

## Part 2: Basics of Cluster Expansions and Getting a Optimal Cluster Expansion

D.D. Johnson, Materials Science & Engineering  
Materials Computation Center, Summer School June 20, 2005

Present: Using **DFT Structural Energies** to get a Cluster Expansion

Goal: Develop ideas for **Cluster Expansions** that are optimal.

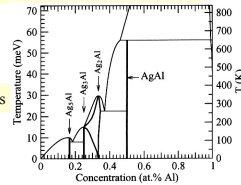
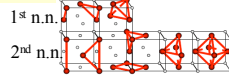
These will be develop/enhanced in remaining lectures.

$E_{DFT}^\sigma$   $\xrightarrow{CE}$   $V_i$   $\xrightarrow{\text{Monte Carlo}}$  Thermodynamics

$$E^\sigma = \sum_i V_i \Phi_i^\sigma$$

Effective Interactions

Cluster correlations



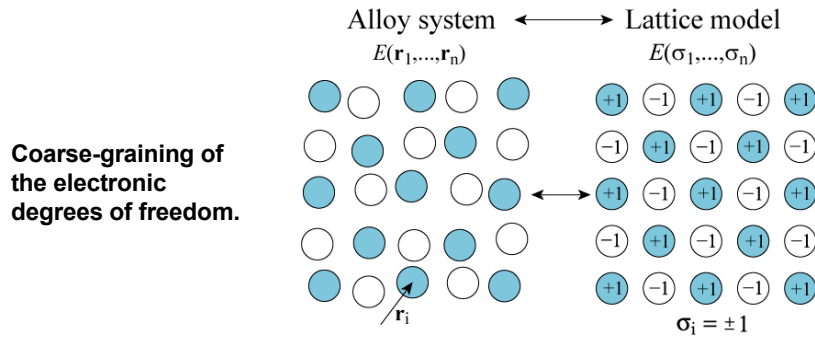
- **Cluster Expansions**: What clusters to use? What is optimal?



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## What is the “coarse-graining” Cluster Expansion concept?



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

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

With structural “correlation fcts”:  $\Phi^{\alpha}(\{\sigma\}) = \sigma_1 \dots \sigma_n$



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## Some “older” References on Cluster Expansion

$$E(\mathbf{V}; \sigma_1, \dots, \sigma_n) = \sum_{\alpha} J_{\alpha}(\mathbf{V}) \Phi^{\alpha}$$

*Just some comments, not meant to be complete! See Reviews*

### Related Effective Interactions for Thermodynamics

Many-body Interactions and effective Interactions

Sanchez and de Fontaine, in *Structures and Bonding in Crystals*, ed. by O'Keefe and Navrotsky (Academic Press, NY, 1981) Vol. 2, 117

First DFT-derived effective Interactions

Connolly, Williams, *Phys. Rev. B* **27**, 5169 (1983)

**Ground-breaking paper:** For an infinite cluster expansion, using a Chebyshev basis, the CE was shown to be complete, in mathematical sense.

Sanchez, Duscetelle and Gratias, "General Cluster Descriptions of Multicomponent Systems," 128 A, 334 (1984).

**BUT ... Cluster Expansion must be truncated for any utility - no longer complete.**

First attempt at DFT-CE with size-mismatch/vibrations included

Terakura, et al., *Phys. Rev. B* **35**, 2169 (1987);  
*J. Phys. CM* **5**, 1473 (1993)

Somewhat of a tutorial in nature but somewhat heavy-handed argument for including explicitly the strain

Alex Zunger, in *Statics and Dynamics of Alloy Phase Transformations*, NATO ASI Series, ed. P.E.A. Turchi and A. Gonis, pg. 361 (1994).

**And many, many, more with Amodor, Ozolins, Wolverton, Asta, Hart, .....**

**Various reviews and commentaries: see references therein**

D. de Fontaine, *Solid State Phys.* **47**, 33 (1994)

Johnson, "Phase stability in Alloys from Density-Functional Methods", in *Encyclopedia of Materials: Science & Technology* (Pergamon, NY, 2002)

Van der Walle and Ceder, "Effect of Lattice Vibration on Alloy Thermodynamics," *Rev. Mod. Phys.* **75**, 11 (2002).

Topical review: Muller, "Bulk and surface ordering phenomena in binary metal alloys," *J. Phys.: Condens. Matter* **15**, R1429–R1500 (2003)

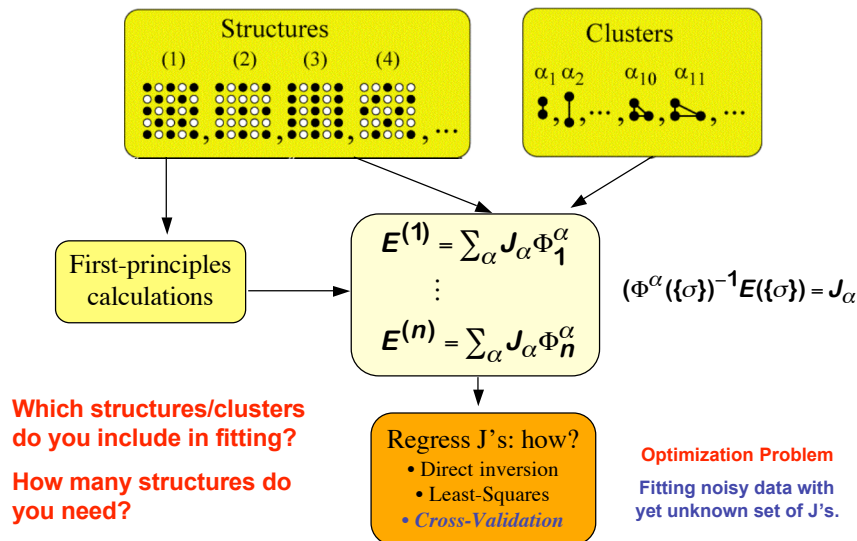
Zarkevich and Johnson, "Reliable First-Principles Thermodynamics via truncated Cluster Expansion, *Phys. Rev. Lett.* **92**, 255702 (2004)



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## Cluster Expansion Procedure



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## Cluster Expansion by Direct Inversion (Connolly-Williams)

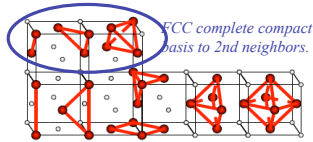
- You choose fixed number of  $n$  cluster (somehow)
- You calculate exactly  $n$  structural energies (well-chosen, guessed...)

$$\begin{aligned} E^{(1)} &= \sum_{\alpha} J_{\alpha} \Phi_{\alpha}^1 \\ &\vdots \\ E^{(n)} &= \sum_{\alpha} J_{\alpha} \Phi_{\alpha}^n \end{aligned}$$

Regress  $J$ 's by Direct inversion

$$(\Phi^{\alpha}(\{\sigma\})^{-1} E(\{\sigma\}) = J_{\alpha}$$

Connolly, Williams, Phys. Rev. B 27, 5169 (1983)



Consider FCC Cu-Au

- Use only near-neighbor interactions, and take all clusters and sub-clusters (forms a local, complete basis for n.n. range).
- Direct Inversion requires 5 structures.
- Cu-Au orders, use simple ordered cells.

There are 5 clusters for which to obtain interactions:  
Empty ( $J_0$ ), point ( $J_1$ ), pair ( $J_2$ ), triplet ( $J_3$ ) and tetrahedron ( $J_4$ ).

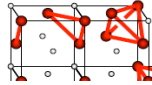


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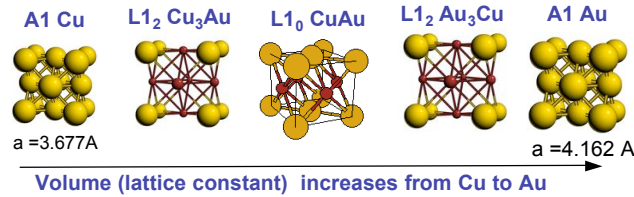


## Connolly-Williams: fcc Cu-Au

Need empty ( $J_0$ ), point ( $J_1$ ), pair ( $J_2$ ), triplet ( $J_3$ ) and tetrahedron ( $J_4$ ).



Direct Inversion requires 5 small unit cell structures.  
Why these? They were known from phase diagram!



What are DFT Formation Energies?

$$E = \begin{pmatrix} 0 \\ -35.6 \\ -64.9 \\ -49.8 \\ 0 \end{pmatrix} \text{meV}$$

See today' lab

What are correlation functions for those structures?

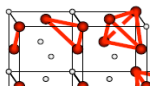
$$\Phi^n(\{\sigma\}) = \sigma_1 \cdots \sigma_n$$



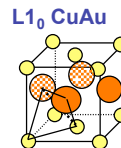
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## Correlation Fct. for L1<sub>0</sub> CuAu



Define variables: Cu as  $\sigma = +1$  and Au as  $\sigma = -1$   
 Consider the 4-atom cell (and up to 4-body)



$$\Phi^0 = 1$$

Always a constant

$$\Phi^1 = \langle \sigma_1 \rangle = 0$$

4 sites:  $[2(+1) + 2(-2)]/4 = 0$

$$\Phi^2 = \langle \sigma_1 \sigma_2 \rangle = -1/3$$

4-atoms x 12n.n. = 48 2-atom clusters

each atom has 4-like n.n. and 8-unlike n.n

$$\frac{1}{48} [32 \cdot (+1)(-1) + 8 \cdot (+1)(+1) + 8 \cdot (-1)(-1)] = -1/3$$

$$\Phi^3 = \langle \sigma_1 \sigma_2 \sigma_3 \rangle = 0$$

Triplets always with  $[2(+1)(+1)(-1) + 2(+1)(-1)(-1)] = 0$

$$\Phi^4 = \langle \sigma_1 \sigma_2 \sigma_3 \sigma_4 \rangle = 1$$

Tetrahedron  $(-1)(-1)(+1)(+1) = 1$

Thus,

$$\Phi^{L10} = \begin{pmatrix} 1 & 0 & -1/3 & 0 & 1 \end{pmatrix}$$

See addendum slides at end for simple way.

You do the others in today' lab

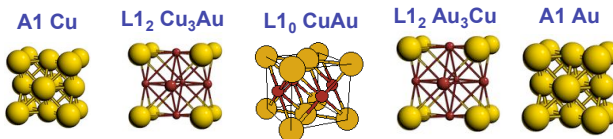


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## Completing the Connolly-Williams: fcc Cu-Au

Direct Inversion to get empty (J0), point (J1), pair (J2), triplet (J3) and tetrahedron (J4).



Correlation functions do not depend on Volume, just structure!

$$J = \Phi^{-1}E \quad \text{with} \quad \Phi^{-1} = \frac{1}{16} \begin{pmatrix} 1 & 4 & 6 & 4 & 1 \\ 4 & 8 & 0 & 8 & 4 \\ 6 & 0 & -12 & 0 & 6 \\ 4 & -8 & 0 & 8 & -4 \\ 1 & -4 & 6 & -4 & 1 \end{pmatrix} \quad E = \begin{pmatrix} 0 \\ -35.6 \\ -64.9 \\ -49.8 \\ 0 \end{pmatrix} \text{ meV}$$

$$\text{So } J = \begin{pmatrix} -45.7 \\ -7.1 \\ +48.7 \\ 7.1 \\ -3 \end{pmatrix}$$

Note that J2 > 0, so system want Cu next to Au: ordering

J4 < 0 very small but favors clustering.

See addendum slide regarding getting energies for any other configurations to which you did NOT fit.



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## Direct Inversions: a few thoughts

- If a cluster expansion is constructed by solving a system of linear equations with equal number of unknown interactions and known formation energies, then by definition this direct inversion has no fit error.

- The least-square error is zero!

- But, what happens when you include more structures (in order to include more physics: configurations and correlations)? Are you predictive?

- If more structures and clusters are added, will these J's change?

$$J = \begin{pmatrix} -45.7 \\ -7.1 \\ +48.7 \\ 7.1 \\ -3 \end{pmatrix}$$

Need to include more structures, without more interactions necessarily.

Best to use Least-Squares (or better) method.



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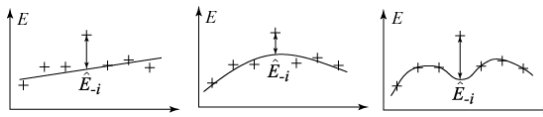
## Cross Validation Score (CV): LS Remove-n Estimator

Fit prediction error  $(CV1)^2 = \frac{1}{N} \sum_{i=1}^n (E_i - \hat{E}(i))^2$

Directly calculated energy

CE predicted energy of structure "j" obtained from fit to n structures: 1, 2, ..., i-1, i+1, ... n  
↑  
i<sup>th</sup> remove  
CV1 or remove-1 estimator.

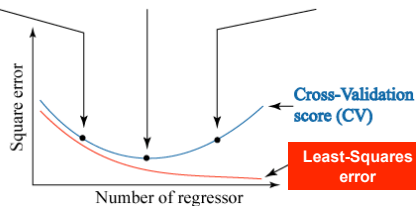
### Example of polynomial fitting via LS and CV1



CV1 is estimate of predictive error.

Ex. references:

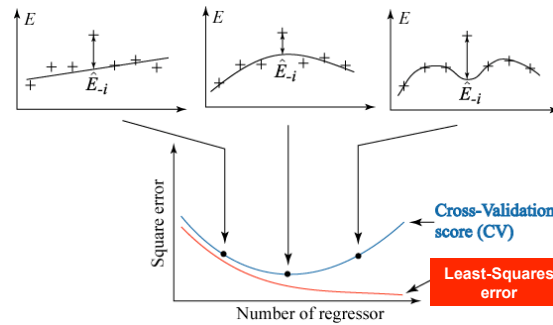
- W. Conover, "Practical nonparametric statistics," Wiley, pp 206-209, 303 (1971).
- M. Stone J. Roy. Stat. Soc. B Met. 36, 111 (1974).
- D.M. Allen, Technometrics 6, 126 (1974).
- CE: Van der Walle, Ceder, J. of Phase Equil. 23, 348 (2002).



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## CV0 = LS is not helpful for predictive power



- Least-squares procedure to reduce fit error essentially *meaningless*.
- Can always add clusters and reduce LS error!



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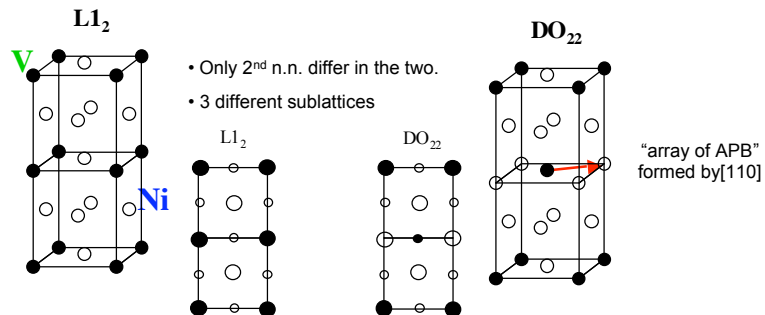


## Uniqueness of CE fit can to be problem: e.g., fcc Ni<sub>3</sub>V

- Ni<sub>3</sub>V has an observed DO<sub>22</sub> ground-state structure.
- Many T = 0 K DFT total energy calculations have been done: DO<sub>22</sub> < L1<sub>2</sub>.  
 $\Delta E(L1_2 - DO_{22}) = 111 \text{ meV}$  (DO<sub>22</sub> lower)

All present and previous calculations agree!

Xu et al. PRB 35, 6940 (1987); Pei et al. PRB 39, 5767 (1989); Lin et al., PRB 45, 10863 (1992),  
Wolverton and Zunger PRB 52, 8813 (1995). Johnson et al., Phys. Rev. B 62, RC11917-20 (2000)



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## DFT and SRO Diffuse Scattering Data

• T=0 K DFT calculations:  $\Delta E(L1_2 - DO_{22}) = 111 \text{ meV}$  ( $DO_{22}$  lower)

• Diffuse scattering (SRO) data:  $\Delta E(L1_2 - DO_{22}) = 10 \pm 5 \text{ meV}$

from  $\Delta\alpha^{-1}$  data at  $T_{\text{expt}} = 1373 \text{ K}$  and  $T_c = 1318 \text{ K}$

Finel et al. NATO-ASI vol. 256 (1993) and Barrachin et al. PRB 50, 12980 (1994)

• DFT Theory estimate 10x larger than experimental assessment!

Is experiment estimate invalid?      Is T=0 K DFT results wrong?

Recall: SRO data is related to Free-Energy change:  $\Delta F = \delta c + \alpha^{-1} \delta c \propto \eta^2 \alpha^{-1}$

$\Delta E(\text{Dis-Ord})$  is linear in  $\eta^2$  (as assumed in experiment).

$$E_{DO_{22}}(\eta) - E_{L1_2}(\eta) \sim \eta^2 [\alpha^{-1}(1,1/2,0) - \alpha^{-1}(100)] - k_B T \Delta S$$

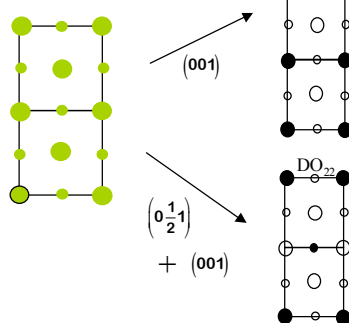


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## Consider the Effects of Partial Order (like in real systems)

A1 (fcc disordered)



$$c_i^y = \frac{1}{4} + \frac{1}{4} \eta_{001} (e^{i2\pi x} + e^{i2\pi y} + e^{i2\pi z})$$

$$c_i^y = \frac{1}{4} + \frac{1}{4} \eta_{001} (e^{i2\pi z}) + \frac{1}{2} \eta_{0\frac{1}{2}1} (\cos 2\pi(y + \frac{1}{2}z))$$

• Based only on SRO,  $\Delta F \sim \eta^2 \alpha^{-1}(k)$  so that ( $\Delta S=0$  for pts and pairs!)

$$E_{DO_{22}}(\eta) - E_{L1_2}(\eta) \sim \eta^2 [\alpha^{-1}(1,1/2,0) - \alpha^{-1}(100)]$$

• As done in experimental analysis, make  $\eta \equiv \eta_{001} = \eta_{01/21}$  (1 LRO parameter)

•  $\eta(T)$  has T-dependence that must be determined from statistical average.



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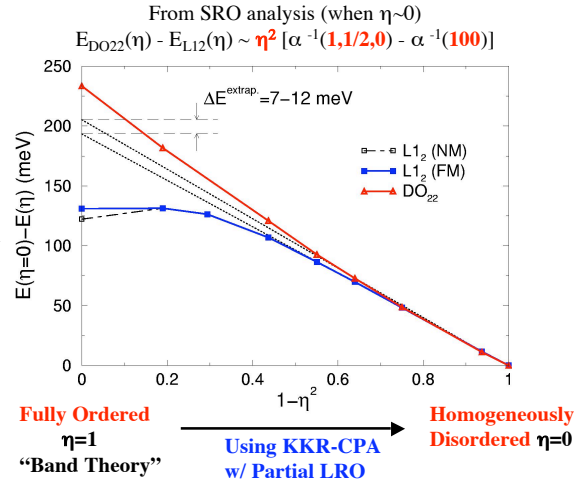
## KKR-CPA: direct calculation of partially-ordered state

- T=0 K DFT get **~100 meV**, now seen to be *not relevant to SRO expt.* that found **10±5 meV**

- ΔE depends on *configuration*, i.e., on LRO parameter for L1<sub>2</sub>, originates from electronic DOS.

- *Extrapolation* from *high-T P-LRO* states yields ΔE from SRO.

(Should not be a general expectation.)



Johnson et al., Phys. Rev. B **62**, RC11917 (2000)



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## KKR-CPA: electronic DOS vs $\eta$ (LRO parameter)

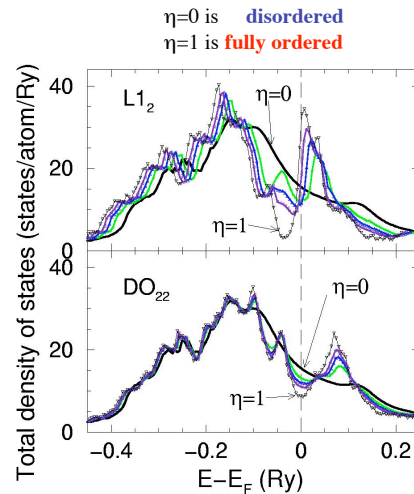
- Band Energy  $\sim \int d\epsilon (\epsilon - \epsilon_F) n(\epsilon)$

$$\Delta E \propto \delta n \propto \delta c \propto \eta$$

- Coulomb Energy  $\Delta E = 0$  as cell and atomic charges same.

- Average DOS  $n(\epsilon) = \sum_s \sum_\alpha c_{\alpha,s} n_{\alpha,s}(\epsilon)$

Symmetry breaking from  $c = c_0 + \delta c$   
 because all  $n_{\alpha,s}(\epsilon)$  about the same.



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## KKR-CPA: electronic DOS vs $\eta$ (LRO parameter)

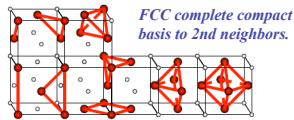
- Experimental measurement is correct.  
**10 meV** is energy associated with SRO.
- T=0 K DFT calculations are correct.  
**111 meV** is energy associated with LRO. **Just not relevant to experiment!**
- Direct SRO (KKR-CPA) calculation gives **8.3 meV**.
- Direct KKR-CPA Energy as function of LRO gives all!  
**7-12 meV** for high-T SRO      **111 meV** for T=0 K LRO
- Experiment and theory were comparing *apples and oranges*.
- But, also previous CE fits incorrectly got **111 meV** for SRO! Why?



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## Optimal Truncated Cluster Expansion: fcc $Ni_3V$



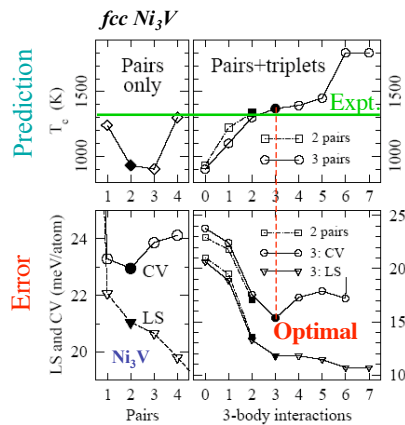
For *variational optimization problem with truncated basis*, one can show:

➤ Include **all smaller  $n$ -body clusters** and **all subclusters**  $\Rightarrow R(n) \leq R(n-1)$ .

✓ basis with a *local compact support*.

➤ **Minimizing CV1-score** then yields optimal CE basis (no 'holes' in basis).

$$CV^2 = \frac{1}{N} \sum_{i=1}^N (E_i - \hat{E}_i^{fit})^2$$



N.A. Zarkevich, D.D. Johnson, *Phys. Rev. Lett.* 92, 255702 (2004)

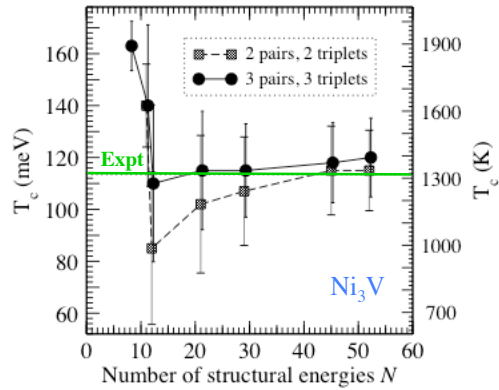
Lecture by Dr. Zarkevich will give more details and other useful items



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**Optimal CE Gives Thermodynamic Predictions that converge to Experimental Data within given CVI-score (accuracy)**



See today' lab



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**CE-Predicted Ni<sub>3</sub>V Structural Energies (meV)**

- CE<sub>3</sub> (3 pairs and 3 triplets)  
LS error = 11.9 meV  
CV error = 15.2 meV  
DFT energy rel. error ~1 meV.
- CE finds *23 long-period superstruc.* lower in energy than L1<sub>2</sub>, which were confirmed by direct DFT calculations.
- Diffraction pts:  $(1 \frac{1}{2m} 0)$ 
  - Hence L1<sub>2</sub> not well described in 2nd truncation, as found by CPA.
- Triplets important, hence, disordered state ≠ SQS.

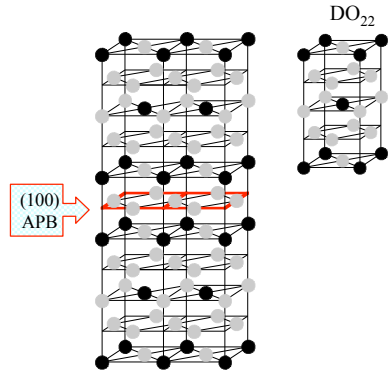
Structure (k-pt)	VASP	CE <sub>3</sub>	dE
<b>DO<sub>22</sub></b> (1 1/2 0) 0	00.0	10.5	10.5
<b>DO<sub>23</sub></b> (1 1/4 0) 2	25.4	35.8	10.4
3	33.7	35.8	2.1
4	43.6	30.6	-13.0
5	46.6	45.3	-1.5
13	79.9	101.0	21.1
14	85.3	95.3	10.0
<b>L1<sub>2</sub></b> (1 0 0) 24	101.2	56.1	-45.1
30	114.2	111.0	-3.2
<b>CE-disordered</b>	-	115.1	-
31	115.4	111.0	-4.4
42	147.8	153.2	5.4
43	148.7	159.5	10.6
44	152.7	137.6	-15.1
<b>SQS<sub>16</sub></b> 45	155.4	152.0	-3.5
46	158.1	153.2	-4.9
47	159.0	144.5	-14.6
52	212.6	197.0	-15.6



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## (001) antiphase boundary (APB) within the $DO_{22}$ phase



In the range of the truncations, the best estimate of APB energies is  $DO_{23} - DO_{22}$ .

$$E^{APB} = 4[E_{CE}^{DO_{23}} - E_{CE}^{DO_{22}}]$$

	DFT	CE
$E^{DO_{23}-DO_{22}}$	25.4	25.3±15
$E^{001\ APB}(\eta=1.0)$	101.6	101.2±15
$E^{001\ APB}(\eta=0.8)$		65±15
$E^{001\ APB}(\eta=0.7)$		50±15
T= 273 K		
expt	T= 273 K	T=900 K
$E^{001\ APB}$	52±20	55±18

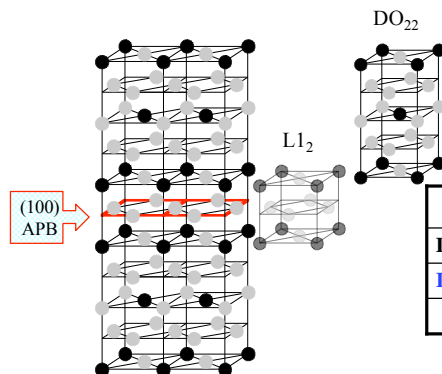
Experimental values are rather independent of temperature, due to limited kinetics.  
~75% partial order there is agreement to experiment.



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## CE not always good: (001) APB from metastable $L1_2$



In the range of the truncations,

$$\begin{aligned} \Delta E_{CE}^{L1_2-DO_{22}} &= E_{CE}^{L1_2} - E_{CE}^{DO_{22}} \\ &= 2[E_{CE}^{DO_{23}} - E_{CE}^{DO_{22}}] = E^{APB} / 2 \end{aligned}$$

	DFT	CE	error
$DO_{23}-DO_{22}$	25.4	25.3	-0.1
$L1_2 - DO_{22}$	101.2	50.5	-50.7
$001\ APB$	101.6	101.1	-0.5

$$\Delta E_{CE}^{L1_2-DO_{22}} \neq \Delta E_{DFT}^{L1_2-DO_{22}}$$

• But because  $L1_2$  is highly metastable, any truncated CE is *suspect versus LRO* unless clusters that distinguish  $L1_2$  from  $DO_{22}$  are included in CE.

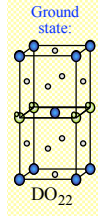
• If you force  $L1_2$  to be fit at perfect LRO without those clusters, then CE is overfit.



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## Optimal Truncated CE results are Robust and Agree with Experiment.



Ni <sub>3</sub> V	Expt.	First-Principles Theory		
		CPA	Cluster Expansion	
			Previous	Present
<b>CE Rule</b>			violated	obeyed
$T_c$ (K)	1318 K		1900 K	1370 K
$E_{(L1_2-DO_{22})}^{SRO\text{-extracted}}$ (meV)	12±5	7-12*	105*	17
CV score (meV)	-	-	-	15
LS error (meV)	-	-	3	12
$E_{(100)APB}$ (meV)	50±20 @273K 55±18 @900K		105	101.6 @ 0K 50-65 @T≠0

Experiment: A. Finel, M. Barrachin, R. Caudron, A. Francois, in *Metallic Alloys: Experimental and Theoretical Perspective*, p. 215-224 (Kluwer, Dordrecht, 1994);  
M. Barrachin *et al.*, PRB **50**, 12980 (1994).

\*CPA: D.D. Johnson, et al., PRB **62**, R11917 (2000).  
\*Previous Cluster Expansion:  
C. Wolverton, A. Zunger, Z.W.Lu, PRB **49**, 16058;  
Z.-W. Lu and A.Zunger, PRB **50**, 6626 (1994);  
C. Wolverton, A.Zunger, PRB **52**, 8813 (1995).



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## Cluster Expansions: Synopsis

- Cluster Expansions are valuable for thermodynamics.
- Need **database** and **optimization** to provide basis with compact local support.
- KKR-CPA provides physical insight to **resolve** previous failures, and CE and KKR-CPA now agree.
- We have **provided a framework** and, now have **toolkit**, to perform such calculations, as long as database is there.

Note:

- 1) **Selectively removing (or adding) structures can make CV smaller, but usually gives bad disordered energy.** Do not choose longer-ranged clusters at the expense of shorter-ranged ones, for they re-weight the interactions, and often can lead to a *smaller* CV1-score but *worse* thermodynamics due to bad disordered energy.
- 2) **Throwing away clusters arbitrarily usually results in the wrong disordered energy. So do not make "holes" in the basis.**

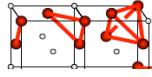
Next Slides: addendum's



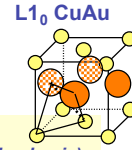
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## Addendum: Correlation Fct. for L1<sub>0</sub> CuAu



Define variables: Cu as  $\sigma = +1$  and Au as  $\sigma = -1$   
Consider the 4-atom cell (and up to 4-body)



For n.n. clusters only: an easy way to count and get correlations.  
Use the 4-atom tetrahedron (translated it gives you structure, as it is fcc with a basis).  
You have 6 edges (all pairs), 4 faces for triplets, and 1 tetrahedron.

Always

$$\Phi^0 = 1 \quad \Phi^1 = \langle \sigma_1 \rangle = 0 \quad \text{4 site average: } [+1 +1 -1 -1]/4 = 0$$

$$\Phi^2 = \langle \sigma_1 \sigma_2 \rangle = -1/3 \quad \text{6-sides with pairs: } [(+1)(+1) + (-1)(-1) + 4(-1)(+1)]/6 = -1/3$$

$$\Phi^3 = \langle \sigma_1 \sigma_2 \sigma_3 \rangle = 0 \quad \text{4-faces with triplets: } [2(+1)(+1)(-1) + 2(+1)(-1)(-1)]/4 = 0$$

$$\Phi^4 = \langle \sigma_1 \sigma_2 \sigma_3 \sigma_4 \rangle = 1 \quad \text{Tetrahedron } [(-1)(-1)(+1)(+1)]/1$$

$$\Phi^{L10} = (1 \quad 0 \quad -1/3 \quad 0 \quad 1)$$



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## Addendum: Connolly-Williams for fcc Cu-Au

We did direct inversion from 5 structures and got interactions  
empty (J<sub>0</sub>), point (J<sub>1</sub>), pair (J<sub>2</sub>), triplet (J<sub>3</sub>) and tetrahedron (J<sub>4</sub>).

$$E(V; \sigma_1, \dots, \sigma_n) = \sum_{\alpha} J_{\alpha}(V) \Phi^{\alpha} \quad \text{With interactions}$$

$$J = \begin{pmatrix} -45.7 \\ -7.1 \\ +48.7 \\ 7.1 \\ -3 \end{pmatrix}$$

Now we can immediately calculation millions!! of other configurations  
with n-th correlations obtained from Monte Carlo to get  $\langle \sigma \dots \sigma \rangle$ .

The simplest one to do by hand is the fully-disordered state  
(homogeneous solid solution - only really at very-very high-T).

$$\Phi^n = \langle \sigma \dots \sigma_n \rangle = \langle \sigma \rangle^n \quad \text{at 50\% Au} = \langle \sigma \rangle^n = 0, \quad \text{for example.}$$

Thus, the energy of the disordered Cu<sub>50</sub>Au<sub>50</sub>  $E^{\text{dis}} = J_0 = -46 \text{ meV}$ .

(Of course, this is incorrect (should be near zero!) because we did not  
take into account size-mismatch, which is large in Cu-Au system.

Simple T<sub>c</sub> estimate would be  $E^{\text{dis}} - E^{L10} = -46 + 66 \sim 20 \text{ eV}$  (~200 K).  
If size-mismatch included it would be ~66 meV (~760 K), close to expt!



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## Addendum: fcc Cu-Au with Occupation Variable

Occupation Variables are better, easier to generalize and more intuitive!

Occupation Variable  $\xi_i = \begin{cases} 1 & \text{if solute} \\ 0 & \text{if not} \end{cases}$  e.g., for Cu<sub>3</sub>Au, Au = 1 (Cu = 0)

Instead of  $E(V; \sigma_1, \dots, \sigma_n) = \sum_{\alpha} J_{\alpha}(V) \Phi^{\alpha}$  use  $E(V; \xi_1, \dots, \xi_n) = \sum_{\alpha} J_{\alpha}(V) \Phi^{\alpha}(\{\xi\})$

Again, correlations for L10 Cu<sub>3</sub>Au: 4-atom cell (and up to 4-body)

Always  $\Phi^1 = \langle \xi_1 \rangle = (0 + 0 + 0 + 1) / 4 = 1/4$   
 $\Phi^0 = 1$  Probability of Au (Concentration)

$\Phi^2 = \langle \xi_1 \xi_2 \rangle = [4 \cdot (1)(0) + 1 \cdot (1)(0) + 1 \cdot (1)(1)] / 6 = 1/6$  Probability of Au-Au pair!

NO probability of Au triplets!  $\Phi^3 = \langle \xi_1 \xi_2 \xi_3 \rangle = 0$

$\Phi^4 = \langle \xi_1 \xi_2 \xi_3 \xi_4 \rangle = 0$  NO probability of Au tetrahedron

$\Phi^{L10} = (1 \quad 1/4 \quad 1/6 \quad 0 \quad 0)$

Exercise: Try re-doing Cu-Au with these variables and get disordered energy. How do things change?

