

*Overview of The Cluster Expansion Method  
Its Foundations and Use in “First Principles  
Thermodynamics”*

Juan M. Sanchez

The University of Texas at Austin

# *A Bit of History and (lost?) Prehistory*

- **Early 70's:** *Cluster Expansion introduced to study prototype order-disorder Phase Diagrams for “generalized” Ising models.*
  - **Early 80's:** *Connolly & Williams propose to use Total Energy calculations to fit the Effective Cluster Interactions (ECI).*
  - **1984:** *Formal development of the Cluster Expansion (SDG basis).*
  - **Early 90's:** *Development of a **general** CE formalism (totally ignored by CE “practitioners” )*
  - **Mid 90's:** *(Gonis et al.) Wait a minute: the physics of the CE in the SDG basis cannot be right; ECIs must depend on concentration! Community response: Total Silence...*
  - **2010:** *Rigorous Development of CE. Shown to be a MDFT and Introduction of VBCE to account for concentration dependence of ECI.*
  - **Now:** *ECIs depend on everything (i.e. all configurational variables). Sorry...*
- Thus, no one has done (or will ever do) a full Cluster Expansion from a finite number of compound energies*

# *The Cluster Expansion*

*Therefore*

# *Some Basic Observations*

*or*

*So, why use any basis other than SDG?*

# *Less Obvious Observations*

PHYSICAL REVIEW B 81, 224202 (2010)



## **Cluster expansion and the configurational theory of alloys**

J. M. Sanchez

*Texas Materials Institute, The University of Texas at Austin, Austin, Texas 78712, USA*

(Received 8 March 2010; published 4 June 2010)

*In other words: in the presence of non-linear terms in concentration, a “truncated” CE in the SDG basis will not work, specially in the implementation of the Connolly-Williams method*

# *A Partial Solution (to account for non-linear concentration dependence)*

*In this representation (VBCE), the expansion coefficients are function of concentration*

# *Periodic Systems*

*Thus:*

*With:*

# Thermo 101

*By Euler's homogeneous function theorem, the total energy  $F = N E$  is given by:*

Or,

*Thus, for a converged CE (in whatever basis) we should have:*

*Which shows that the ECIs will not only depend on concentration but also on all the higher order correlations (i.e. SRO)*

*Pair Potential Model* At constant volume the Cluster Expansion in the SDG basis is EXACT

# *Energies of 627 fcc compounds*

# *Exact Euler Derivatives*

*SDG Basis (Variables are  $z_{n0}$ )*

*Variable Basis: (Variables are  $z_{nx}$ )*

# *CE in SDG Basis vs **Exact** Euler Derivatives*

# *Variable Basis Cluster Expansion*

# *Comparison of **SDG CE** , **VBCE** and **Exact** Euler Derivatives*

*SDG Basis*

*Variable Basis*

# *The Bottom Line*

What is a *truncated* CE in the SDG basis?

- A Taylor expansion to *first order* in the configurational variables ( $x$  and  $z_{n0}$ ) about the random state at  $x=0$ !

What is a *truncated* VBCE?

- A Taylor expansion to *first order* in the configurational variables  $z_{nx}$  about the random state at concentration  $x$ !

*Can we do better?*

- *Yes! Include higher order terms in the Taylor expansion*

# *Taylor Expansion: SDG vs Variable Basis*

*Taylor Expansion in the SDG Basis*

*Taylor Expansion in VB*

# *Taylor Expansion of the Euler Derivatives compared to Exact values*

*SDG Basis*

*Variable Basis*

*Fe-Co (Original Fit)* Published: A. Díaz-Ortiz et al., *Phys. Rev B*, 73, 224208, (2006)

- DFT (PAW)
- CE (SDG)

Variational CE (VCX) \_\_\_\_\_

# Fe-Co Phase Diagram: CVX with 14 clusters CVM Approximation: 15Points + 4 Octahedra

bcc

• Exp.  
CE (SDG)

B2

## Issues

- Energy Scale: 50 K  $\square$  4.3 meV
  - Probable Cause: using wrong thermodynamic variables for relaxed structure
  - Solution: All-electron calculations (LAPW) with Volume relaxation ONLY
- Shape
  - Probable Cause: SDG CE
  - Solution: Taylor Expansion in the VB

# Fe-Co Revisited

- *Unpublished Data (A. Díaz-Ortiz)*
  - *Un-relaxed energies for the 70 Structures*
  - *Plus the energies of an additional set of 23 un-relaxed structures*

## Next

1. *Do the Taylor Expansion in the Variable Basis using 70 un-relaxed structures. Does the PD change?*
2. *Use the CE (TVB) to calculate the energies of the 23 un-relaxed structures not used in the fitting. Is there agreement with the DFT energies?*

*Second order Taylor Expansion*  
*First and Second neighbor pairs*

# *The Energy and the ECIs (Euler Derivatives) in the VB*

# *The Fe-Co Phase Diagram*

bcc

B2

bcc

B2

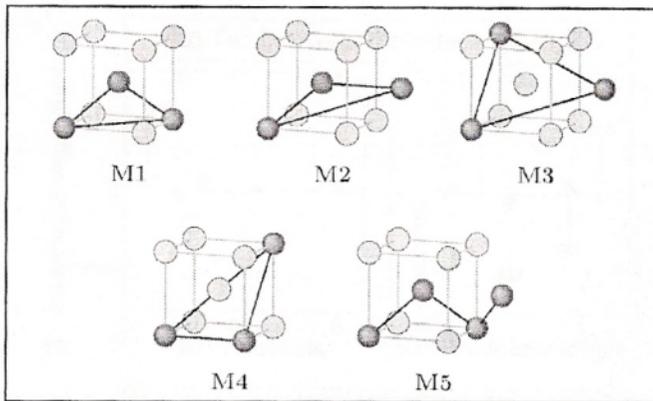
# *“Predicted” Energies for 23 un-relaxed Structures*

# Mo-Ta

Published: V. Blum & A. Zunger, *Phys. Rev. B*, 70, 155108 (2004)

Converged “Mixed Base” CE:

Empty, Point, 8 Pairs  
Plus



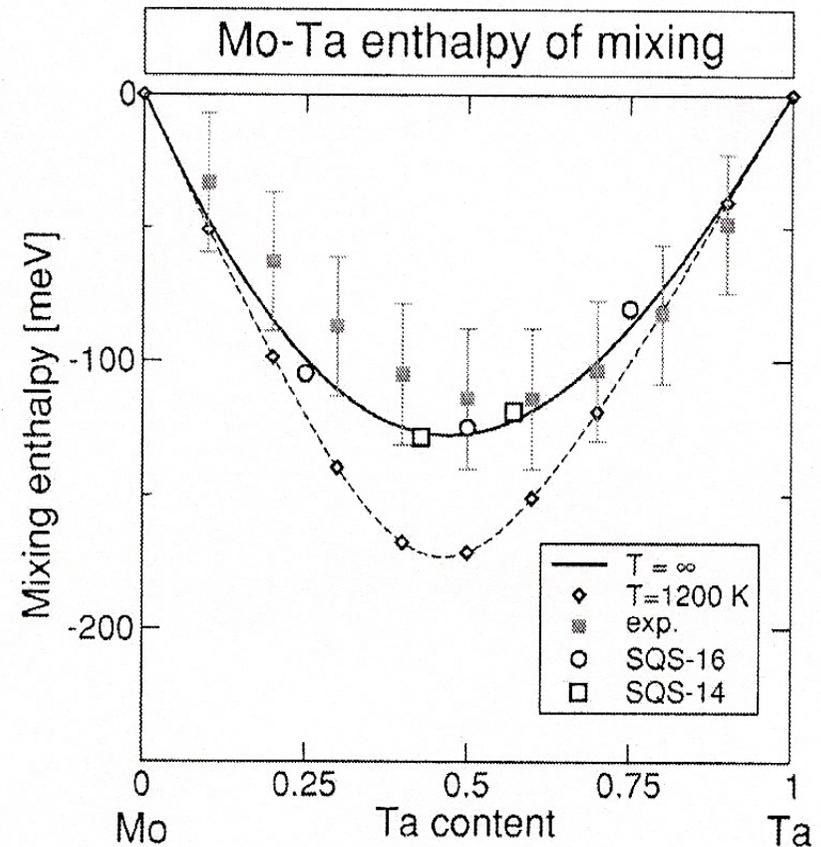
Fitting Error  $\approx 2.5$  meV

**B2 Structure**

ELAPW = -195 meV  
EVASP = -205 meV

**C11b Structure**

MoTa<sub>2</sub>:  $\delta E_{rel} = -7.1$  meV  
Mo<sub>2</sub>Ta:  $\delta E_{rel} = -23.4$  meV



“underestimating the truth”

# *The Four Issues with the Mo-Ta Calculations:*

1. *Accuracy of Projector Augmented Wave Potentials (VASP): Not a major issue unless accuracies below 10 meV are required.*

*Solution: All-electron calculations: LAPW (WIEN)*

1. *Description of the energies of fully relaxed structures using a CE with the space group symmetry of the disordered phase: Major conceptual problem (i.e. uses the wrong thermodynamic variables for the relaxed structures!)*

*Solution: DO NOT relax the structures (except for volume relaxation)*

1. *Use of a truncated CE in the SDG basis: CE does not converge. Assumes constant Euler derivatives or ECIs. Equivalent to a Taylor expansion to first order about the 50/50 random state.*

*Solution: Use a higher order Taylor expansion about the random state at each concentration  $x$  (a high order Variable Basis CE)*

1. *Number of structures (56) is not enough for a meaningful VB Taylor expansion.*

*Solution(s): Calculate more energies or overdimension the LSF and “regularize”*

# *Addressing Issues 1) and 2)*

# *The Art of Fitting*

- *Basic Principles:*

- *Use as many clusters as you can afford: 6 pairs + all clusters in the octahedron (17 clusters in all)*
- *Control non-linear terms through regularization (**but with minimum bias**)*

*Mo-Ta: 2nd order Taylor expansion in the VB*

# *Mo-Ta Enthalpy @ 1200 K*

□ Experimental

—□— Taylor VBCE  
Random (TBVCE)

—□— Blum & Zunger

# Conclusions

- *The most important result of the CE: Gives all configurational variables for an alloy with a given space group symmetry.*
- *At least three approximate versions of the CE:*
  - *SDG Basis ( $\mu = 0$ ): MDFT, ECIs are constant, good phenomenological model.*
  - *VBCE ( $\mu$  matched to concentrations): Wavelet Transform ECIs depend on concentration, better phenomenological model?*
  - *Taylor expansion in the VB: ECIs depend on all configurational variables. Might lead to a quantitative First Principles Thermodynamic Theory*

## *Issues that need to be considered (re 30 years of use of the CE):*

- *The configurational variables typically used in the CE are the wrong variables to describe fully relaxed structures*
- *A truncated CE in the SDG basis is a good phenomenological model (but*