A FIRST-PRINCIPLES APPROACH TO DESIGNING THERMODYNAMIC PROPERTIES OF MATERIALS

Alain Pasturel

CNRS-INPG (Grenoble)

E-mail: alain.pasturel@inpg.fr

Coauthor: Noel Jakse

Acknowledgements

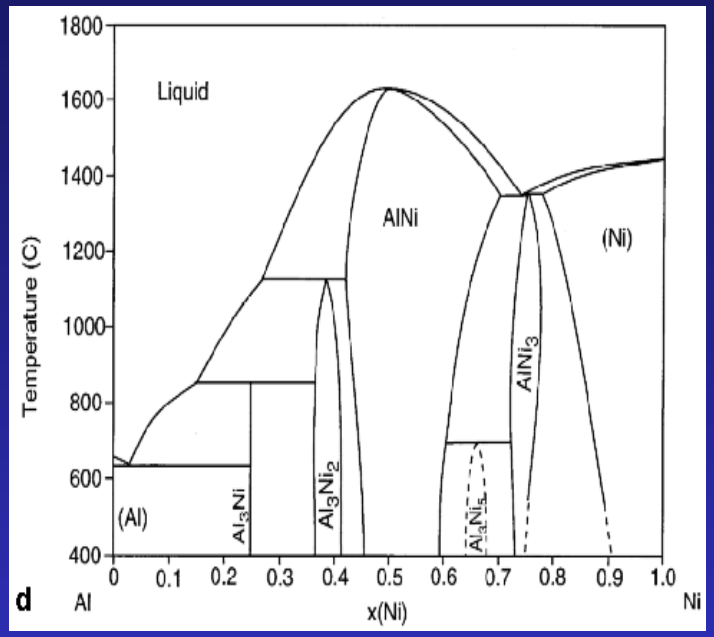
- P. Barberis, C. Berne, C. Colinet, N. Dupin, S. Fries, J. Hafner, G. Kresse, C. Lemaignan, A. Pisch, R. Podloucky, G. Robert, B. Siberchicot, M. Sluiter, B. Sundman, J.F. Wax, W. Wolf

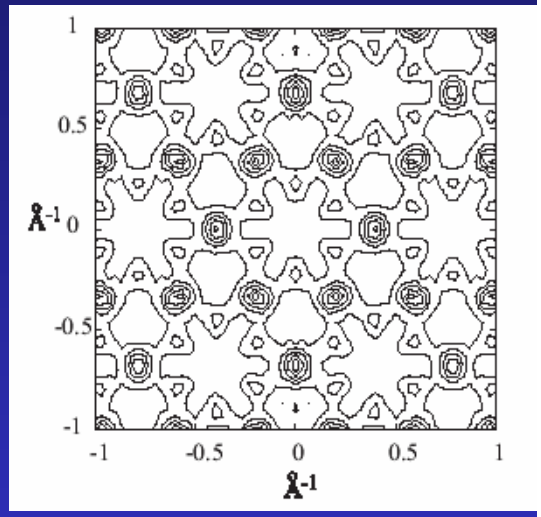
- Computational Resources: IDRIS, CINES and PHYNUM-CIMENT

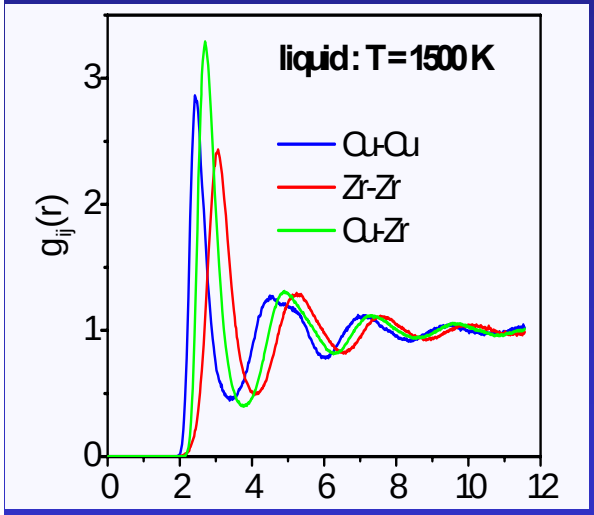
- CNRS, INPG and UJF

WHAT can first-principles thermodynamic calculations do for you?

Composition-temperature phase diagrams







Liquid Structures

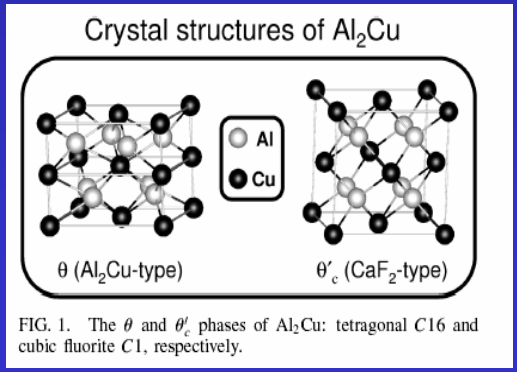


FIG. 1. The θ and θ'_c phases of Al_2Cu: tetragonal $C16$ and cubic fluorite $C1$, respectively.

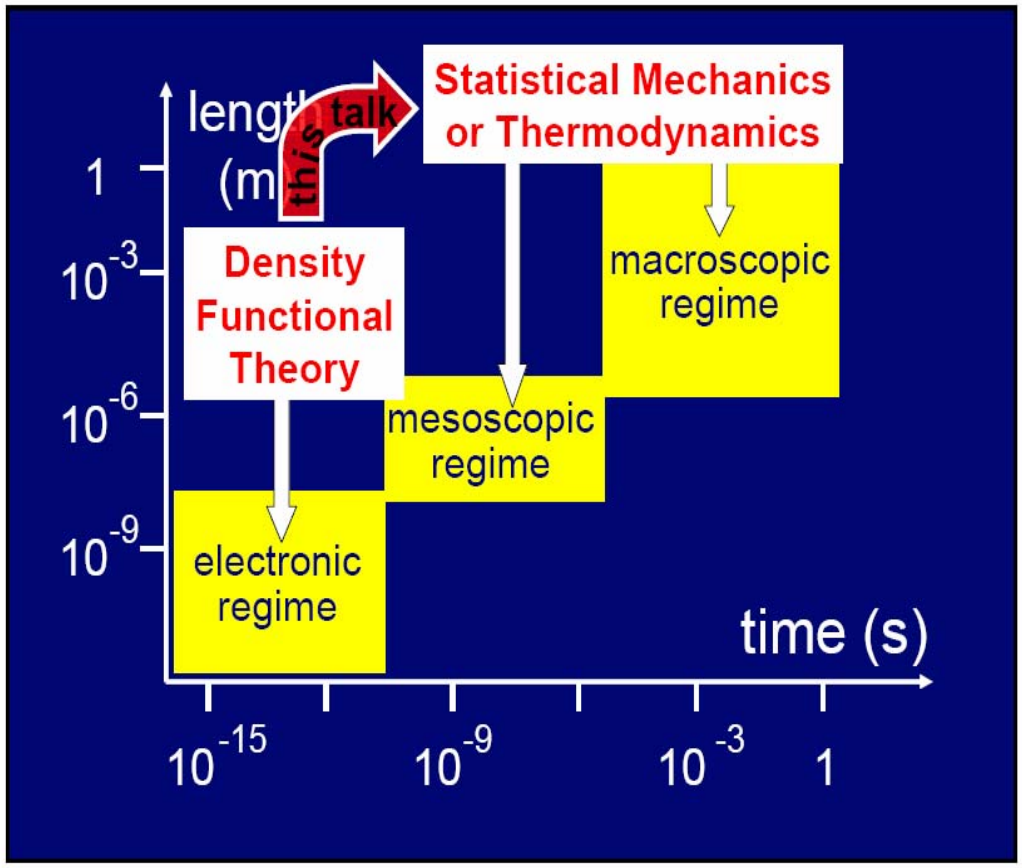
Short-range order in solid solutions

Thermodynamics of stable and metastable solid phases,

HOW can it be done?

Main Objective:

Thermodynamic models, whose forms are constrained by theoretical considerations and whose parameters are physically reasonable, are more reliably extrapolated than arbitray polynamonials fit to data in a small P, T, composition range.



Multi-scale integrated Method

Plan

1. *Ab Initio* Calculations: a Brief Overview

A. Atomistic Simulations: Terminology
B. Density functional theory (DFT).
C. Predicting Structures: The Energy scales

2. Ab initio Thermodynamics:

A. Solid Part:
   Ordering-Disordering Phenomena (Ising Models and CE)
   Lattice dynamics (Quasiharmonic)
B. Liquid Part:
   Molecular Dynamics
   Local Order

3. From Ab initio to CALPHAD:

A. Data bases
B. Functionals and Models

Part I
Ab Initio Calculations: a Brief Overview

A. Simulation Methods: Terminology

Classical – described by classical (Newtonian) mechanics.

Quantum – described by the Schrödinger equation (or its analogues).

Quantum electronic effects – exchange-correlation, antisymmetry of the wavefunction, Heisenberg uncertainty principle, electronic kinetic energy. ALWAYS IMPORTANT!

Atomistic methods – electrons are not considered. Instead, INTERATOMIC interactions, parameterised by some functions, are used.

Semiempirical methods – simplified quantum-mechanical treatments (some effects neglected, some approximated).

Hartree-Fock – exact exchange, neglect of correlation.

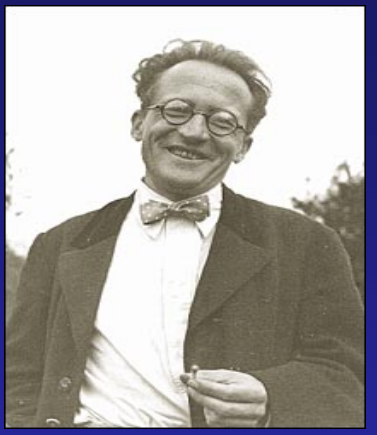
Density functional theory – in principle exact, in practice approximate for both exchange and correlation.

Quantum Monte Carlo – nearly exact method with a stochastic procedure for finding the many-body wavefunction.

B. Density Functional Theory

Energy from quantum mechanics?

SOLVING the Schrödinger Equation



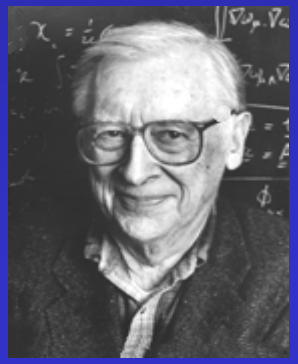
$$H\psi = E\psi$$

Born-Hoppenheimer approximation:

$$[-1/2\nabla^2 + v_{e\text{-}n} + v_{e\text{-}e}]\psi_{el} = E\psi_{el}$$

Further approximations! One-electron theories!

Wave functions or Density Functional



1998 Nobel Prize Winners

John Pople Walter Kohn

Density Functional Theory (DFT)

Hohenberg & Kohn (1964):

Electron density $\rho(\mathbf{r}) = |\psi|^2(\mathbf{r})$ UNIQUELY determines the energy and ALL ground-state properties.

Don't need the wavefunction at all !!!!!

There exists a universal functional $E[\rho]$.

$$E = E_{\text{kin}} + E_{\text{e-n}} + \tfrac{1}{2}\int \rho(\mathbf{r})\,d\mathbf{r} \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\,d\mathbf{r}' + E_{\text{xc}}$$

BUT: The functional is unknown:

Non-trivial: E_{kin} and E_{xc}.

Density Functional Theory (DFT)

Kohn & Sham Method (1965)

Introduce one-electron ϕ_i orbitals to get E_{kin}

$$E_{kin} = -1/2\Sigma< \phi_i|\nabla^2|\phi_i> \qquad (1)$$

Errors of (1) put in the exchange-correlation energy.

The theory is *in principle* exact. ***BUT*** $E_{xc}[\rho]$ is unknown and must be approximated.

The band structure given by this method does not have a strict physical meaning.

Approximations

The MOST USED approximations: LDA and GGA:

LDA: E_{xc} from $\rho(\mathbf{r})$ while GGA: E_{xc} from $\rho(\mathbf{r})$ & $\nabla\rho(\mathbf{r})$.

For metallic systems GGA is overall better than LDA for cohesive properties (lattice parameters, cohesive energies, elastic constants : (**see Fe with Chu-Chun Fu**).

But Neither LDA nor GGA are perfect :

DO NOT WORK for strongly correlated systems (e.g., late transition metal oxides, sulfides,actinides, …).

FAILS to describe Van der Waals interactions, excited states, band gaps,

C. Predicting Structures: Energy Scale

High accuracy required to predict physical behavior

V element : Atomic energy: -1894.074 Ry

BCC V : Energy: -1894.7125 Ry

Cohesive Energy: 0.638 Ry (0.03% of total E)

FCC/BCC difference: 0.02 Ry (0.001% of total E)

ALLOYS: Mixing and Ordering energies are also a few mRy

For Phase Stability, need DFT relative error ~ 0.1 mRy!!!!

(in Temperature Units $K_B T$: 1 mRy= 158 K)

Physical behavior correct due to large cancellation of errors

HOW IT WORKS : $D0_{22}$ - $TiAl_3$

$\Delta_f E$ (kJ/mol of atoms)	Method	Reference
-40.5	LMTO-ASA, LDA	Hong et al.
-41.5	FLAPW, LDA	Fu
-41.9	FPLMTO, LDA	Asta et al.
-39.6	FLASTO, LDA	Watson and Weinert
-39.3	VASP, USPP, GGA	Colinet and Pasturel
-36.6	Calorimetry	Kubaschewski and Dench
-35.6	Calorimetry	Kubaschewski and Heymer
-37.0	Calorimetry	Stuve and Ferrante
-36.6	Calorimetry	Meschel and Kleppa
-39.2	Calorimetry	Nassik et al.

Lattice parameters	Method	Reference
a= 3.790 A°, c/a= 2.24	FPLMTO, LDA	Asta et al.
a= 3.80 A°, c/a= 2.242	FLASTO, LDA	Watson and Weinert
a= 3.844 A°, c/a= 2.247	VASP, USPP, GGA	Colinet and Pasturel
a= 3.790 A°, c/a= 2.23	MBPP-LDA	Bester and Fähnle
a= 3.849 A°, c/a= 2.236	experimental	Braun and Ellner

Technicalities: Things to Think about

FOLLOW TUTORIALS: (Chu-Chun Fu and Guillaume Lucas)

Basis set: local or plane-wave, completeness.

All-electron or pseudopotential.

Reciprocal space (Brillouin zone) sampling.

Supercell Techniques

Precision, convergence.

MAIN PROGRAMS FOR CRYSTALS:

SIESTA. http://www.uam.es/departamentos/ciencias/fismateriac/siesta/

ABINIT. http://www.abinit.org/ **VASP**. http://cms.mpi.univie.ac.at/vasp/

CPMD. http://www.cpmd.org **PWSCF**. http://www.pwscf.org

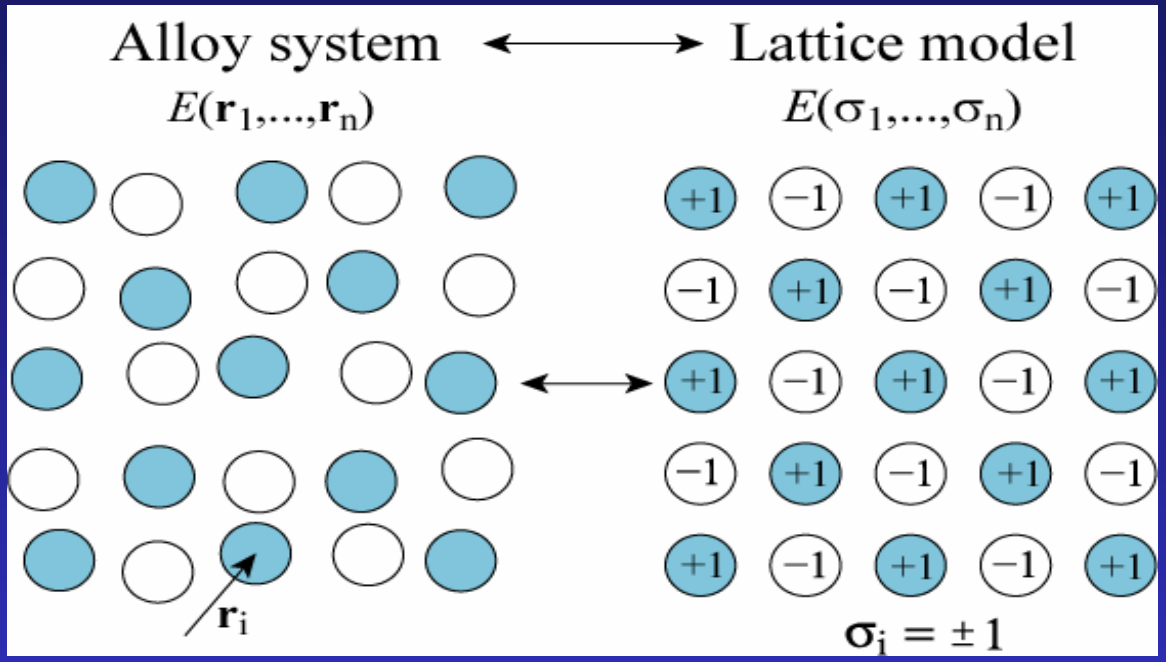
WIEN. http://www.wien2k.at/ **CASTEP**. http://www.cse.clrc.ac.uk/Activity/UKCP

CRYSTAL. http://www.cse.dl.ac.uk/Activity/CRYSTAL

Part II
Ab Initio Thermodynamics

A.1 Ising Model and Cluster Expansion

Coarse-graining of the electronic degrees of freedom.

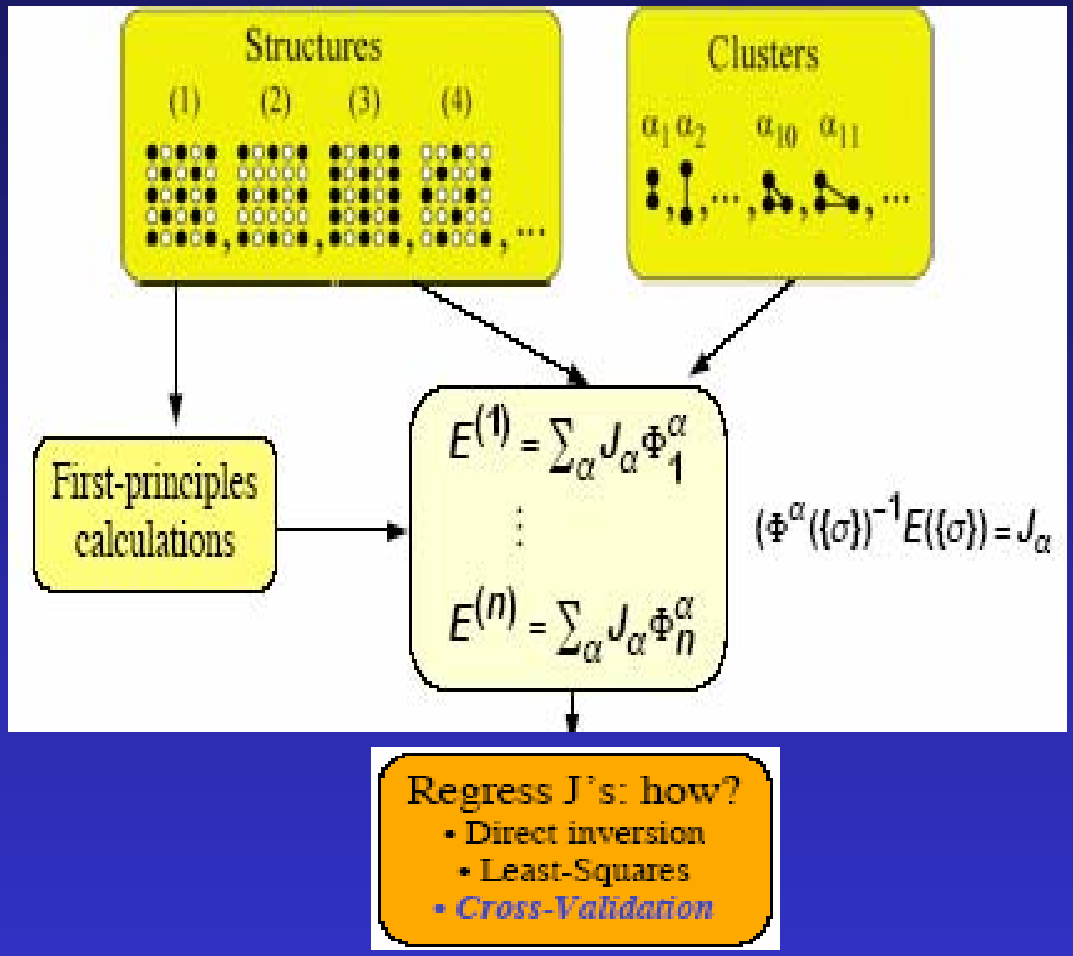


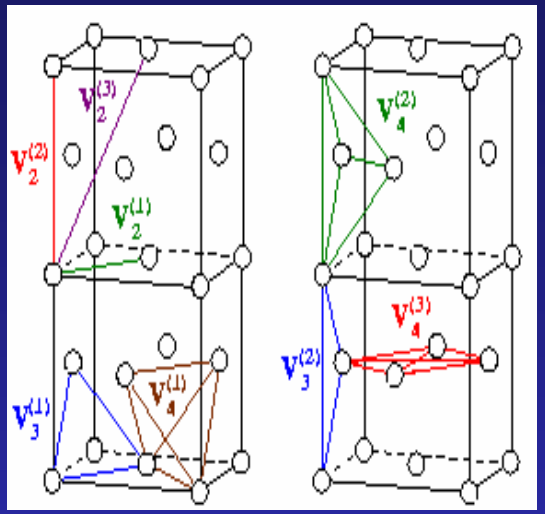
$$E(\sigma_1,\ldots\sigma_n) = J_0 + \frac{1}{1!}\sum_{\{i\}} J_i\sigma_i + \frac{1}{2!}\sum_{\{ij\}} J_{ij}\sigma_i\sigma_j + \frac{1}{3!}\sum_{\{ijk\}} J_{ijk}\sigma_i\sigma_j\sigma_k + \cdots$$

Succinctly written as: $E(\sigma_1,\ldots\sigma_n) = \sum_\alpha J_\alpha \Phi^\alpha$

With structural "correlation fcts": $\Phi^n(\{\sigma\}) = \sigma_1\cdots\sigma_n$

THE CLUSTER EXPANSION FORMALISM





Which structures and which clusters to include in the fit?

REF: PRB45, 7677 (1992); J. of Phase Equilibria 15,330 (1994); PRB 52, 15176 (1995); PRB 56, 552(1997);review published in the Science of Complex Alloy Phases, ed. P.Turchi and Massalski, p409 (TMS, Warrendale, PA, USA)2005.

THE CLUSTER EXPANSION FORMALISM

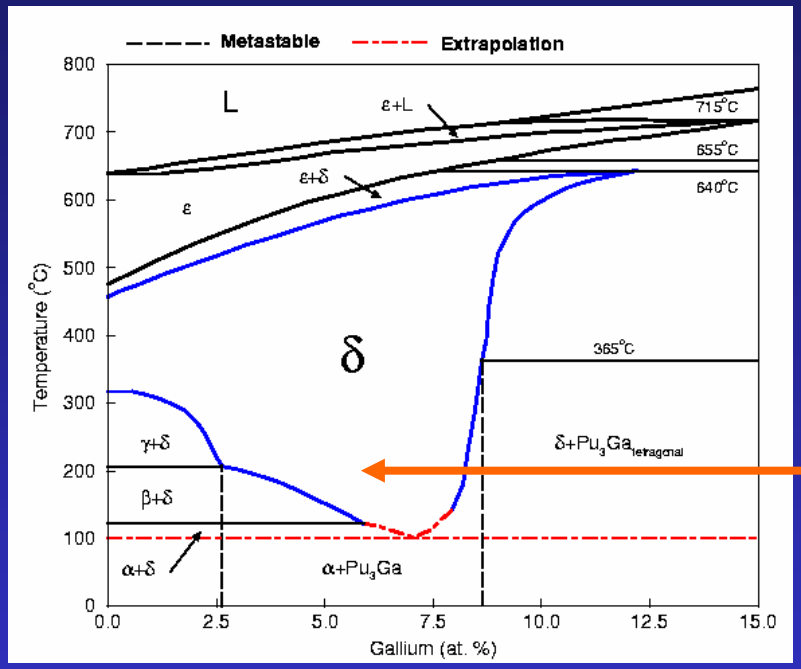
How to pick the interactions

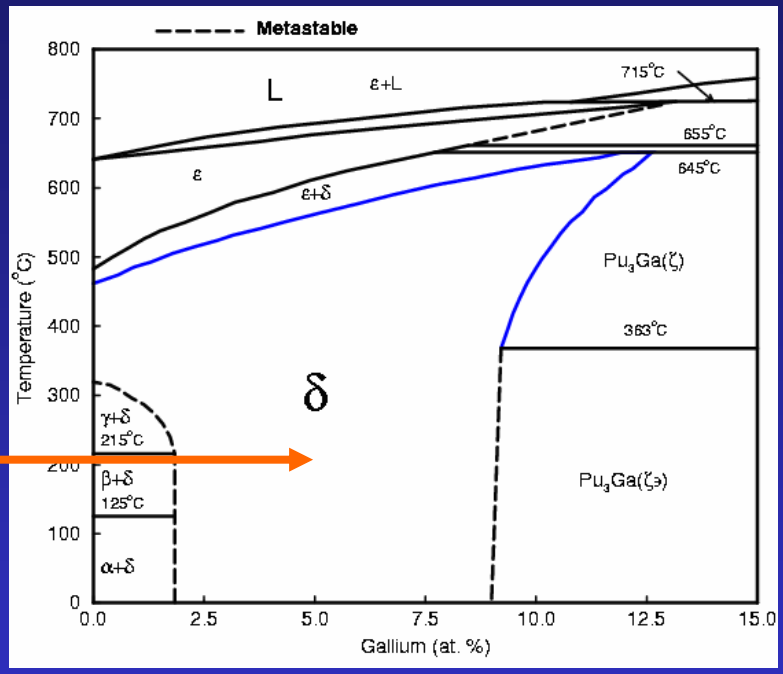
- By physics “intuition”—dangerous (and physics shouldn’t be an “art”)
- Formal hierarchy (converges way too slow to be practical)
- Systematic “guessing”—hierarchal approach

  (Phys. Rev. B 73, 174204 2006)
- Evolutionary Optimization

  (Zunger et al, Nature materials 2005)
- See also I. Abrikosov ‘s talk for other techniques

CEF: APPLICATION TO THE Pu-Ga PHASE DIAGRAM

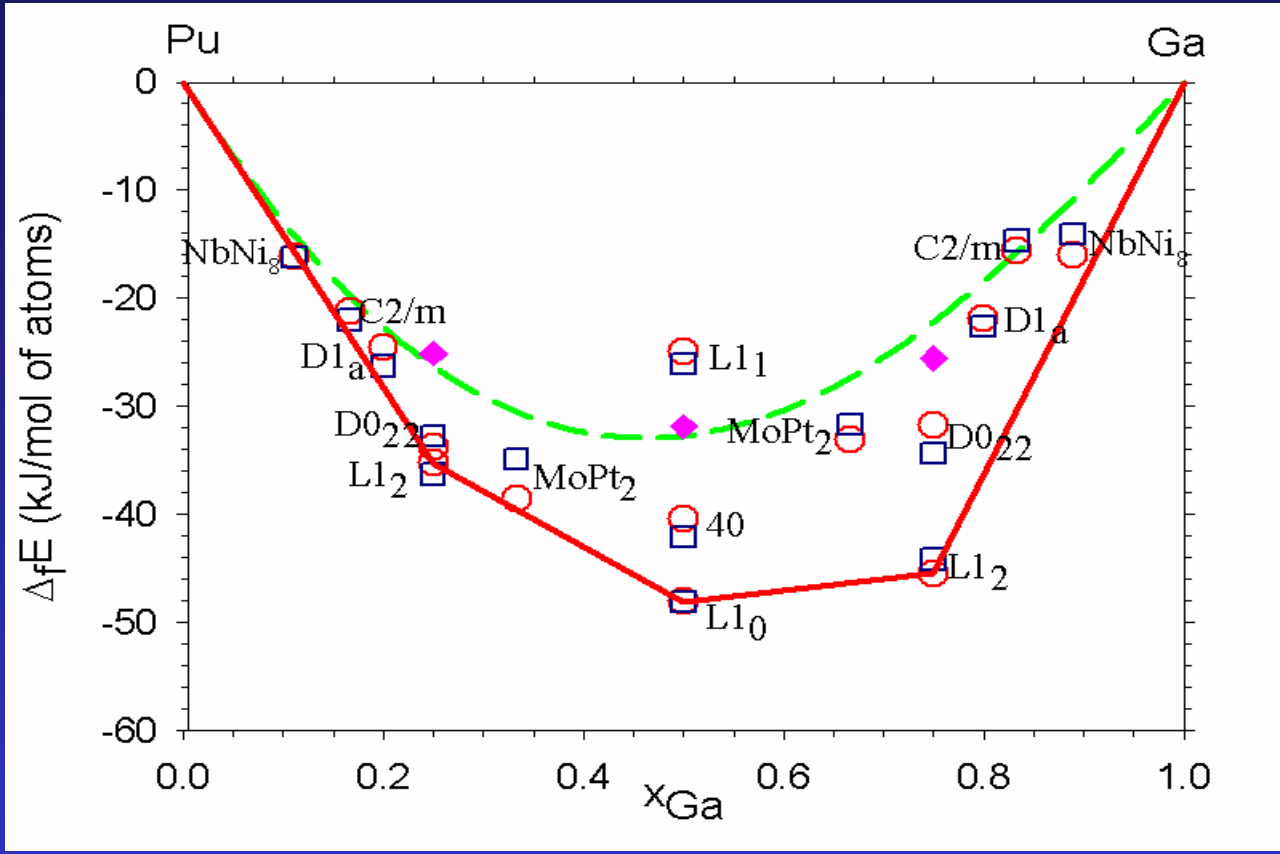




Russian P. D. [Chebotarev et al]

American P.D. [Ellinger et al]

CEF: APPLICATION TO THE Pu-Ga PHASE DIAGRAM



○ : direct values (from ab-initio calculations)

□ : indirect values (calculated using the effective cluster interactions)

— — : Energy of mixing of the disordered δ solid solution

Pink diamonds: Energies of formation of special quasirandom structures (SQS)

CEF: APPLICATION TO THE Pu-Ga PHASE DIAGRAM

Three dimensional Ising-like Hamiltonian: $E_{tot}^{S} = \sum_{\alpha} m_{\alpha} V_{\alpha} \xi_{\alpha}^{S}$

- strong first nearest neighbor pair effective interaction $V_2^{(1)}$

Configurational entropy (see G. INDEN)

Ideal solid solution: $S / Nk = -\sum_{i} x_i \ln x_i$

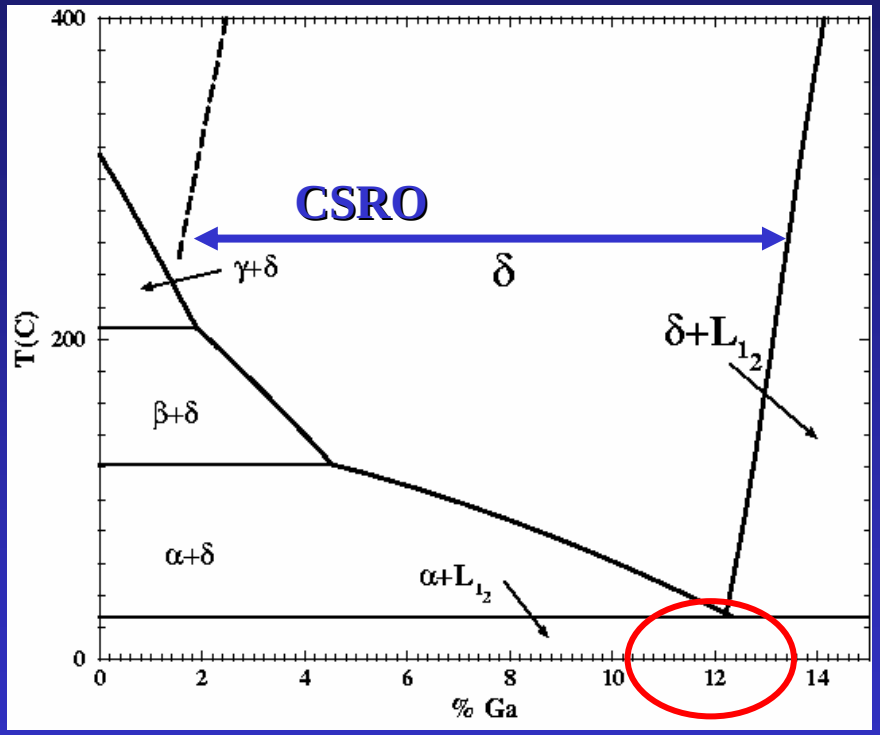
Cluster variation method: regular tetrahedron

approximation in the fcc solid solution:

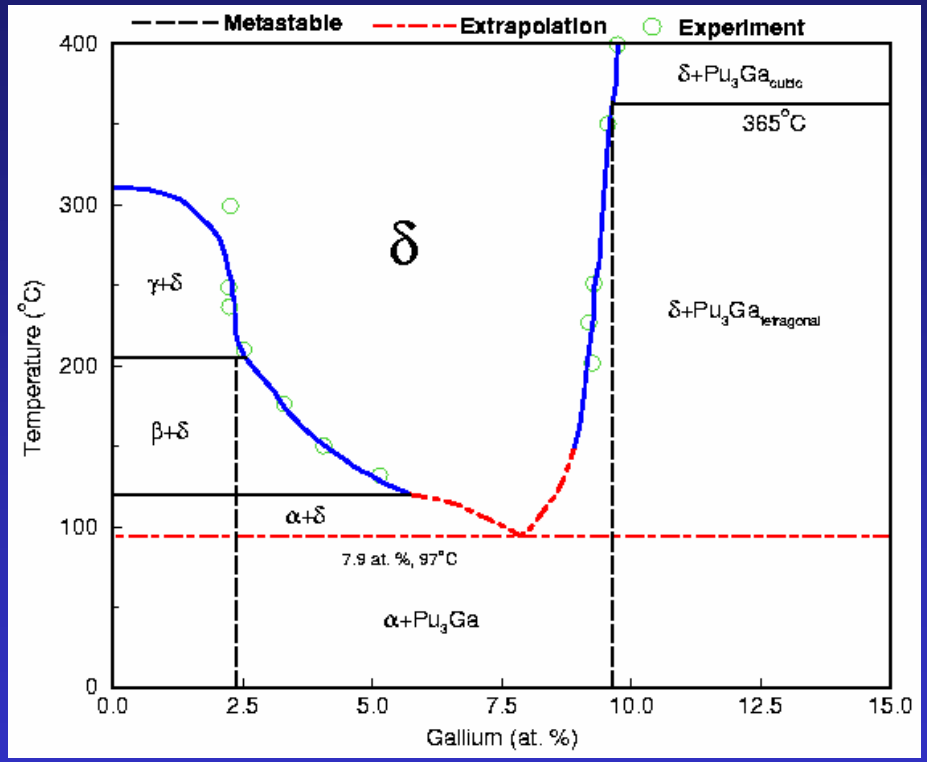
$$S / Nk = -2 \sum_{ijkl} p_{ijkl} \ln p_{ijkl} + 6 \sum_{ij} p_{ij} \ln p_{ij} - 5 \sum_{i} p_i \ln p_i$$

CEF: APPLICATION TO THE Pu-Ga PHASE DIAGRAM

Theoretical



Experimental



REF: PRB 68, 75109 (2003); MSMSE 12, 693 (2004); Phil Mag. B84 1877 (2004); MRS 802, DD64(2004)
J. Phys. Cond. Mat. 15, 8377 (2003); Euro. Phys. Lett. 71, 412 (2005)

A.2 First-Principles Lattice Dynamics

Linear response perturbation method:

accurate but expensive, limited to small systems, (S. Baroni et al. PRL 58, 1861(1987))

Supercell method:

approximate but applicable to large systems (K. Parlinski et al. PRL, 78, 4063(1997)

Thermodynamic Properties (Quasiharmonic App.)

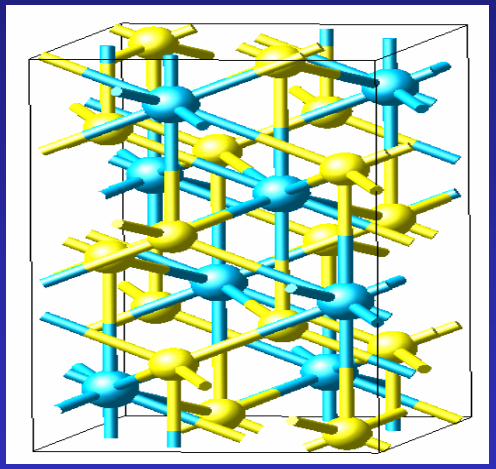
$$F(T) = E_0 + \int_0^{\omega_{max}} \frac{1}{2}\hbar\omega\, g(\omega)d\omega + k_B T \int_0^{\omega_{max}} \ln[1-\exp(-\frac{\hbar\omega}{k_B T})]g(\omega)d\omega$$

Intrinsic Anharmonicity at High T (E_{vib} ~T^2) : Molecular Dynamics

First-Principles Lattice Dynamics

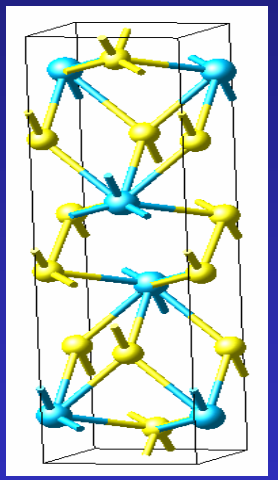
Polytypisme of $TiSi_2$.

C54: ground state



Experimental background:

C49: metastable

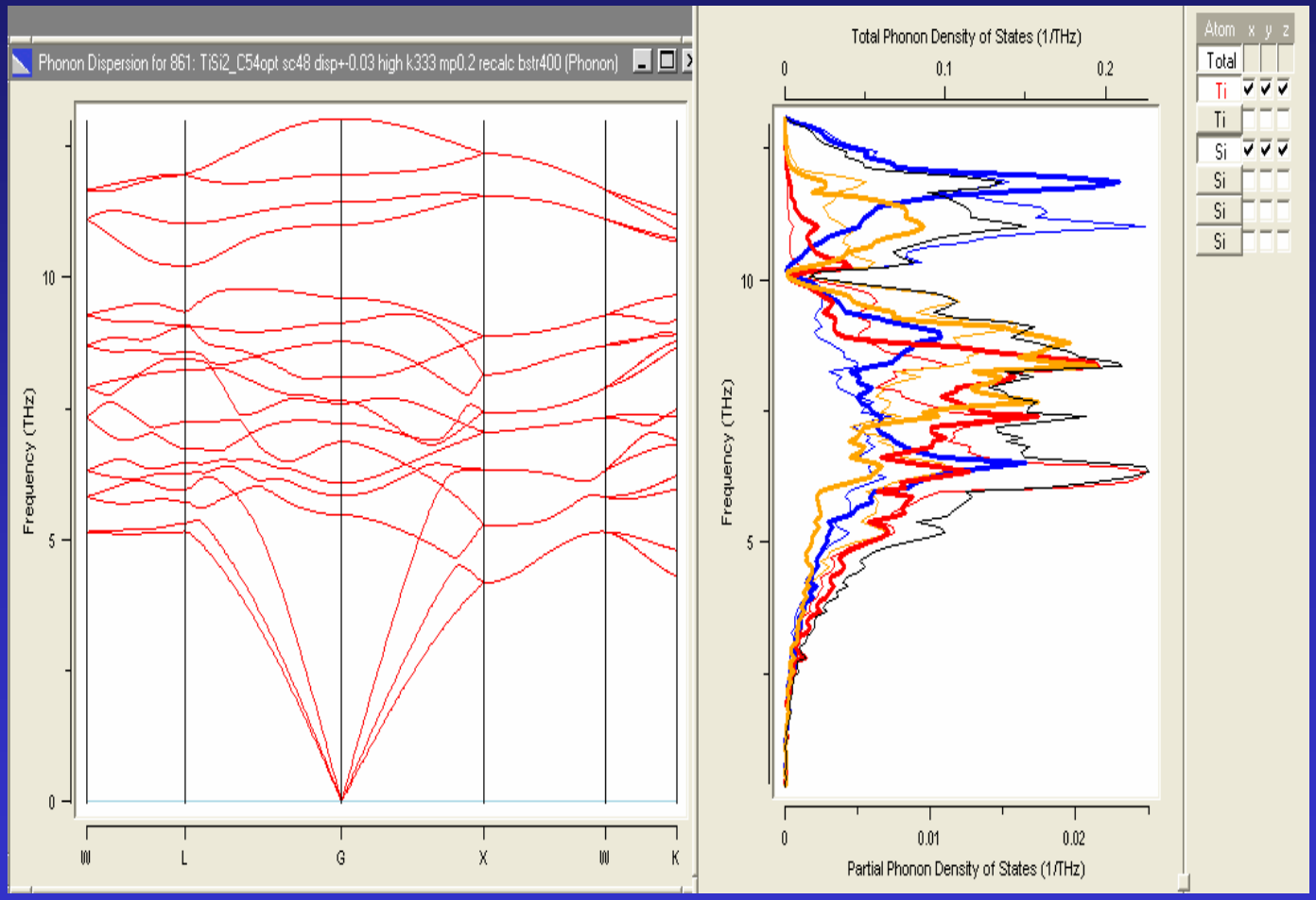


Ab initio results a T=0K: C49 ground state

APL 87, 41910 (2005)

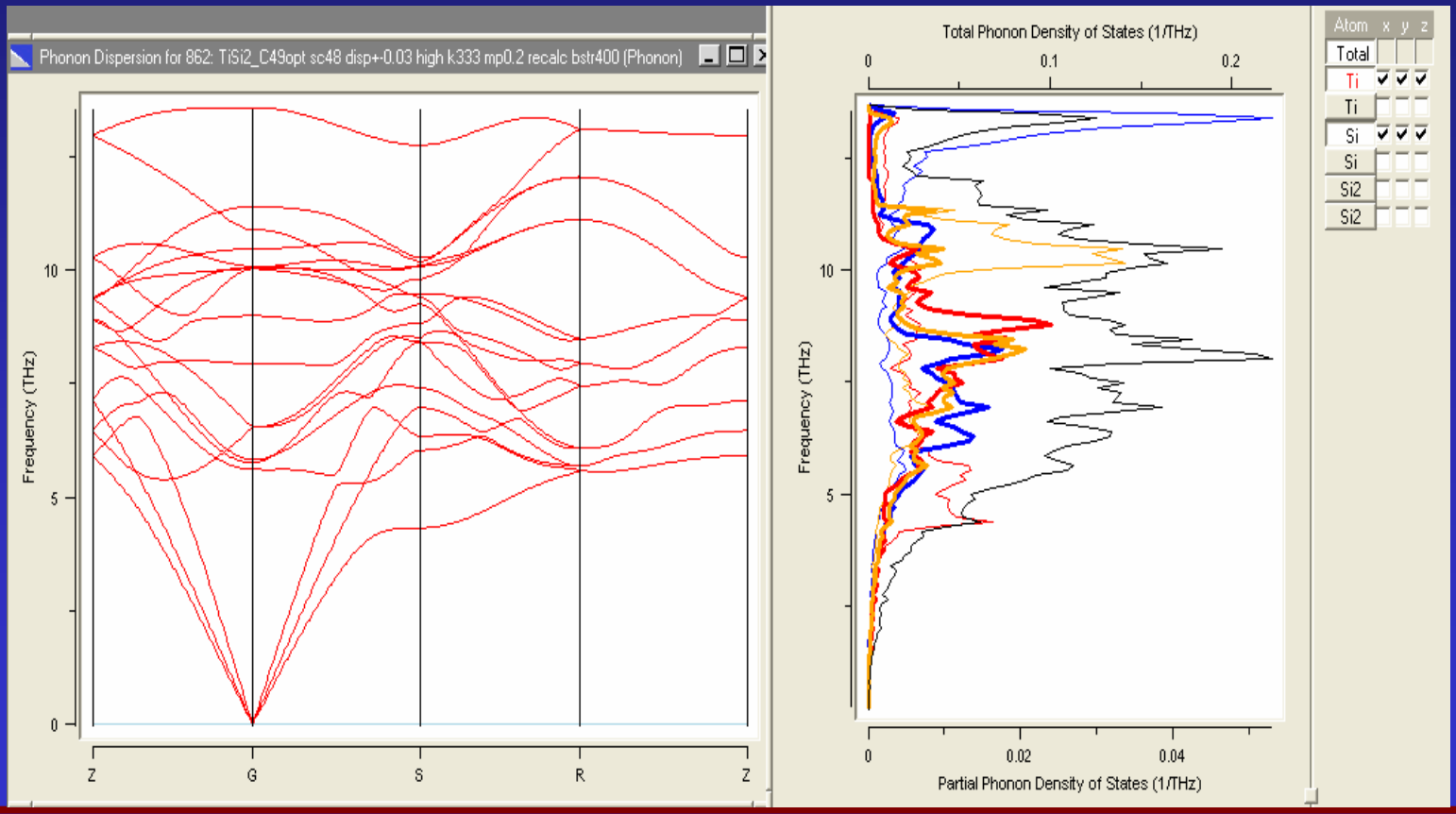
First-Principles Lattice Dynamics

Phonons of TiSi2 C54

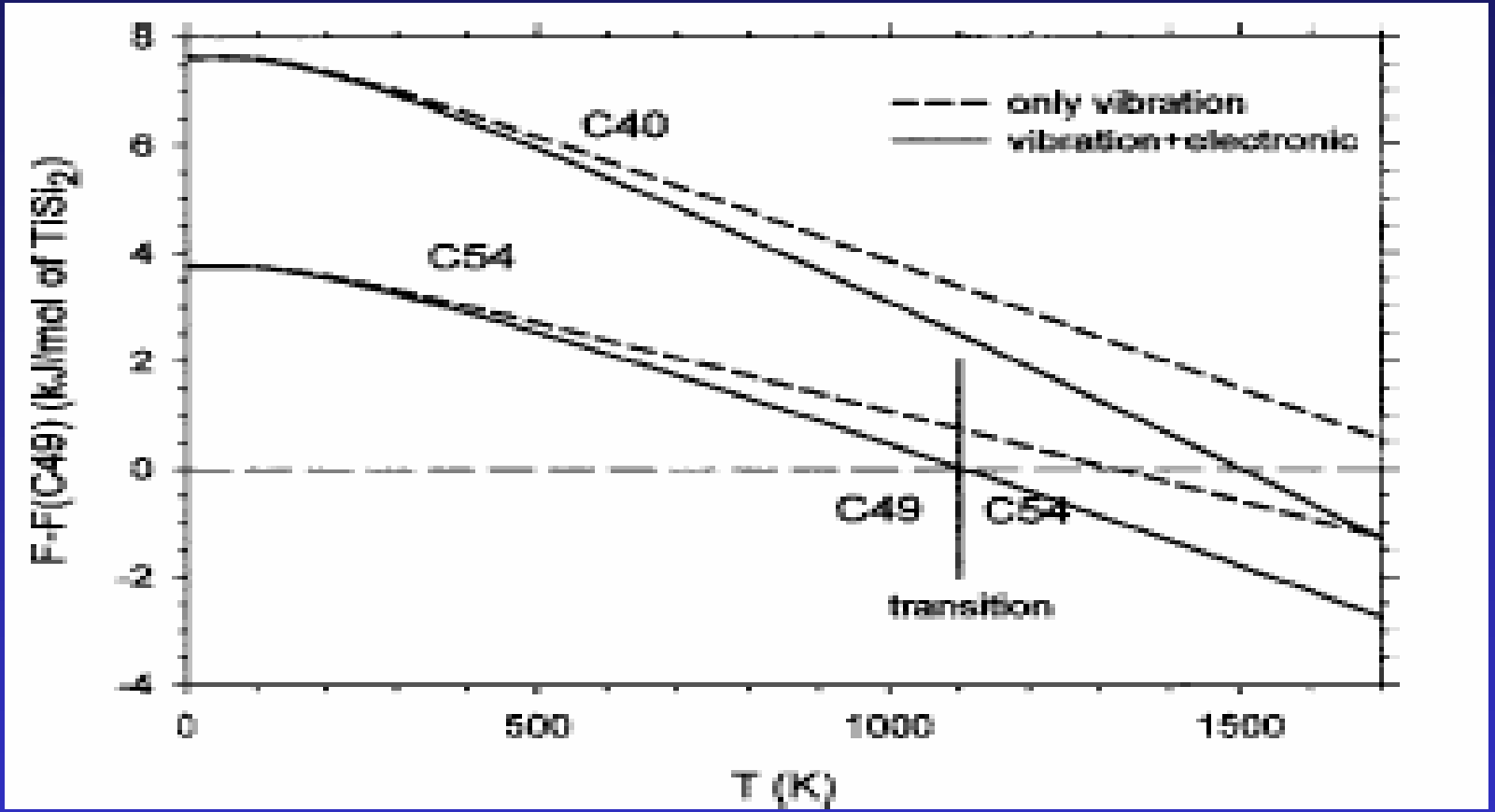


First-Principles Lattice Dynamics

Phonons of TiSi2 C49



First-Principles Lattice Dynamics



Phase transition : C49 >C54: 1100K
Reassesment of the Ti-Si Phase diagram !!!!!

B LIQUID STATE: ab initio MD

Structure UNKNOWN : Molecular Dynamics

- <u>CENTRAL ASSUMPTIONS:</u>
- Atomic nuclei are classical objects.
- Electrons give effective interaction potential (computed explicitly or approximated implicitly).

- <u>COMPUTATIONS:</u>
- Initialize positions and momentum (boundary conditions in space and time).
- Solve F= mγ to determine r(t), v(t) Newton (1667-87)
- *NVT* and NPTensembles
- Ab initio: at each step calculate forces quantum-mechanically.
  Car-Parrinello Scheme versus Born Hoppenheimer
  Usually DFT Plane-wave methodology

LIQUID STATE

What can be studied with MD ?

- Local Structure : Chemical and topological short-range order
- Dynamics : Diffusion, Viscosity
- Thermodynamics: the free energy is calculated from thermodynamic integration or thermodynamic perturbation theory

Ab Initio MD:

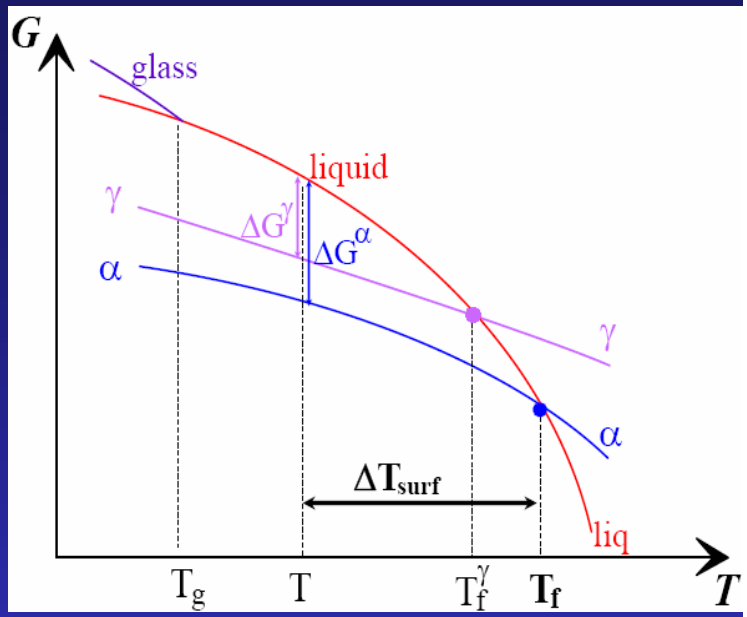
- Very expensive: Restricted in simulation time (30-50 ps) and size (~300 atoms)
- Necessary when chemical transformations (bond forming/breaking) occur.

CLASSICAL NUCLEATION MODEL

Competition between :

** ΔG_V : difference of the Gibb's energies of liquid and solid (< 0)

** γ : solid-liquid interfacial energy (> 0)



Activation Energy for Nucleation:
γ main factor

$$\Delta G^{*} = \frac{16}{3}\pi \frac{\gamma^{3}}{(\Delta G_V)^{2}}$$

IDEA: High γ when local structure of melt incompatible with the translational invariance of crystalline solids

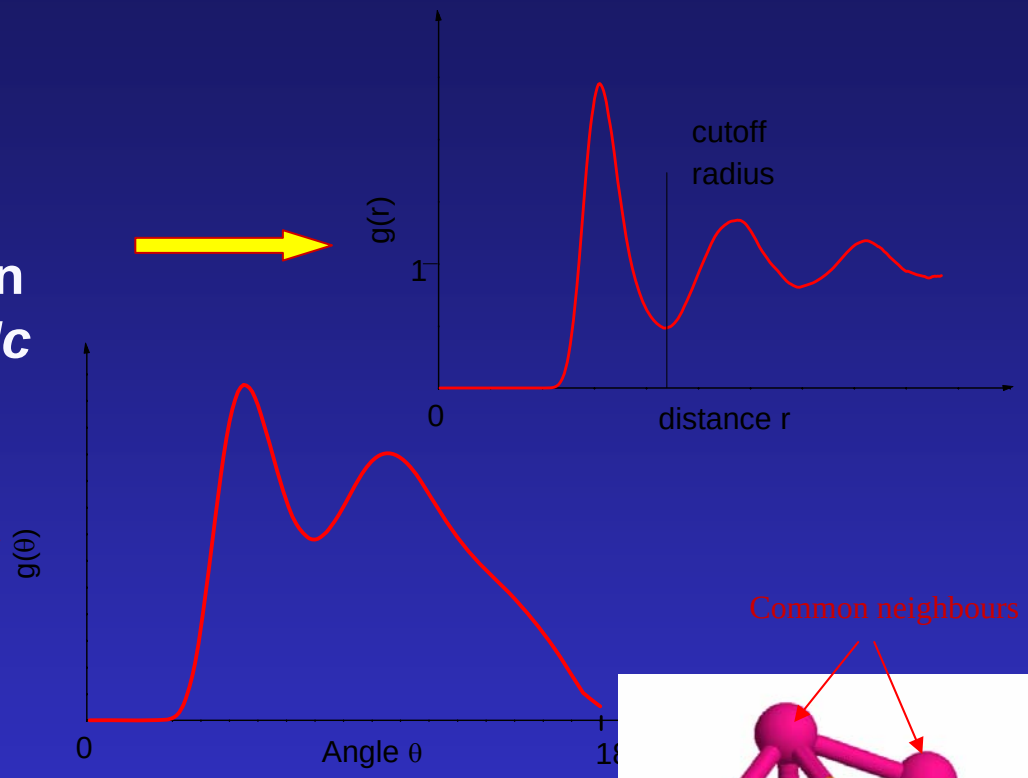
LOCAL STRUCTURE

ANALYSIS

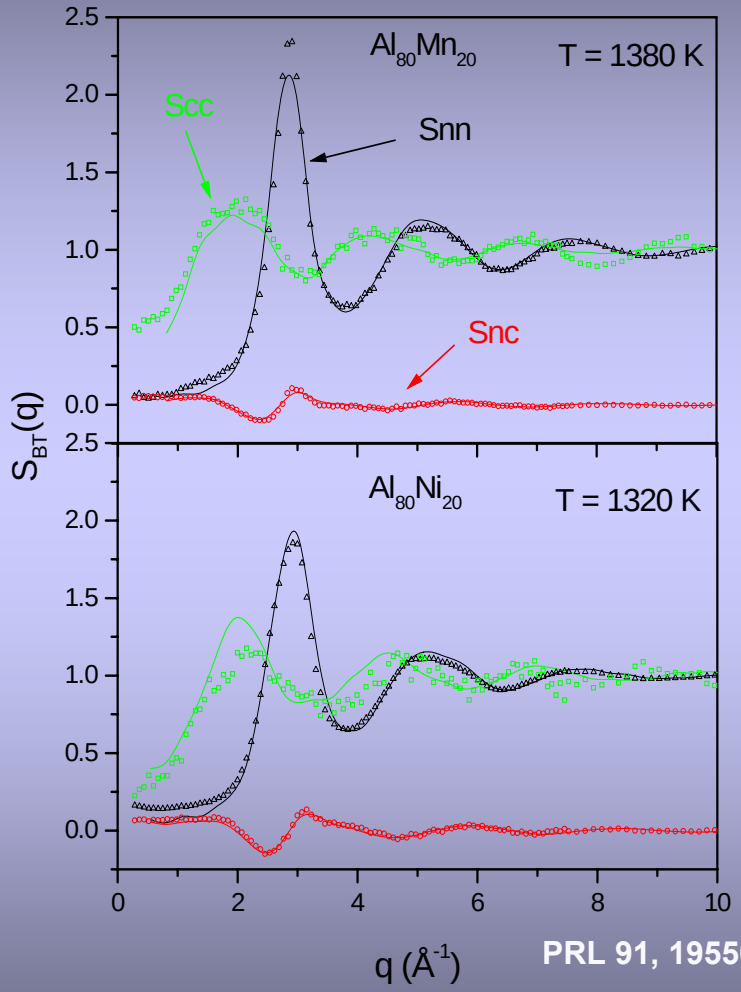
*The length and number of the bonds : pair-correlation function *g(r)* and coordination number *Nc*

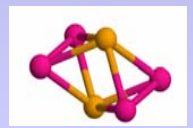
*The direction of the bonds : bond-angle distribution *g(θ)*

*The common-neighbour analysis : a 3D local structure



Structural Properties of $Al_{80}Mn_{20}$ and $Al_{80}Ni_{20}$ alloys





	$Al_{80}Ni_{20}$		$Al_{80}Mn_{20}$	
Pairs	Total	Ni	Total	Mn
1551	0.14	0.25	0.18	0.37
1541	0.15	0.10	0.14	0.13
1431	0.25	0.34	0.21	0.21
1421	0.05	0.04	0.03	0.02
1422	0.10	0.07	0.10	0.05
1201	0.02	0.00	0.03	0.00
1211	0.01	0.00	0.01	0.00
1301	0.02	0.01	0.02	0.00
1311	0.10	0.06	0.08	0.02
1321	0.06	0.04	0.07	0.02
1331	0.00	0.00	0.00	0.00
1441	0.03	0.07	0.04	0.08
1661	0.03	0.01	0.03	0.06
1771	0.00	0.00	0.00	0.00
1881	0.00	0.00	0.00	0.00
2101	1.81	1.96	1.75	1.71
2211	1.00	1.17	0.93	1.08
2321	0.18	0.10	0.15	0.06
2331	0.59	0.65	0.64	0.76
2441	0.13	0.08	0.13	0.11

PRL 91, 195501 (2003); APL 83, 4734 (2003); J. Chem Phys 120, 6124 (2004);
PRB 70, 174203 (2004), PRL, 93, 207801 (2004), JCP 123, 104508 (2005)

Part III
From Ab Initio to CALPHAD

A. Data Base

ESSENTIAL TO CALPHAD METHODOLOGY

Models which simultaneously include constraints imposed by phase equilibria, calorimetry, and crystal chemistry are more reliable than those based on any one source alone.

Experimental Phase diagrams often determined from phase equilibria and crystal chemistry only.

Include ab initio data in Data base:

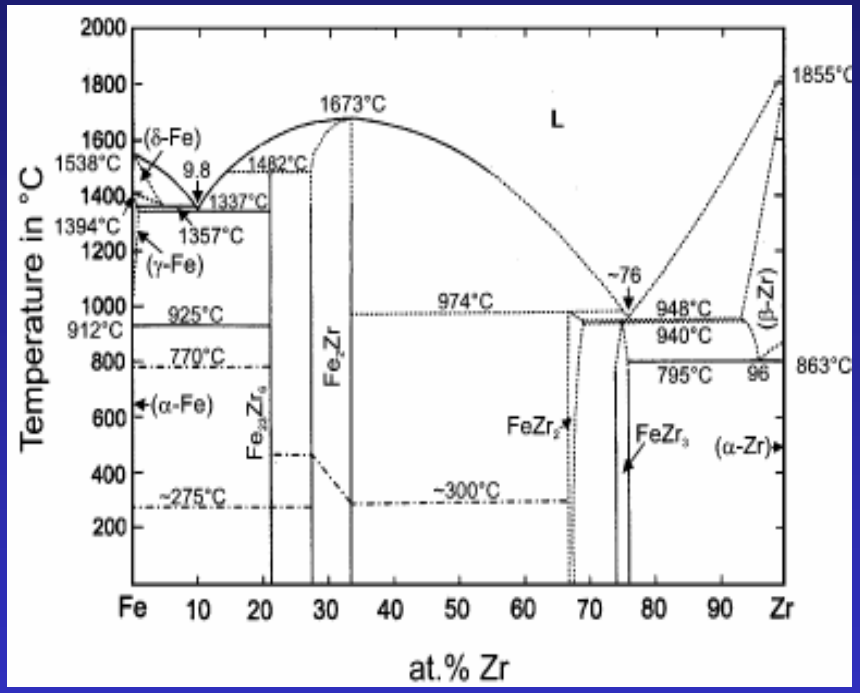
- to improve accuracy of thermodynamic predictions

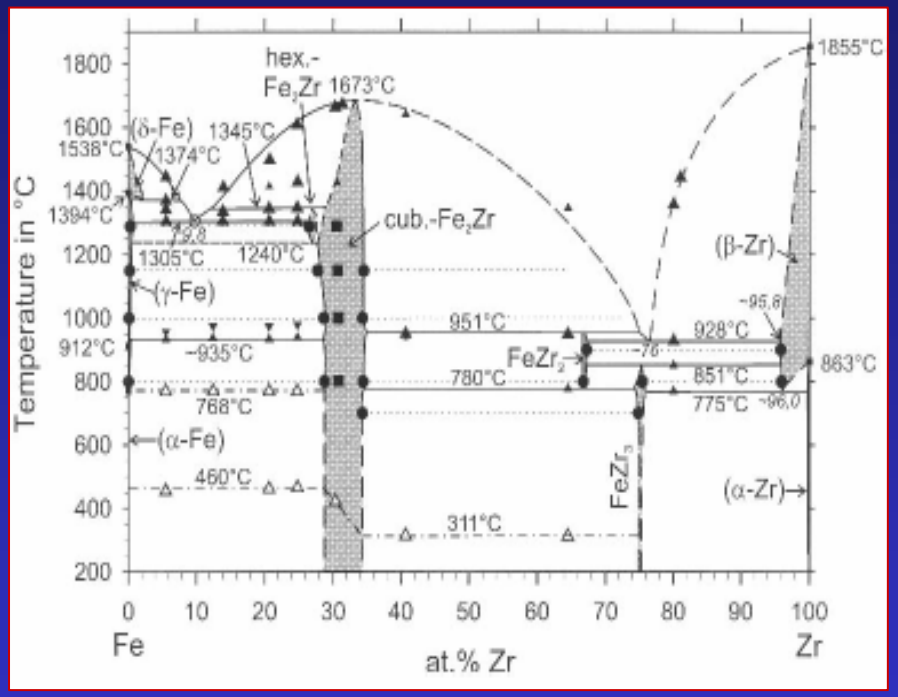
(provide energy, ground state analysis, free energy …)

- allows data mining and prediction of compounds for unknown systems (Curtarolo et al. PRL 2005)
- help to built better functional or models

(see also A. Caro's talk)

Phase Diagram Fe-Zr: Data Base

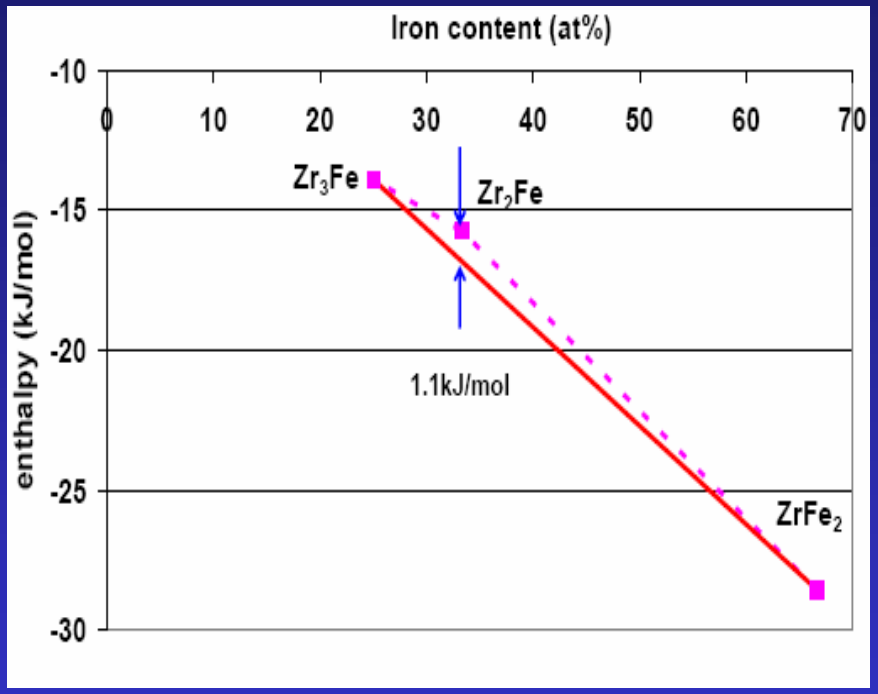


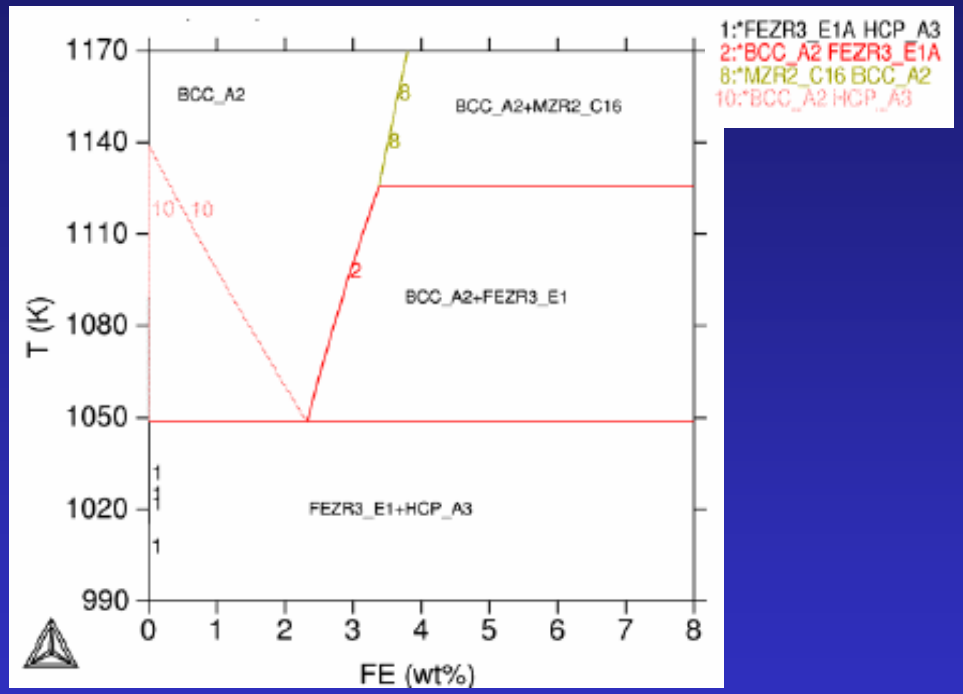


M. Jiang et al. J. Phase Equil. 2001

Stein et al. J. Phase Equil. 2002

Phase Diagram Fe-Zr : Zircobase





Ab initio calculations computed rich-part of the Zr-Fe diag.

P. Barberis et al. ASTM N°1467, 129 (2006)

B. FUNCTIONALS and MODELS

Models must have forms constrained by
Theoretical Considerations

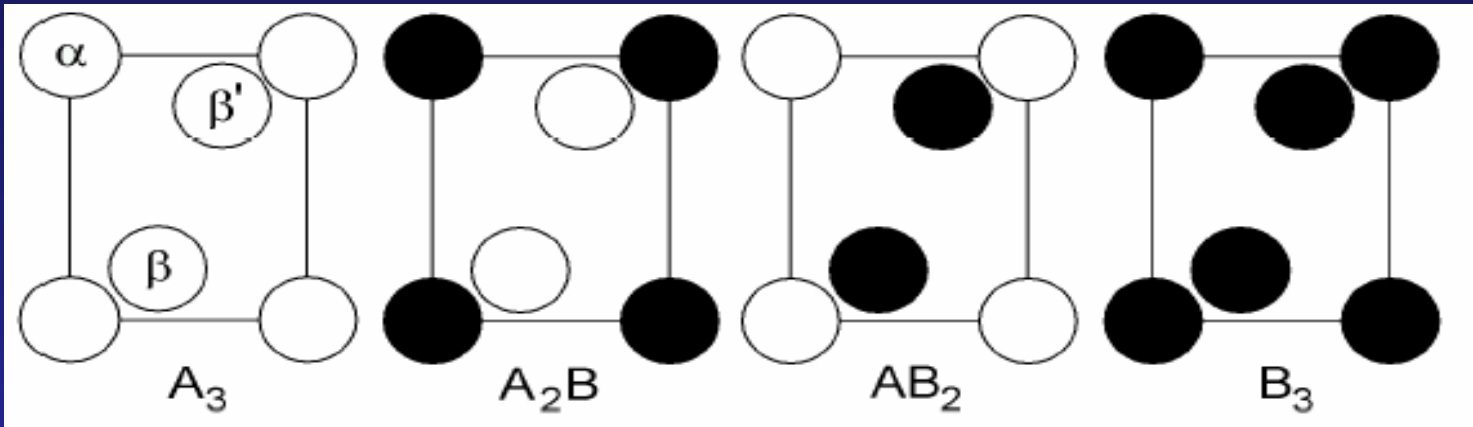
Compound Energy Formalism (CEF)

Parametric thermodynamic model to modelling

- Interstitial Solutions
- Non-stoichiometric compounds
- Ordering effects.

based on the existence of several sublattices
(inequivalent sites in the unit cell) in a crystalline phase

Compound Energy Formalism



Energy: Mixture of Hypothetical Compounds

$$E_{CEF} = \sum_{c} f_c E_c$$

Entropy: Randomness on each Sublattice

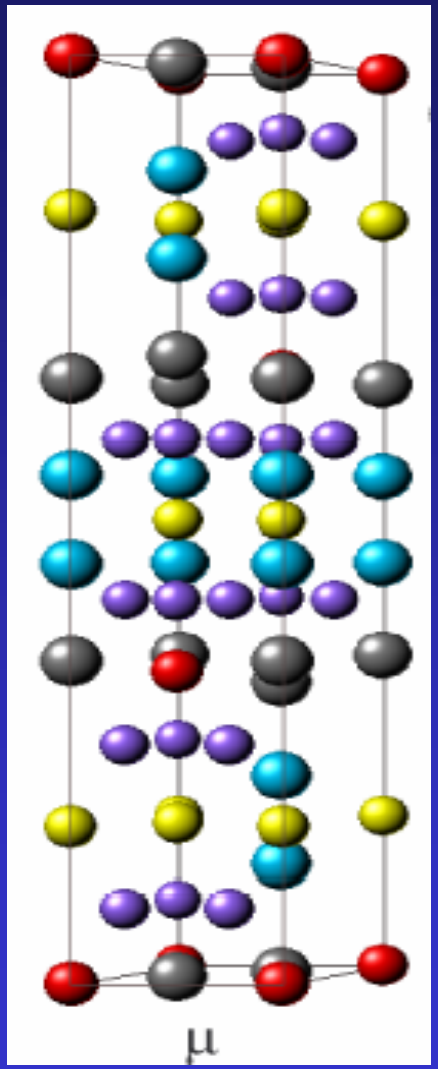
$$S_{CEF} = \sum_{\alpha} f_\alpha S_{random}(\alpha)$$

f_α : fraction of sites of type α

f_c : fraction of compound c : determined by minimizing F_{CEF}

COMPARE to CE-CVM to validate no SRO on each sublattice

μ Ni-Nb Phase



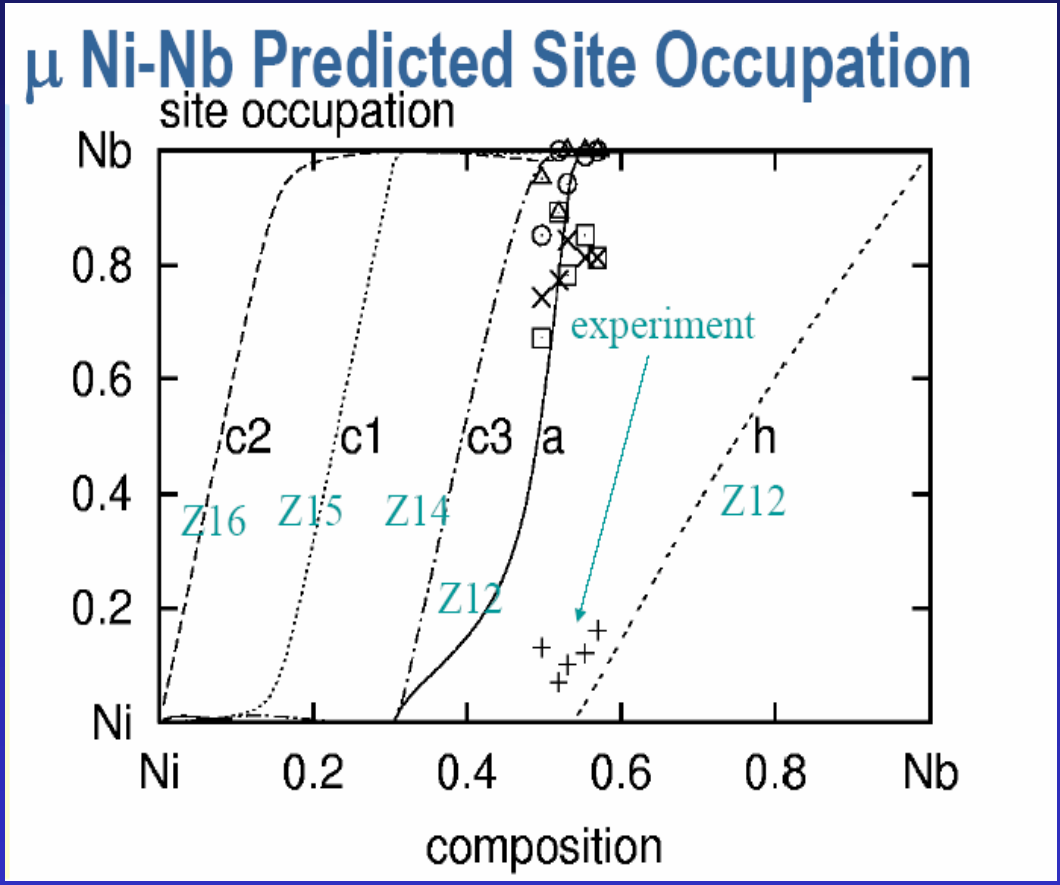
μ Ni-Nb Site Occupation Models

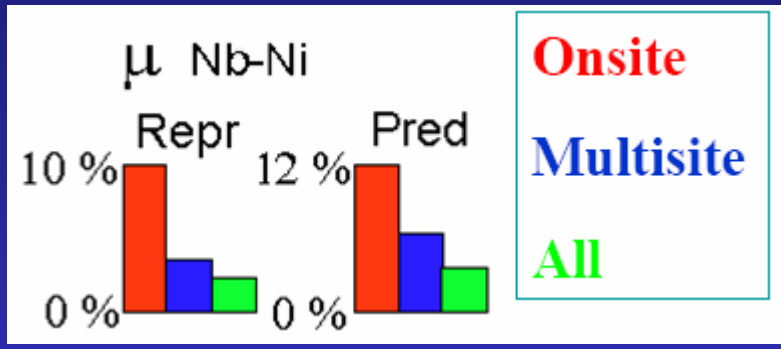
Table 2: Models for site occupation in the μ phase (Fe_7W_6 prototype). Element A represents the larger sized, early TM such as W, and element B represents the smaller sized, late TM such as Fe.

	sites					composition		Reference
Wyckoff	3a	$6c_1$	$6c_2$	$6c_3$	18h	min	max	
CN	12	15	16	14	12			
General	A,B	A,B	A,B	A,B	A,B	A_{13}	B_{13}	[23]
Ideal	B	A	A	A	B	A_6B_7	A_6B_7	[56, 58]
Model I	A,B	A	A	A	A,B	A_{13}	A_6B_7	[60, 61]
Model II	A,B	A	A	A,B	A,B	A_{13}	A_4B_9	[60]
Model III	A,B	A,B	A	A,B	A,B	A_{13}	A_2B_{11}	[60, 62, 61]
Model IV	A,B	A	A	A,B	B	A_7B_6	A_4B_9	[60, 62, 61]
Model V	A,B	A,B	A	A,B	B	A_7B_6	A_2B_{11}	[62]

CALPHAD: Many Models – all alike and still different!

μ Ni-Nb Phase



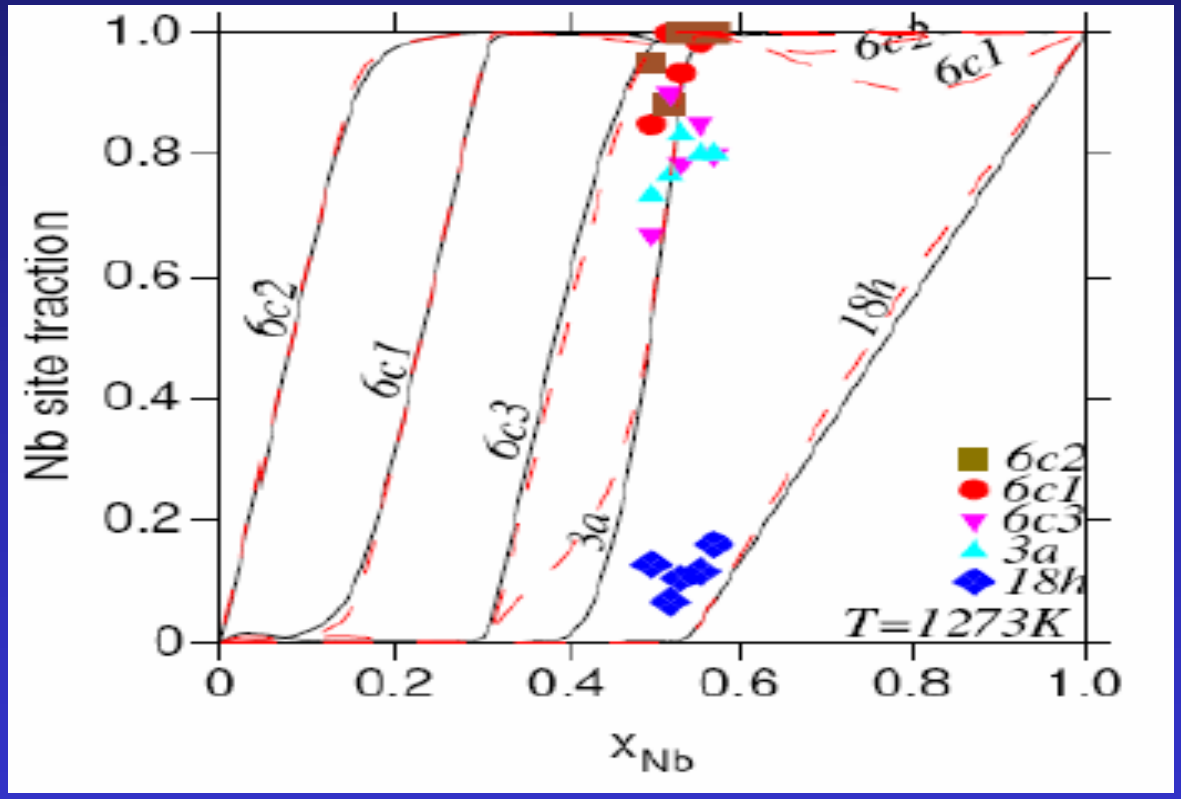


CE+CVM results : *PRB 67, 174203 (2003)*

μ Ni-Nb Phase

Comparison between CE-CVM and CEF results

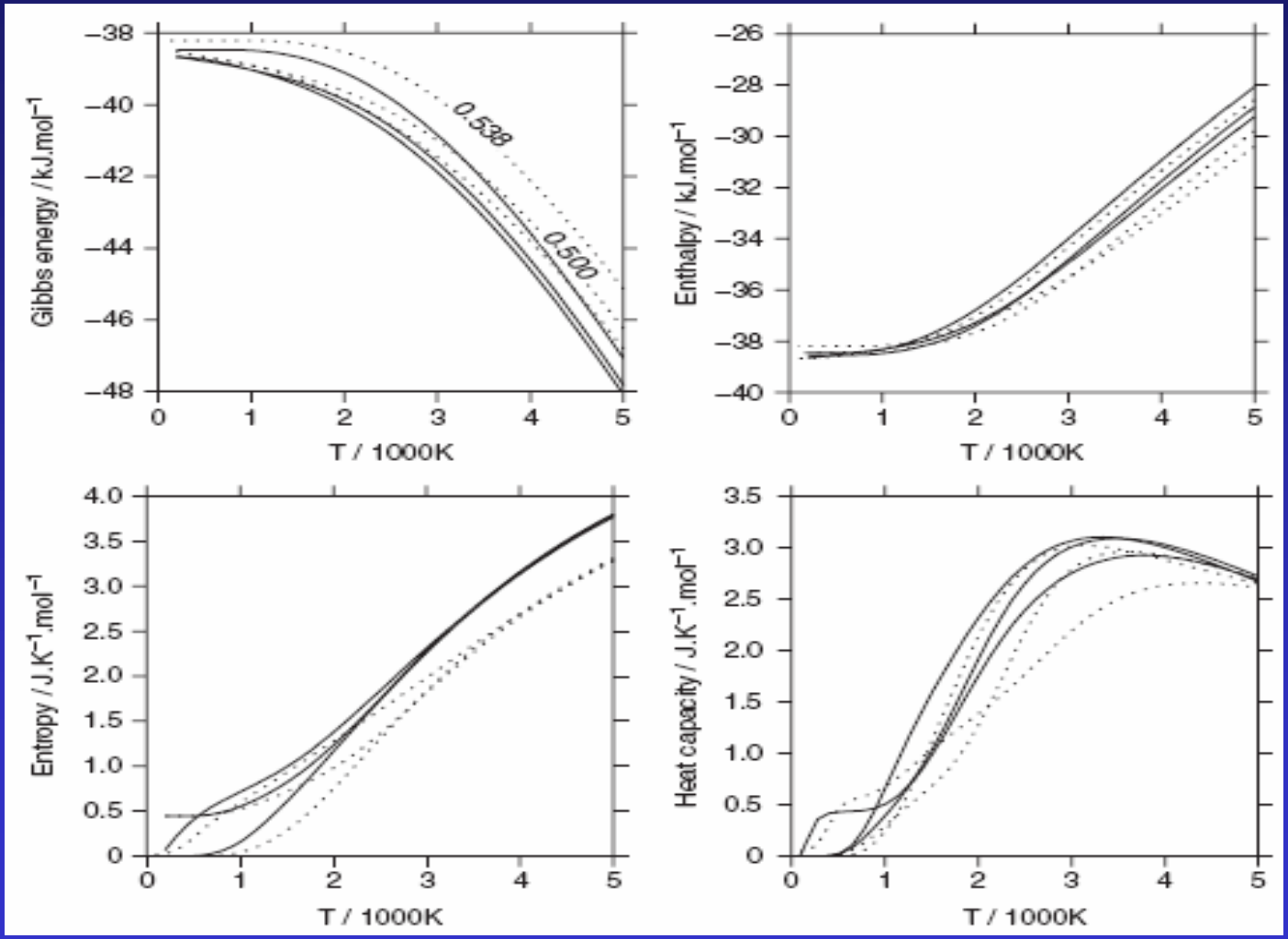
Site Occupancies



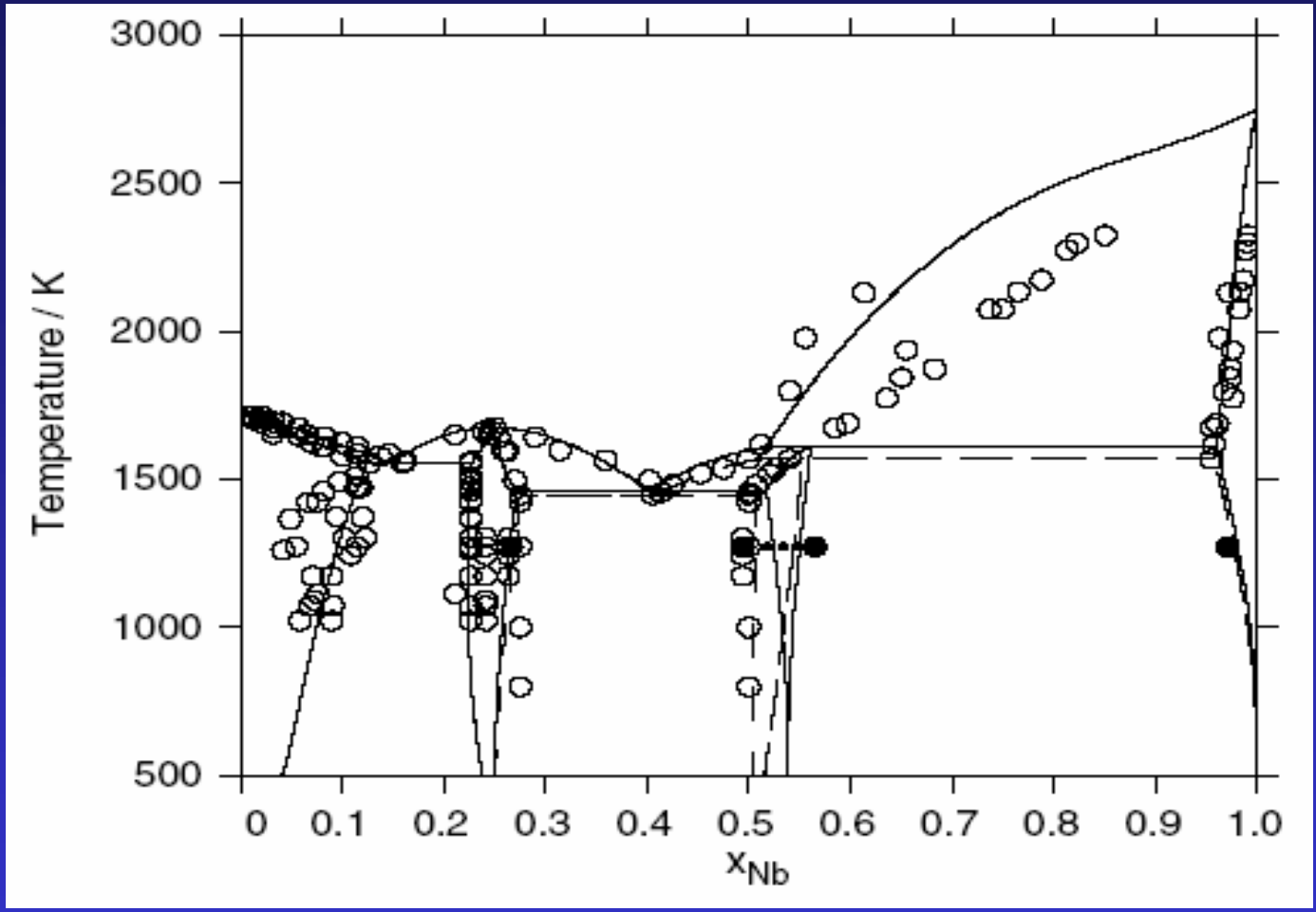
Phil Mag. 86, 1631 (2006)

μ Ni-Nb Phase

Thermodynamic Data



Ni-Nb Phase Diagram



Experiments from Bolcavage et al . J. Phase Equil. 1996 and Joubert et al. Calphad 2002

Conclusion

Essential tools for *ab initio* alloy thermodynamics:

- The cluster expansion (configurational effects)
- Phonon spectra (vibrational effects)
- SRO in liquid (amorphous) phases

Thermodynamic properties can now
be calculated with a precision comparable to measurements
(More accurate Data bases and better functionals)

Future directions:
Coupling ab initio calculations with CALPHAD method
for multicomponent systems.