologist (tight-binding mappings)

Outline

- Realistic descriptions of large-scale nanostructures from first-principles

- Mapping electronic structure-calculations into model Hamiltonians
  - Ising-like models for alloys
  - Tight-binding orbitals for functionalized nanotubes (electronic-structure LEGO bricks)

Why semiconductor alloys ?

- Technological interest: tunability of materials properties. Strained layer epitaxy (Prof Fitzgerald)

Array of vertical cavity lasers

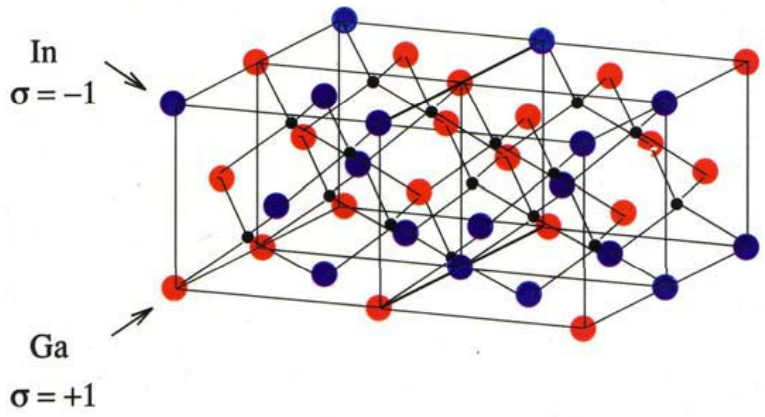
- Scientific interest: spontaneous multilayer ordering

Superspot reflections

Band-gap/lattice parameter

Configurational Statistical Mechanics

- Energy of a configuration ?



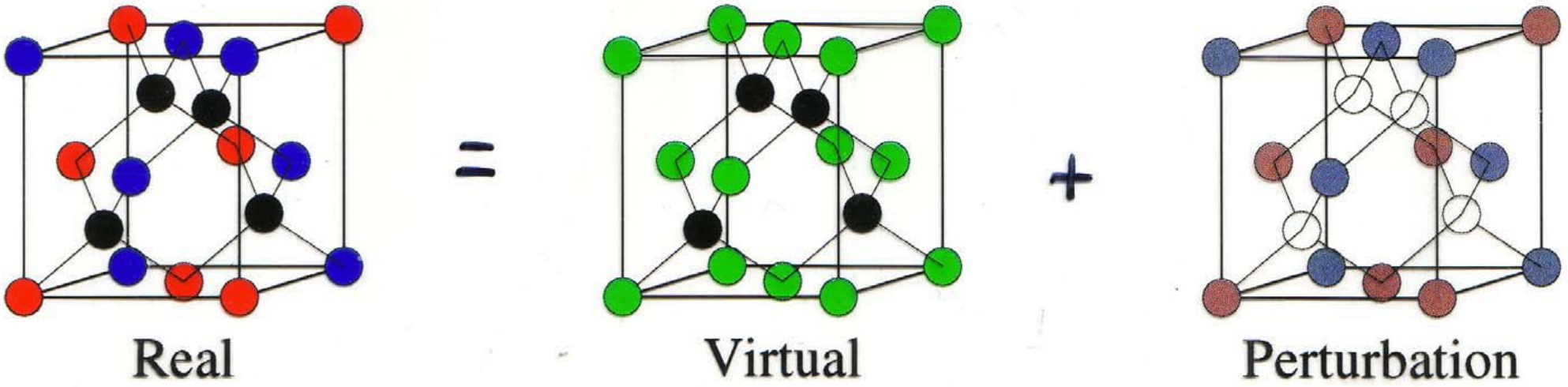
Linear-response

- Thermodynamic properties ?

$$P[\sigma] = \frac{e^{-\beta E[\sigma]}}{Z}$$

Monte Carlo

Disorder as a perturbation



Disorder as a perturbation

Configurational variables

$$\{\sigma_{\mathbf{R}}\} = \begin{cases} +1 & \text{if Ga in } \mathbf{R} \\ -1 & \text{if In in } \mathbf{R} \end{cases}$$

External potential

$$V_{ext}(\mathbf{r}) = \underbrace{\sum \left(\frac{1}{2}(v_{Ga} + v_{In})(\mathbf{r} - \mathbf{R}) \right)}_{V_0(\mathbf{r})} + \underbrace{\sum \sigma_{\mathbf{R}} \left(\frac{1}{2}(v_{Ga} - v_{In})(\mathbf{r} - \mathbf{R}) \right)}_{\Delta V(\mathbf{r}) \equiv \sum \sigma_{\mathbf{R}} \Delta v(\mathbf{r} - \mathbf{R})}$$

Perturbation (external potential):

$$V_0 \Rightarrow V_0 + \lambda \Delta V$$

Response (charge density):

$$n_0 \Rightarrow n_\lambda = n_0 + \lambda n_1 + \ldots$$

Hellmann-Feynman Theorem:

$$\frac{\partial E}{\partial \lambda} = \int n_\lambda(\mathbf{r}) \frac{\partial V(\mathbf{r})}{\partial \lambda} d\mathbf{r}$$

Total Energy:

$$E_\lambda = E_0 + \lambda \underbrace{\int n_0(\mathbf{r}) \Delta V(\mathbf{r}) d\mathbf{r}}_{1^{\text{st}}\text{order}} + \frac{\lambda^2}{2} \underbrace{\int n_1(\mathbf{r}) \Delta V(\mathbf{r}) d\mathbf{r}}_{2^{\text{nd}}\text{order}} + \ldots$$

$$\Delta V_{\text{ext}}$$

$$\Downarrow$$

$$\Delta V_{SCF}(\mathbf{r}) = \Delta V_{\text{ext}}(\mathbf{r}) + e^2 \int \frac{\Delta n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\, \mathrm{d}\mathbf{r}' + \Delta n(\mathbf{r})\, \mu'_{XC}(n(\mathbf{r}))$$

$$\Downarrow$$

$$[-\nabla^2 + V_{SCF}(\mathbf{r}) \ - \epsilon_v]\Delta\psi_v(\mathbf{r}) = [\Delta V_{SCF}(\mathbf{r}) - \langle\psi_v|\Delta V_{SCF}|\psi_v\rangle]\psi_v(\mathbf{r})$$

$$\Downarrow$$

$$\Delta n(\mathbf{r}) = 2\sum \psi_v^*(\mathbf{r})\, \Delta\psi_v(\mathbf{r})\, \theta(\epsilon_F - \epsilon_v)$$

Perturbation (external potential):

$$V_0 \Rightarrow V_0(\mathbf{r}) + \sum \sigma_{\mathbf{R}} \Delta v(\mathbf{r} - \mathbf{R})$$

Total energy:

$$E(\{\sigma_{\mathbf{R}}\}) = E_0 + K \sum_{\mathbf{R}} \sigma_{\mathbf{R}} + \frac{1}{2} \sum_{\mathbf{R},\mathbf{R}'} \sigma_{\mathbf{R}} J(\mathbf{R}-\mathbf{R}') \sigma_{\mathbf{R}'}$$

The interaction constants are determined from the ground-state density n_0 and the linear response n_1:

$$K = \int \Delta v(\mathbf{r}) n_0(\mathbf{r}) d\mathbf{r}$$

$$J(\mathbf{R} - \mathbf{R}') = \int \Delta v(\mathbf{r} - \mathbf{R}) n_1(\mathbf{r} - \mathbf{R}') d\mathbf{r}$$

Expansion in the substitutions *and* the displacements:

$$E = E_0 + K\sum \sigma_{\mathbf{R}} + \frac{1}{2}\sum \sigma_{\mathbf{R}} J \sigma_{\mathbf{R}'} + \\ + \frac{1}{2}\sum \mathbf{u}_{\mathbf{R}} \cdot \mathbf{\Phi} \cdot \mathbf{u}_{\mathbf{R}'} - \sum \mathbf{u}_{\mathbf{R}} \cdot \mathbf{F} \sigma_{\mathbf{R}'}$$

At equilibrium the forces must vanish:

$$-\frac{\partial E}{\partial \mathbf{u}_{\mathbf{R}}} = 0 \quad \Rightarrow \quad \mathbf{u}_{\mathbf{R}} = \mathbf{\Phi}^{-1} \cdot F \sigma_{\mathbf{R}}$$

The Hamiltonian is rewritten as :

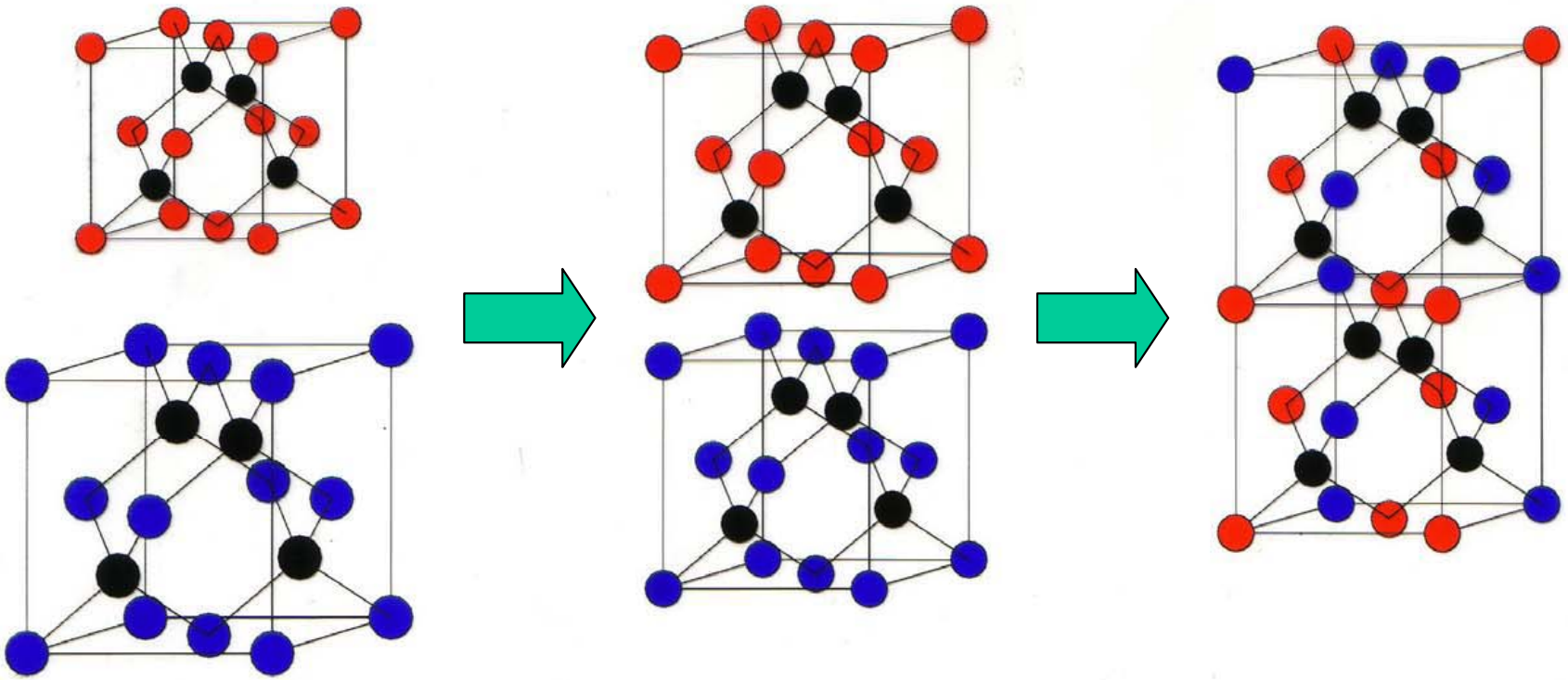
$$E^{relax}[\{\sigma_{\mathbf{R}}\}] = E_0 + K\sum \sigma_{\mathbf{R}} + \frac{1}{2}\sum \sigma_{\mathbf{R}} \widehat{J}(\mathbf{R}-\mathbf{R}') \sigma_{\mathbf{R}'}$$

with renormalized $\widehat{J} = J - \mathbf{F} \cdot \mathbf{\Phi}^{-1} \cdot \mathbf{F}$

Formation Energies

Elastic Step

Configurational Step



Formation Energies

The energy of the alloy at its equilibrium volume is compared to the energy of the same quantity of bulk materials at their equilibrium volumes :

$$E(\{\sigma_{\mathbf{R}}\},\Omega_{eq}) - xE_{GaP}(\Omega_{GaP}) - (1-x)E_{InP}(\Omega_{InP})$$

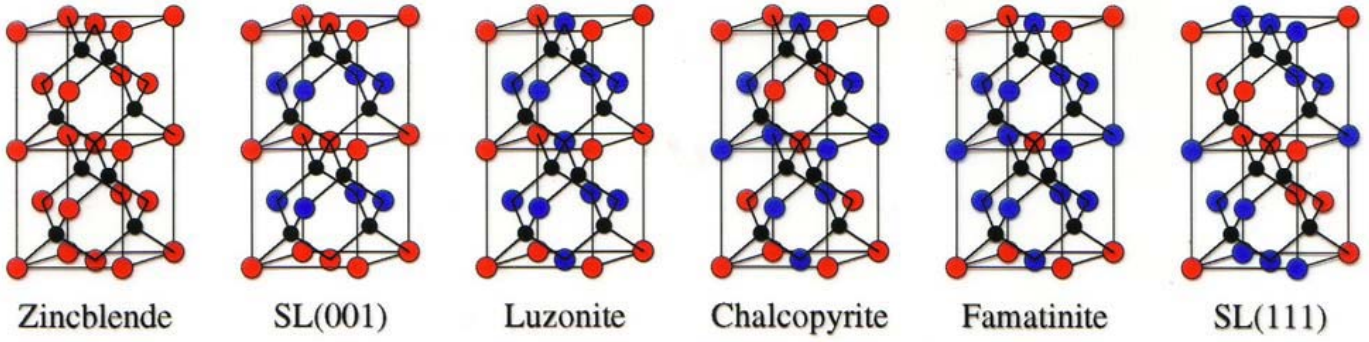
It is decomposed in an **elastic term** (equation of state) and a **configurational** one (linear response at fixed volume)

$$\Delta E_{elast}(x,\Omega_{eq}) + \Delta E_{config}(\{\sigma_{\mathbf{R}}\},\Omega_{eq})$$

Full DFT vs. linear response

Equilibrium lattice parameters a_0 are in atomic units and the chemical formation energies ΔE_{config} are in meV/atom

Structures		Relaxed atoms SCF a_0	SCF ΔE	LRT a_0	LRT ΔE
SL[001]$_{1+1}$	$Ga_2In_2P_4$	10.603	-39.3	10.606	-38.3
Luzonite	Ga_3InP_4	10.420	-31.8	10.421	-33.7
Luzonite	$GaIn_3P_4$	10.783	-27.4	10.788	-24.3
Chalcopyrite	$Ga_2In_2P_4$	10.598	-51.6	10.599	-49.7
Famatinite	Ga_3InP_4	10.420	-38.2	10.418	-39.9
Famatinite	$GaIn_3P_4$	10.781	-33.0	10.785	-29.4
SL[111]$_{1+1}$	$Ga_2In_2P_4$	10.616	-29.1	10.613	-28.4
Random	$Ga_nIn_nP_{2n}$			10.602	-41.6



Compressible Ising model, with long-range interactions on a FCC lattice

Supercell of 1024 atoms, at fixed P, T and difference in chemical potentials $\Delta\mu$.

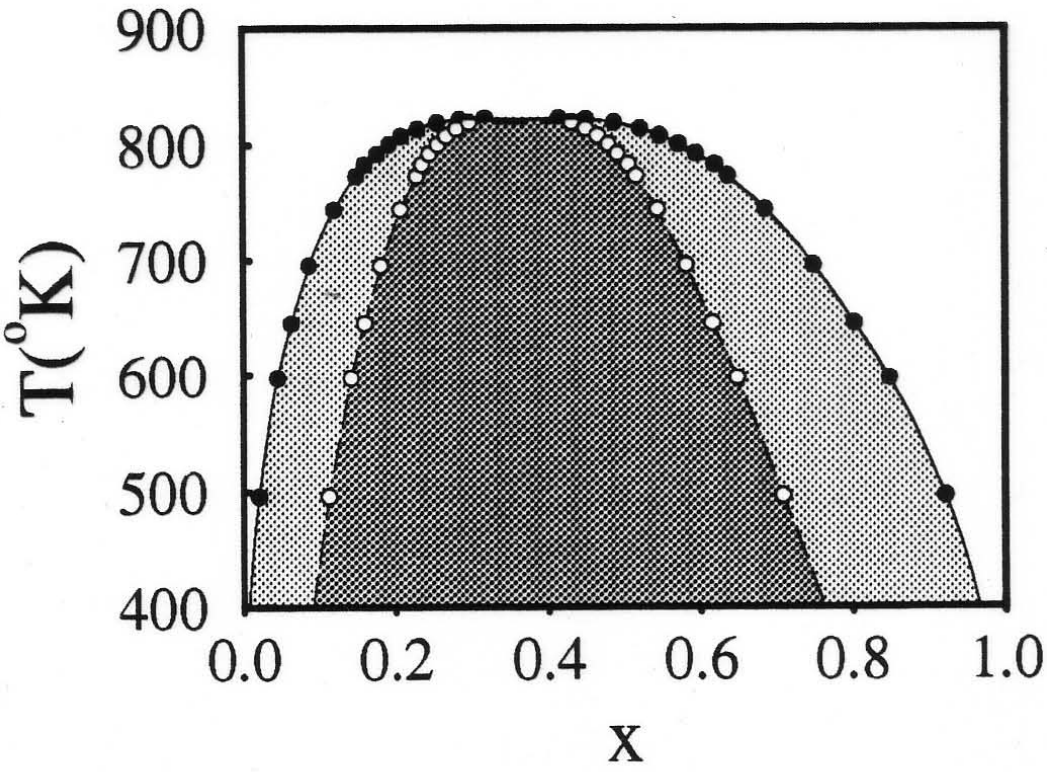
$$\sigma_{\mathbf{R}} \Rightarrow -\sigma_{\mathbf{R}} \quad \text{and} \quad V \Rightarrow V + \Delta V$$

Thermodynamic Integration

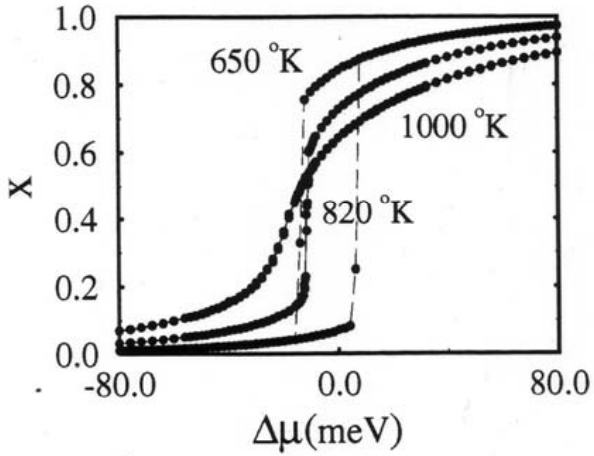
$$G(B) - G(A) = \int_A^B \left(\frac{\partial G}{\partial N}\right)_{T,P} dN = \int_{x_A}^{x_B} \langle \Delta\mu(x) \rangle dx$$

Phase Diagram from Thermodynamic Integration

Phase diagram

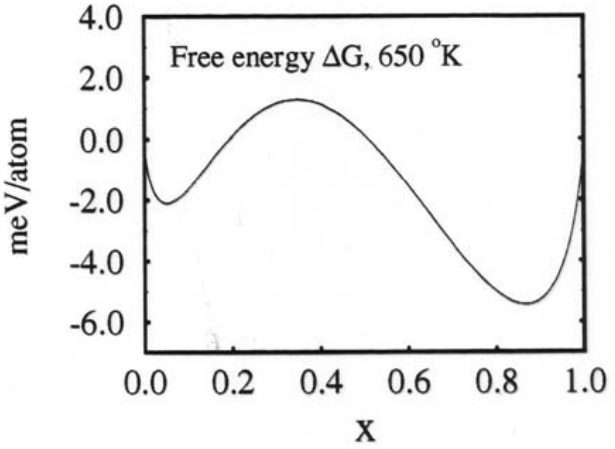


Monte Carlo simulations :
$\langle x \rangle = \langle x \rangle(\Delta\mu)$



$\Downarrow$

$G(x) = \int \Delta\mu(\xi) d\xi$:
common tangent



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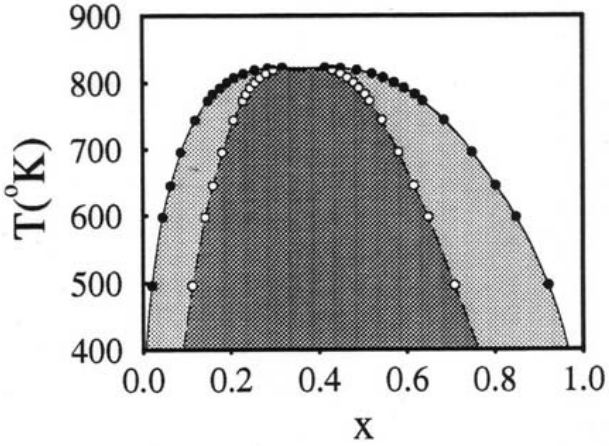
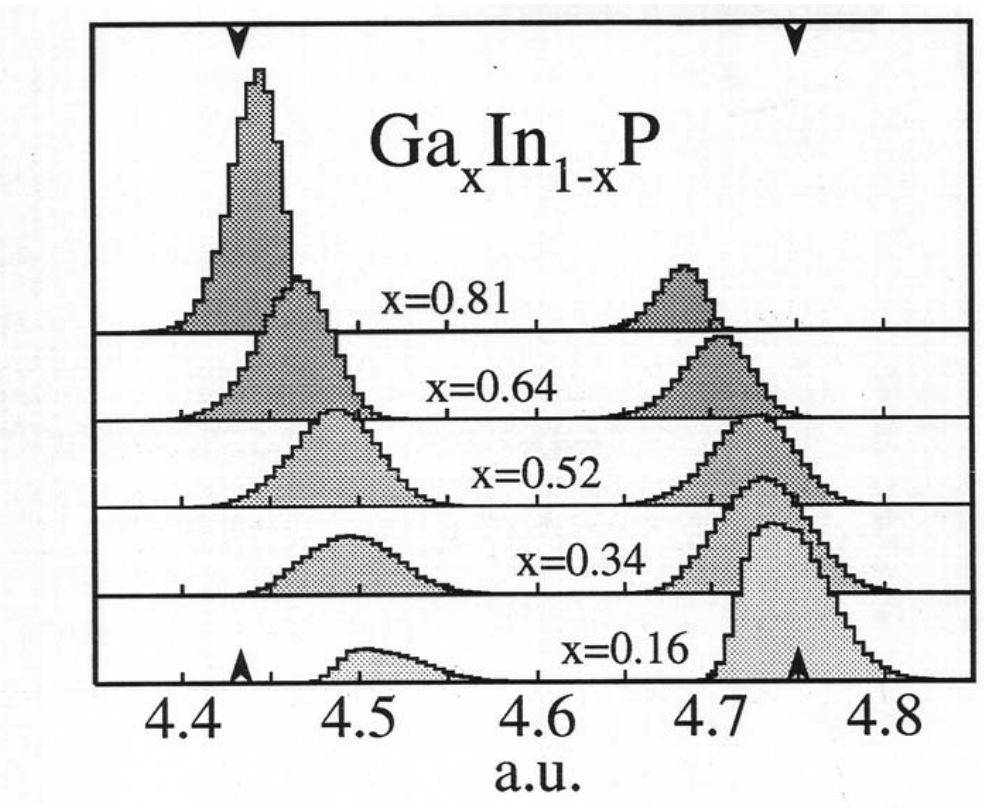
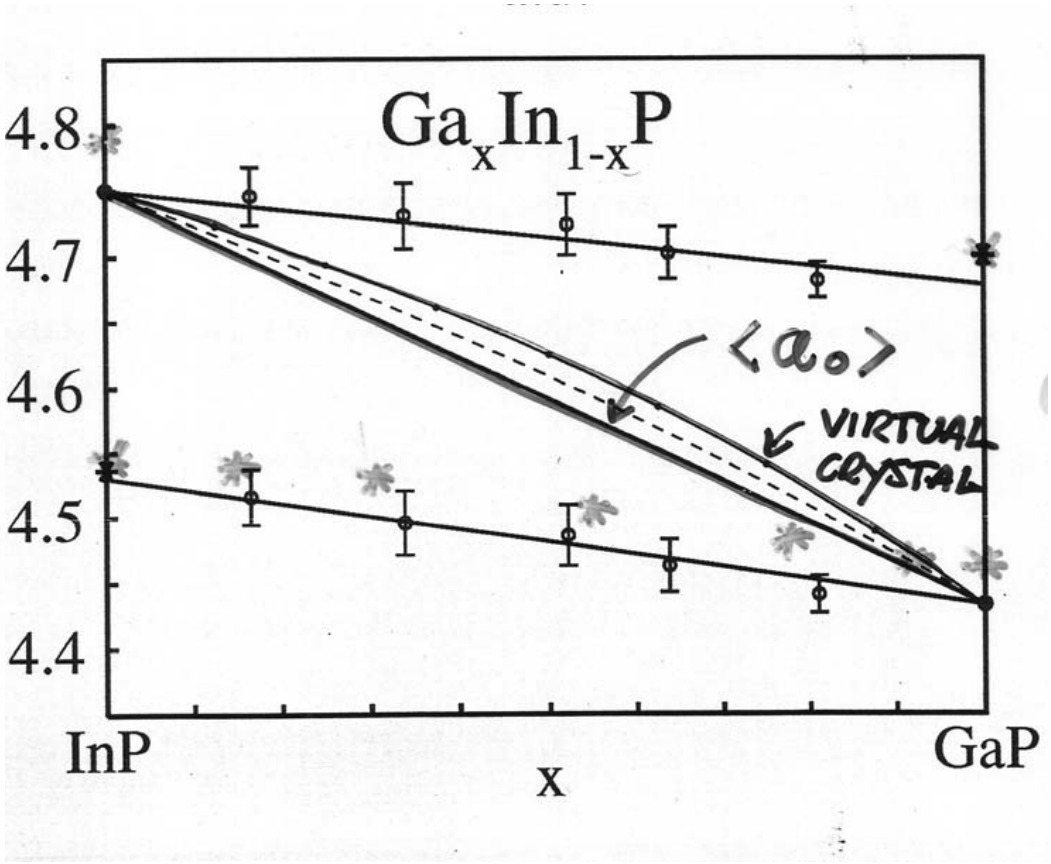
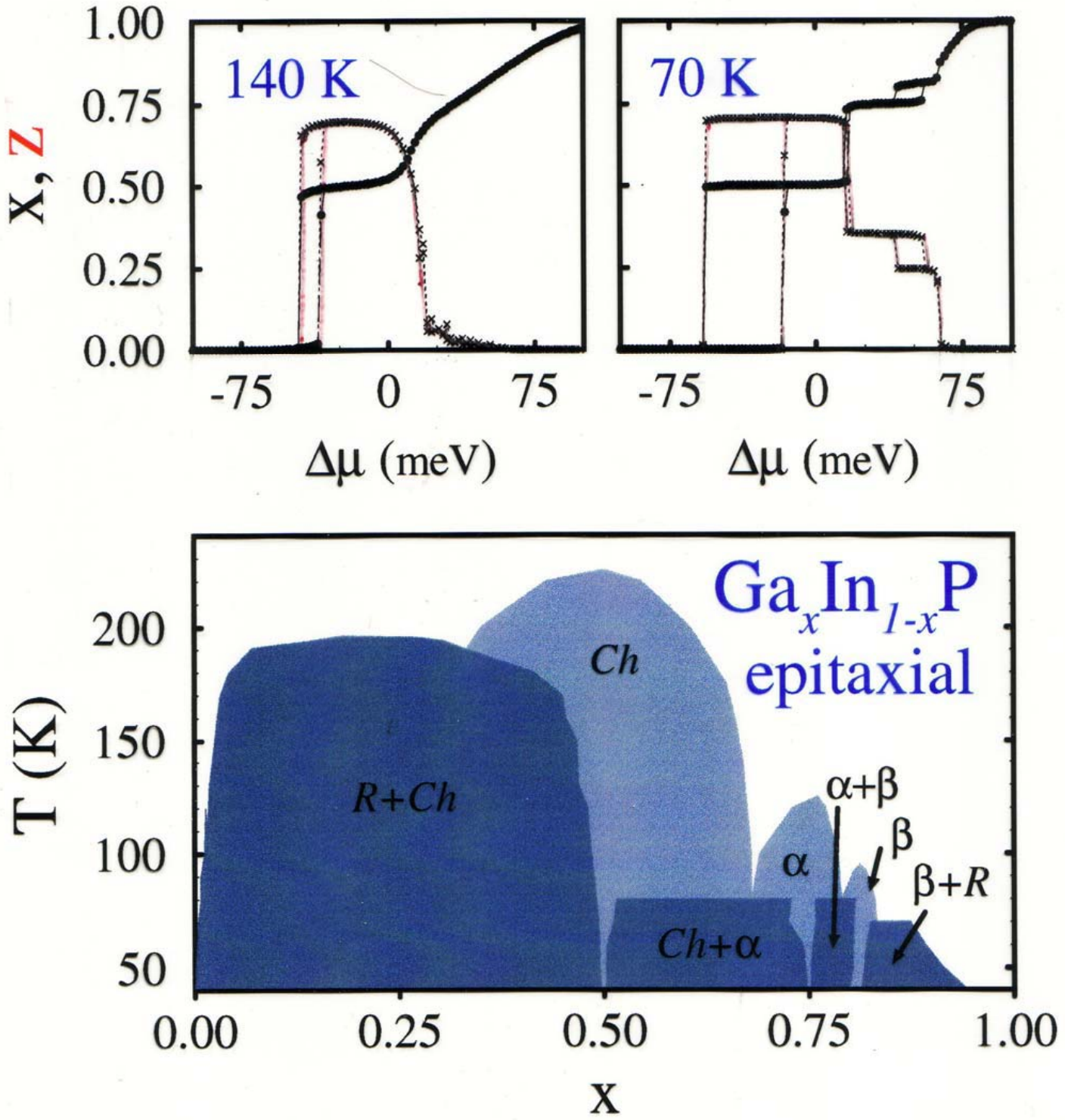
Phase diagram



Computational EXAFS






1.00
0.75
0.50
0.25
0.00
X, Z
140 K
70 K
-75
0
75
Δμ (meV)
Ga$_x$In$_{1-x}$P
epitaxial
Ch
R+Ch
α+β
β
α
β+R
Ch+α
200
150
100
50
T (K)
0.00
0.25
0.50
0.75
1.00
x