IDEAS FROM MULTI-STATE MEAM APPLIED TO THE Pu-Ga SYSTEM

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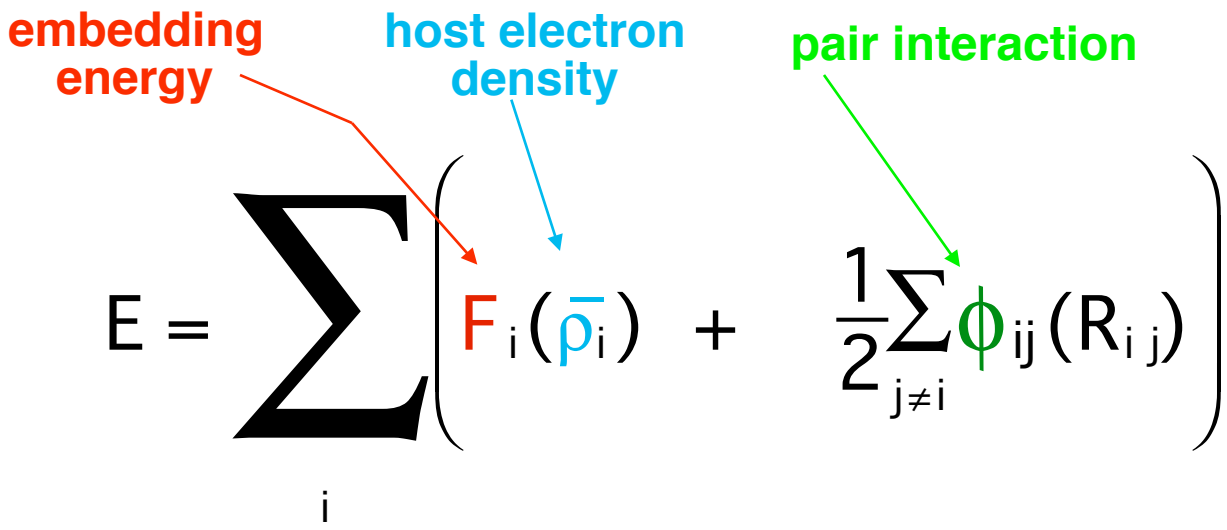
OUTLINE

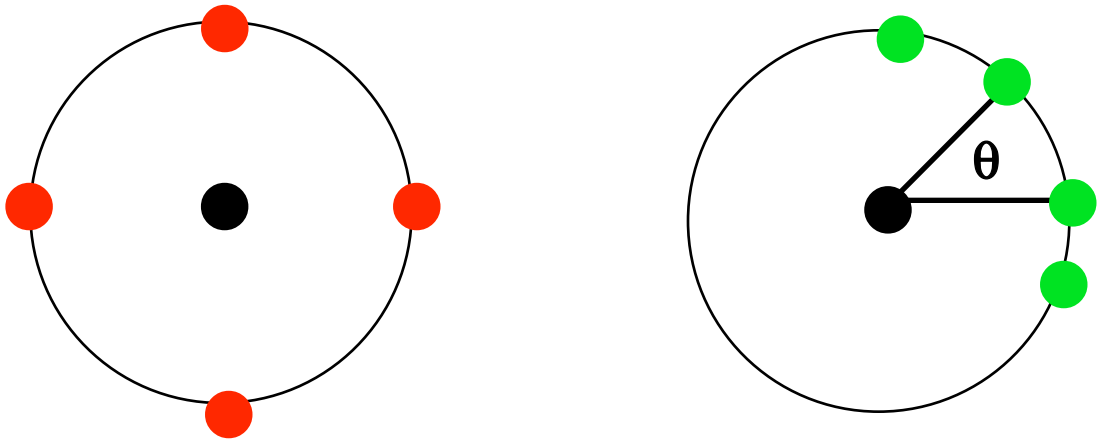
- **Modified EAM (MEAM)**
- **Multi-State MEAM**
- **Application to the Pu-Ga System**

WE ARE ALL FAMILIAR WITH THE EMBEDDED ATOM METHOD FORMALISM



COMPLEX MATERIALS REQUIRE THE ADDITION OF ANGULAR FORCES

- **EAM uses a linear superposition of spherically averaged electron densities**
- **MEAM allows the background electron density to depend on the local symmetry**



MEAM USES A LINEAR COMBINATION OF WEIGHTED SQUARES OF PARTIAL ELECTRON DENSITIES

$$\overline{\rho} = \rho^0 \sqrt{1+\Gamma}$$

$$\Gamma = \sum_{l=1}^{3} \overline{t}^{\,l} \left(\rho^l / \rho^0\right)^2$$

$$\left(\rho^l\right)^2 = \sum_i \rho^{al}\left(R_{ik}\right) \sum_j \rho^{al}\left(R_{kj}\right) P_l^0\left(\cos\left(\theta_{ikj}\right)\right)$$

For alloys, the weighting factors are taken as a function of the local environment and the atomic weighting factors

WE DEVELOPED MS-MEAM AND APPLIED IT TO Cu

- **First Principles data base (VASP)**
- **Almost identical formalism to MEAM**
- **Almost no ad-hoc functions**

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MS-MEAM/MEAM FORMALISM COMPARED

MS-MEAM

$$\bar{\rho}_i^2 = \left(\rho_i^0\right)^2 + \sum_{l=1}^{3}\left[\left(\rho_i^{l+}\right)^2 - \left(\rho_i^{l-}\right)^2\right]$$

MEAM

$$\bar{\rho}_i^2 = \left(\rho_i^0\right)^2 + \sum_{l=1}^{3}\left[\bar{t}^{\,l}\left(\rho_i^l\right)^2\right]$$

+ ad-hoc equation for $\bar{t}$

WE NOW PARAMETERIZE THE ATOMIC ELECTRON DENSITIES

MS-MEAM

$$\rho_\alpha^{al\pm}(R) = \rho_{0\alpha}^{a} a_\alpha^{l\pm} \exp\left[-\beta_\alpha^{l\pm}\left(\frac{R}{R_{0\alpha}} - 1\right)\right]$$

MEAM

$$\rho_\alpha^{al}(R) = \rho_0^{a} \exp\left[-\beta_\alpha^{l}\left(\frac{R}{R_{0\alpha}} - 1\right)\right]$$

where we can relate the a's and β's in MS-MEAM to the t's and β's in MEAM

$$\left.\begin{aligned} a_\alpha^{l+} &= \sqrt{t_\alpha^{l}}, \quad \beta_\alpha^{l+} = \beta_\alpha^{l} \\ a_\alpha^{l-} &= \sqrt{-t_\alpha^{l}}, \quad \beta_\alpha^{l-} = \beta_\alpha^{l} \end{aligned}\right\} \begin{aligned} t_\alpha^{l} &> 0 \\ t_\alpha^{l} &< 0 \end{aligned}$$

MEAM FOR Pu WAS GENERALLY SUCCESSFUL – BUT SOME PROBLEMS APPEARED

- **Properties reproduced**
  - **complex crystal structures**
    - ➢ **α (monoclinic) stable at RT**
  - **unusual volume behavior**
    - ➢ **δ (fcc) has largest volume/atom**
- **Problems**
  - **at 0K hcp required to be more stable than fcc (in contradiction with recent first principles calculations)**
  - **large partial dislocation separation predicted (in conflict with TEM in alloys)**

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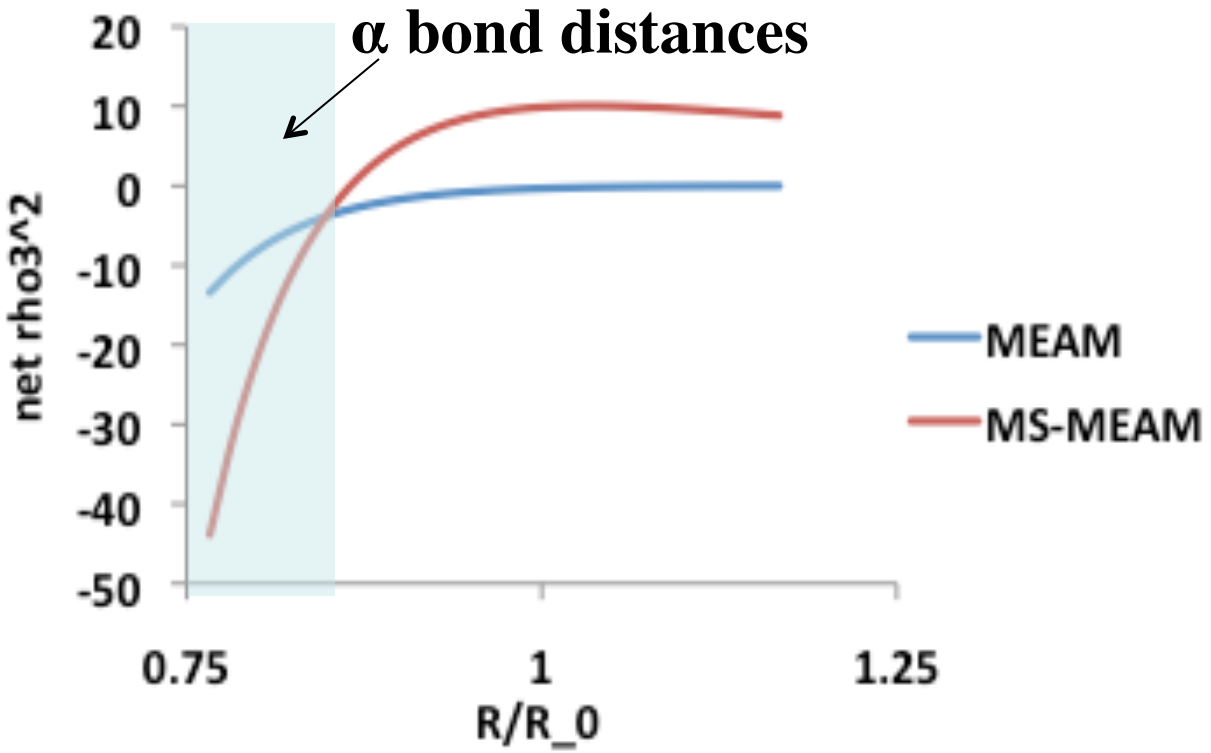
CHANGE TO MS-MEAM FORMALISM APPEARS TO BE SUCCESSFUL

- **All MEAM parameters (or equivalent) retained except:**

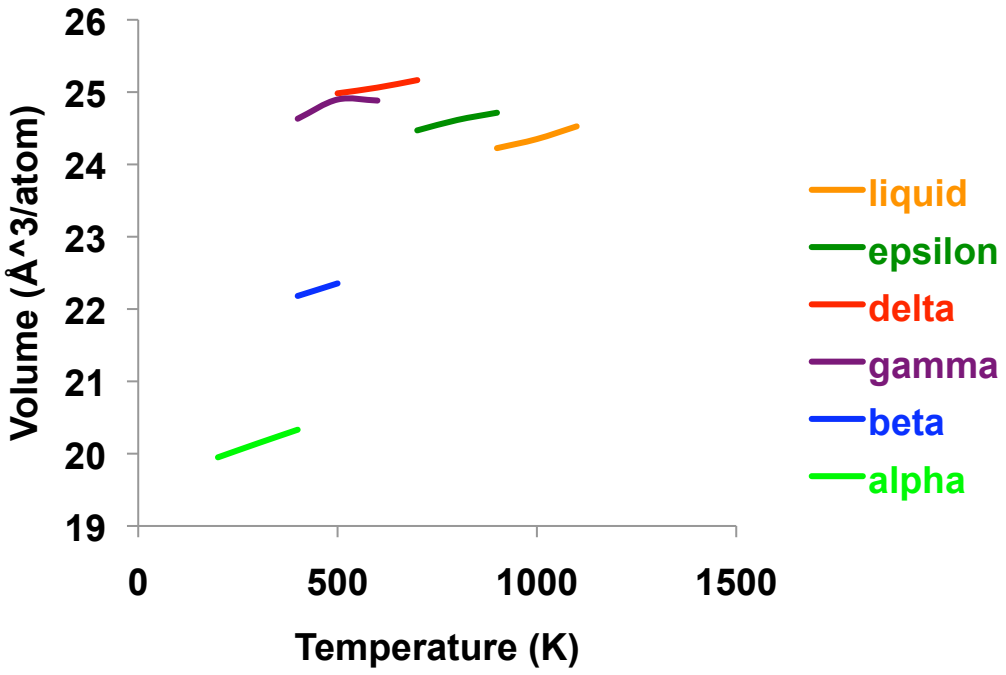
MEAM → **MS-MEAM**

$$\beta_{Pu}^{3} = 9; t_{Pu}^{3} = -0.8 \Rightarrow \begin{matrix} \beta_{Pu}^{3+} = 0.9; a_{Pu}^{3+} = 3.5 \\ \beta_{Pu}^{3-} = 7; a_{Pu}^{3-} = 1.54 \end{matrix}$$

RESULTANT CHANGE IN f-PARTIAL ELECTRON DENSITY



PREDICTED VOLUMES MIRROR EXPERIMENT



- δ predicted to have largest volume/atom
- volume decrease upon melting
- γ volume predicted higher than experiment

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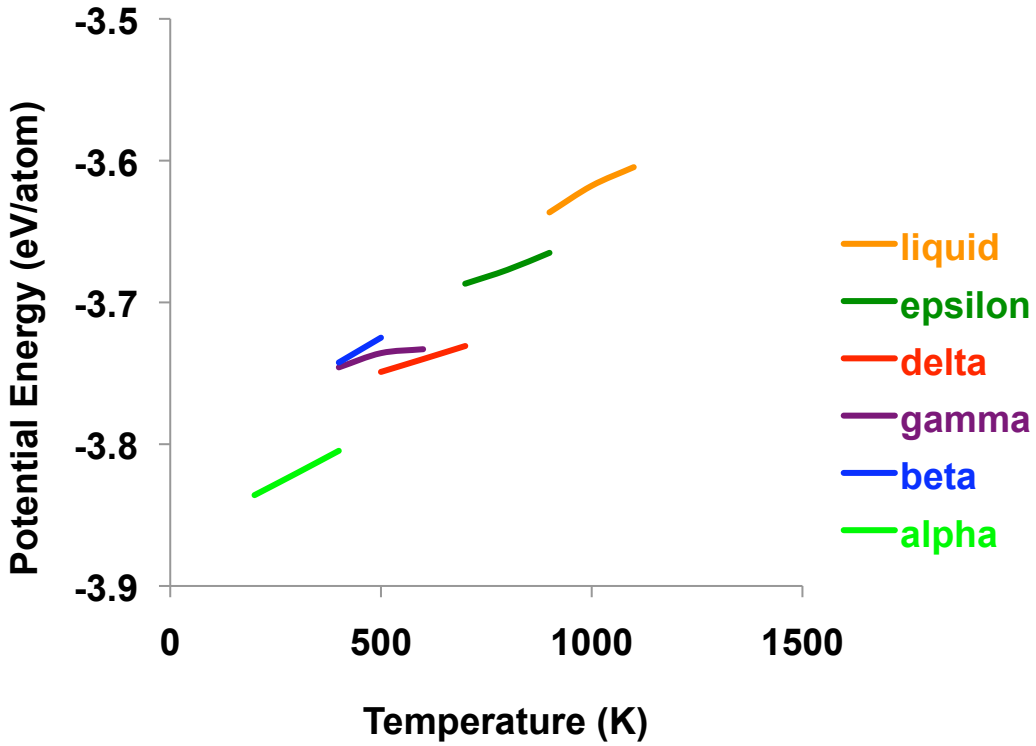
PREDICTED PHASE STABILITY IN GOOD AGREEMENT WITH EXPERIMENTAL PHASE DIAGRAM



- **Ordering of phases is correct except for β and γ**
- **Free energies determine phase boundaries**

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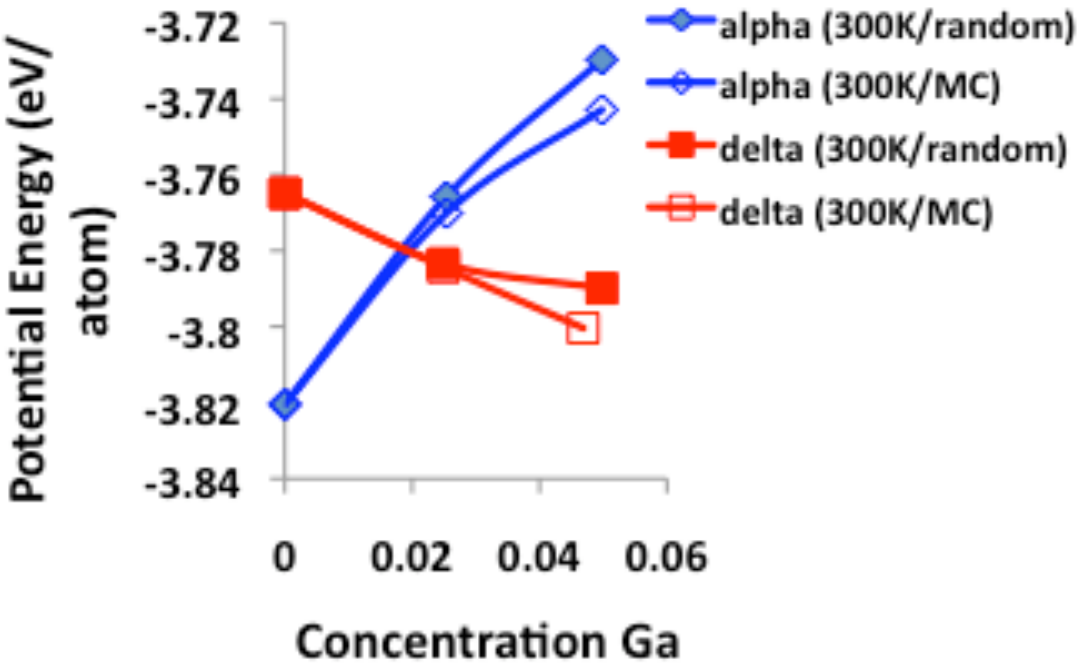
REASONABLE DEFECT ENERGIES NOW FOUND FOR δ

	MS-MEAM	F.P.
Stacking fault energy	158 mJ/m^2	
(111) surface energy	412 mJ/m^2	
Vacancy formation energy	1.28 eV	
hcp-fcc energy difference	0.04 eV/atom	0.07-0.13

MEAM PARAMETERS RETAINED FOR Ga AND Pu-Ga

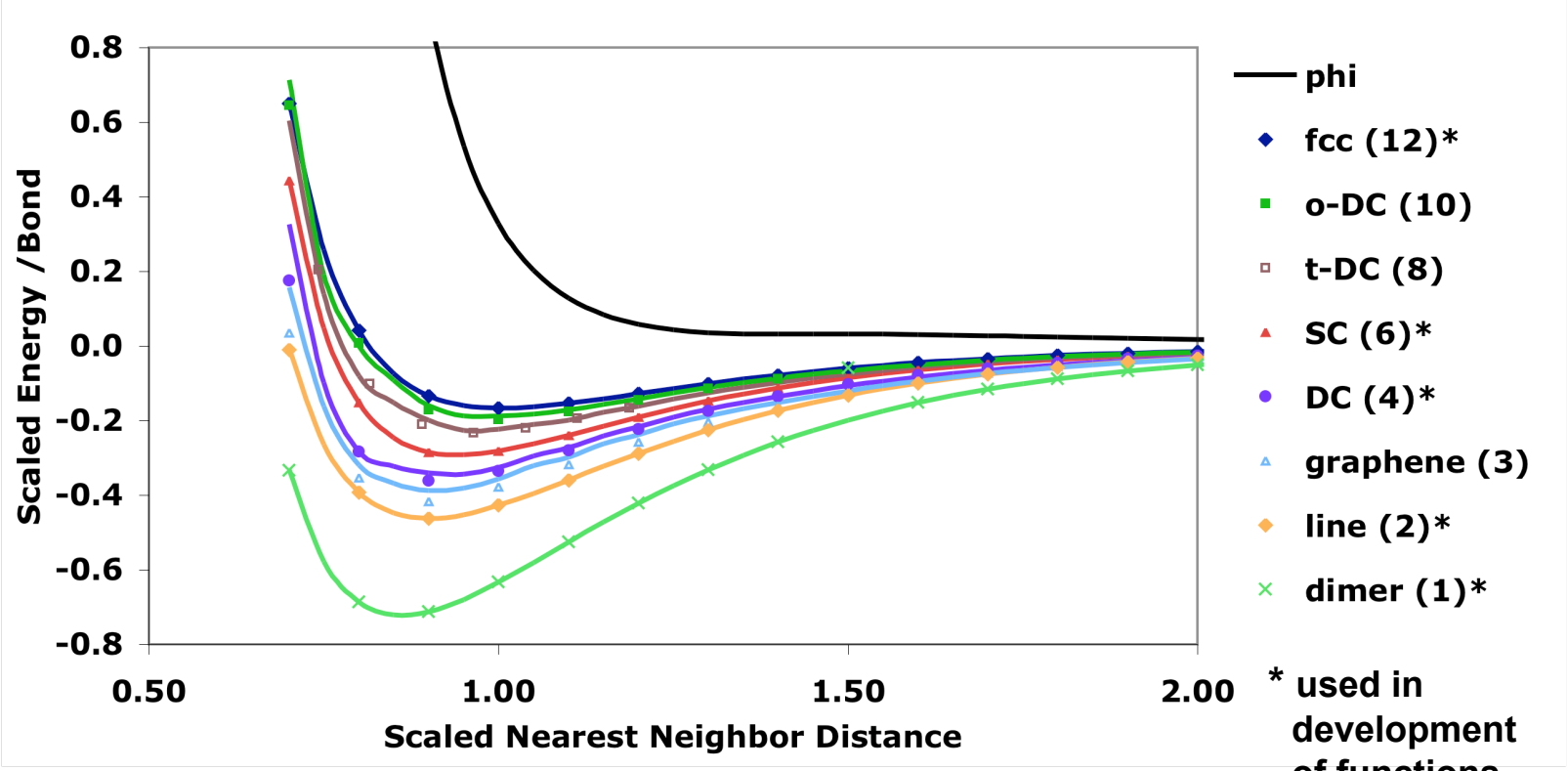


Ga stabilizes δ w.r.t. α as seen in experiment

CONCLUSION

As suggested by MS-MEAM, including both positive and negative f-partial electron densities for Pu leads to a more physical model for the Pu-Ga system

MS-MEAM IS PREDICTIVE FOR ENERGY vs. NN DISTANCE



coordination 1-12

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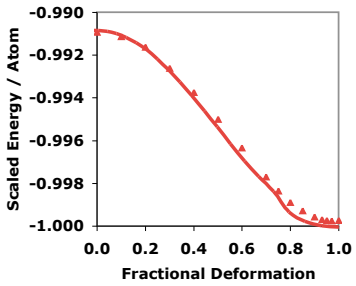
TRANSFORMATIONS ARE A SERIOUS TEST OF TRANSFERABILITY



beam(4)
t-DC(6)

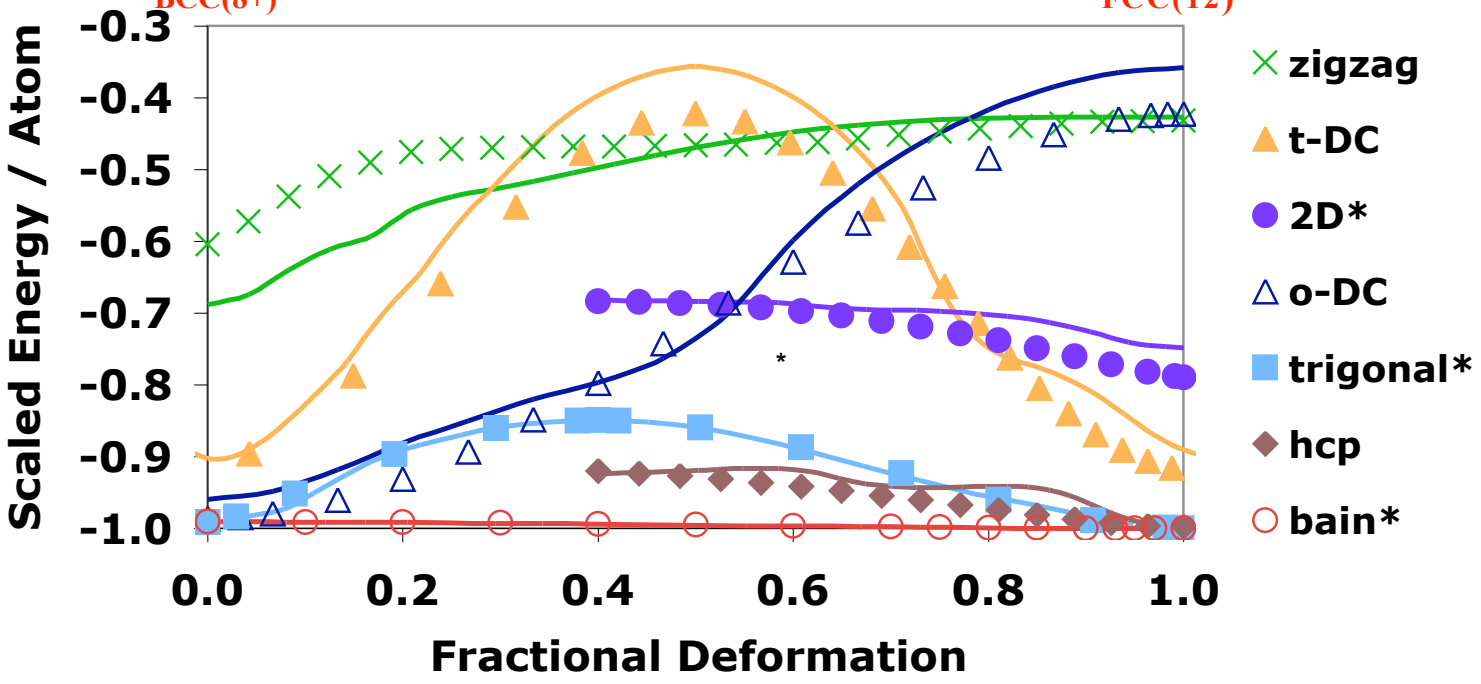
o-DC(10)
BCC(8+)

BCC(8+)

DC(4)
2D-square (4)

SC(6)
cubic(6)

line(2)
t-DC(8)
2 D - h e xagonal (6)
DC(4)
FCC(12)
HCP(12)
FCC(12)



* used in development of functions

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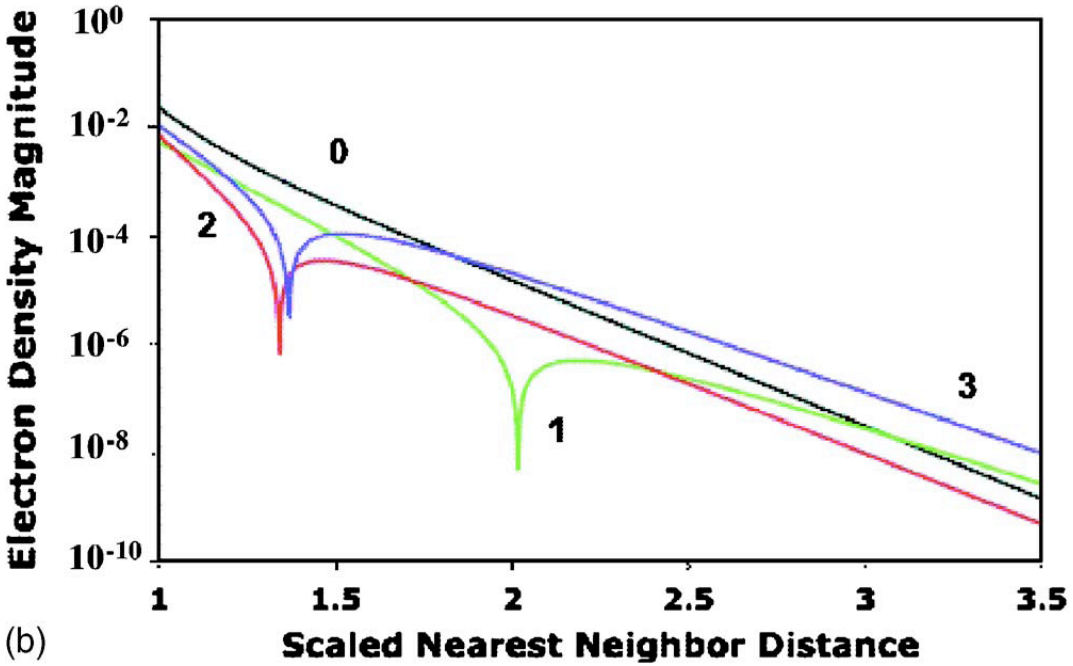
WE LEARNED THE PARTIAL ELECTRON DENSITIES CHANGED SIGN



- **In contradiction with MEAM formalism**
- **Slightly new formalism required**

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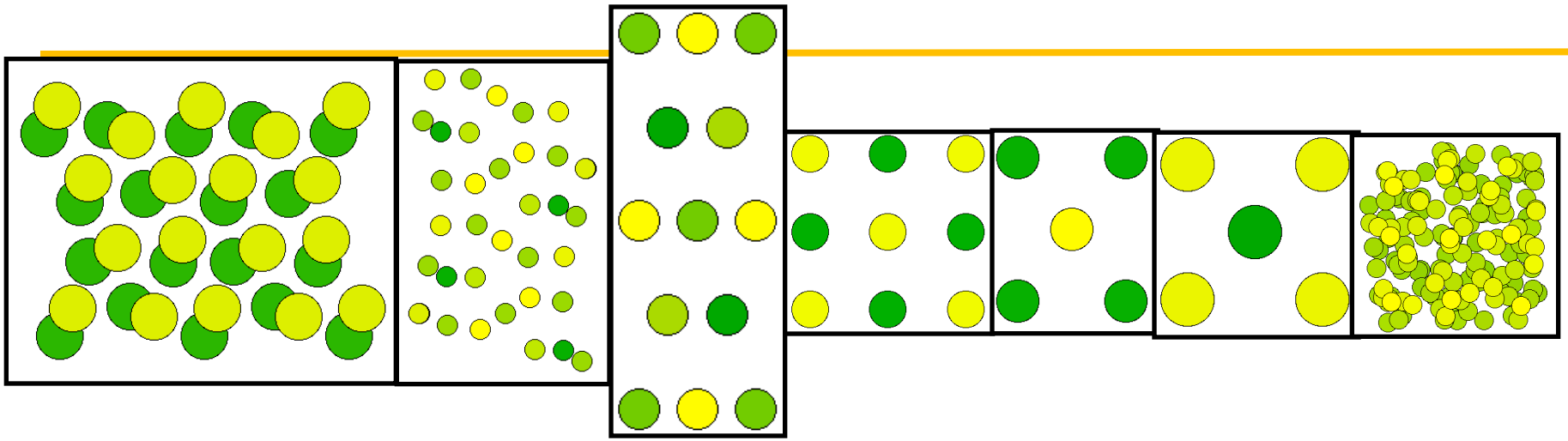
Pu HAS SEVEN STABLE PHASES



0		388		473	583		725		753		913	T(K)
	α		β		γ	δ		δ’		ε		L
	monoclinic		monoclinic		distorted diamond	fcc		distorted bcc		bcc		liquid

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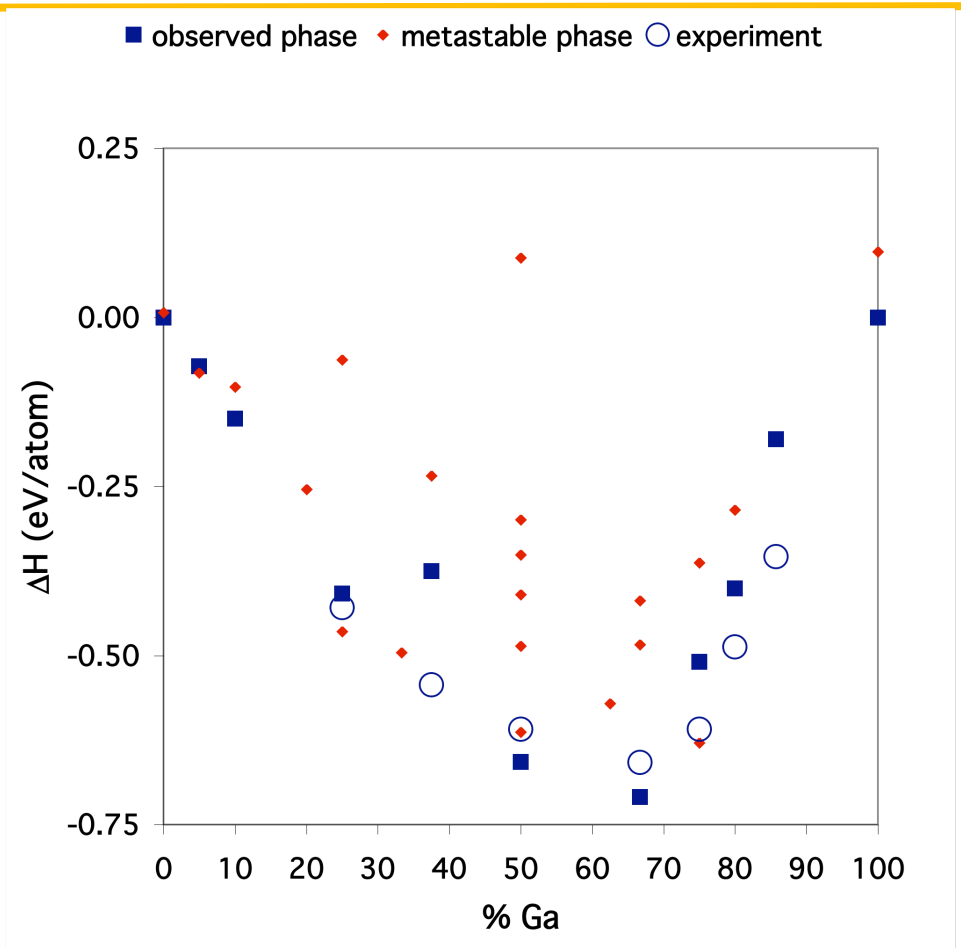
PREDICTED STABILITY OF Pu-Ga ALLOYS AGREES WITH EXPERIMENT



- Enthalpy relative to pure elements
- T = 0 K; P = 0
- 36 alloys / crystal structures investigated

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