Thermal vacancy thermodynamics and ordering kinetics in B2 AB intermetallics

COST 535, COST P19

Rafał Kozubski, Andrzej Biborski, Łukasz Zosiak

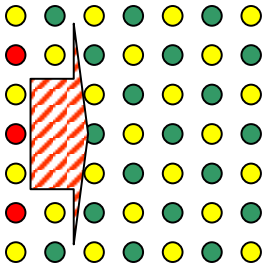
Interdisciplinary Centre for Materials Modelling,
M. Smoluchowski Institute of Physics,
Jagellonian University
Krakow, Poland

Outline:

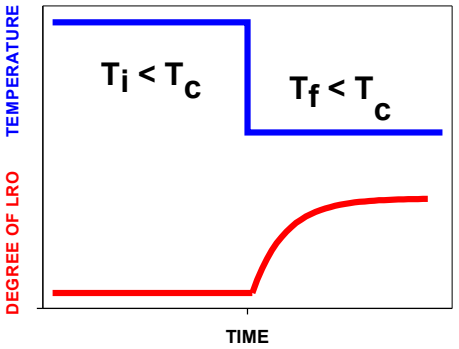
- „Order-order” kinetics
- NiAl – surprising experimental result
- MC simulations with temperature-dependent vacancy concentration
- Model for vacancy thermodynamics
- Results

DIFFUSION AND „ORDER-ORDER" kinetics

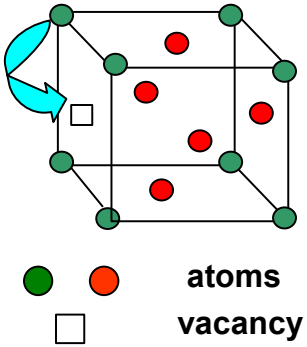
in intermetallics

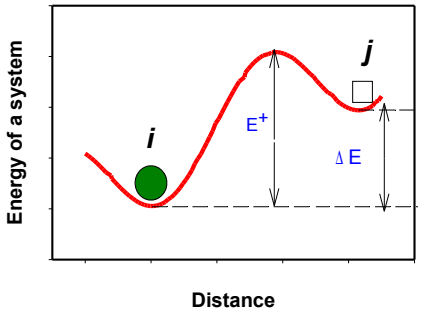


A-atoms
B-atoms
A-tracer atoms



COMMON ELEMENTARY MECHANISM:
atomic jumps to vacancies





SPECIFIC FEATURES: correlation of atomic jumps

DIFFUSION

Minimisation of the energetic cost of local LRO perturbation by jumping atoms:

„six-jump-cycle", ASB, triple defect mechanism, antisite diffusion etc.

ORDER-ORDER kinetics

Formation of equilibrium atomic configuration:

generation/elimination of antisite defects

CONCLUSION: BOTH METHODS YIELD COMPLEMENTARY INSIGHT INTO ATOMIC JUMP DYNAMICS

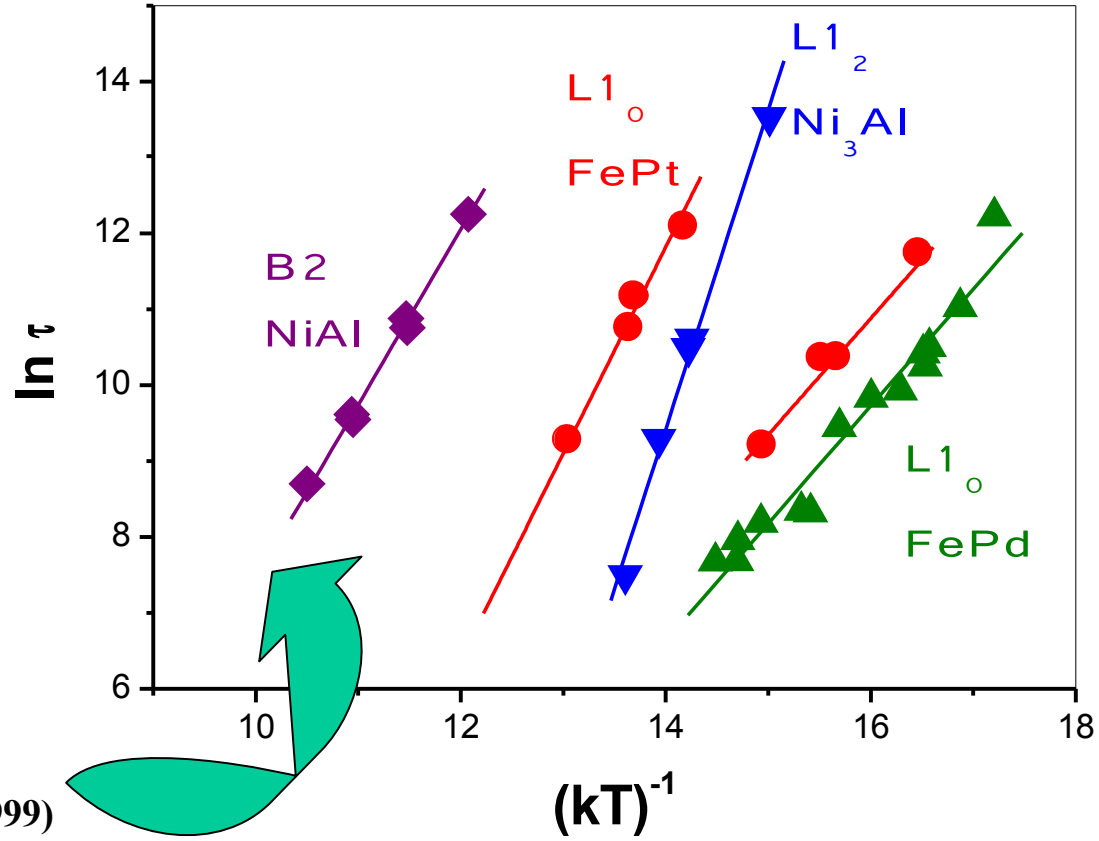
SYNTHESIS: analysis of „order-order" relaxation isotherms in bulk intermetallics

Process markedly slower than in Ni_3Al despite extremely high vacancy concentration:

Ni_3Al: $C_V=10^{-9}$ at $T=T_m/2$

NiAl: $C_V=10^{-2}$ at $T=T_m/2$

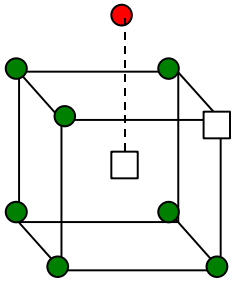
H.-E. Schaefer et al., *Intermetallics*; 7, 277, (1999)



R.Kozubski et al., *Intermetallics*, 11,897-905,(2003).

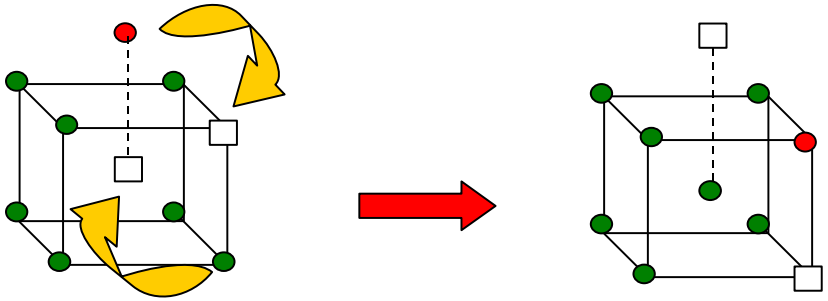
GENERATION OF ANTISITE DEFECTS without perturbing superlattice geometry:

Initial (starting) configuration:



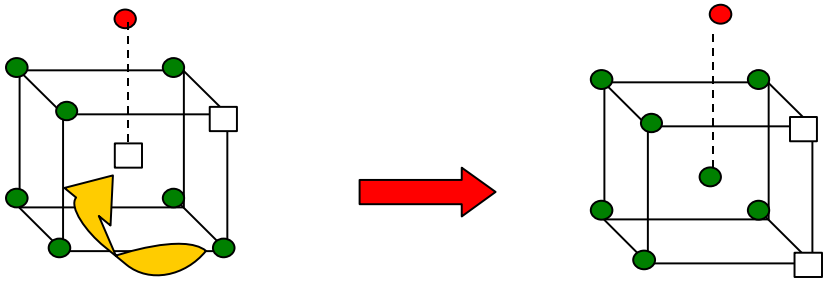
pair of V_A and V_B vacancies

Variant 1: generation of A_B and B_A antisite pairs



Result:
pair of V_A and V_B vacancies
+
pair of A_B and B_A antisites
Process may continue !

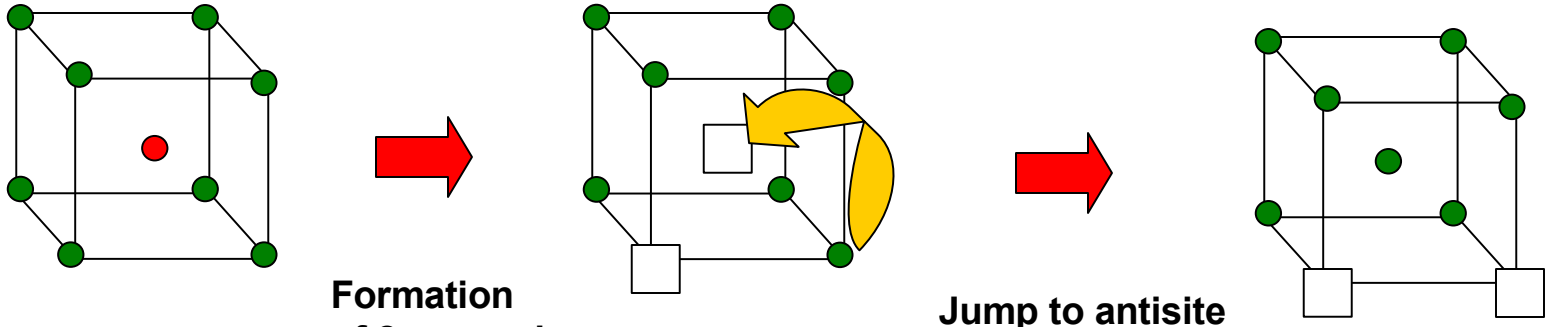
Variant 2: generation of triple defects



Result:
pair of V_A vacancies
+
single A_B antisite
„triple defect"
Vacancies almost immobile !
Condition:
$E_F(V_B) >> E_F(A_B)$

„ORDER-ORDER" KINETICS IN TRIPLE-DEFECT B2-ORDERED AB SYSTEMS:

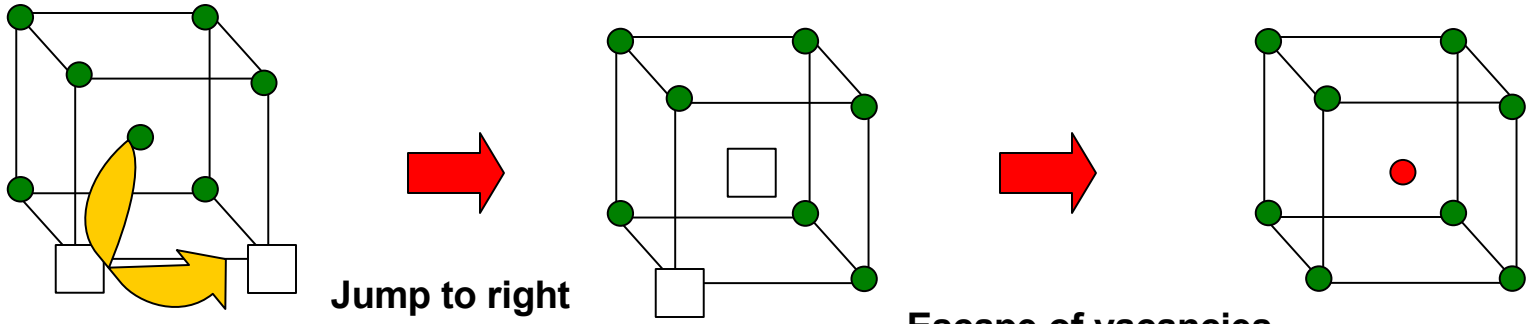
DISORDERING (GENERATION OF ANTISITE DEFECTS):



Formation of 2 vacancies
Very high E_F

Jump to antisite position
Low E_M

ORDERING (ELIMINATION OF ANTISITE DEFECTS):



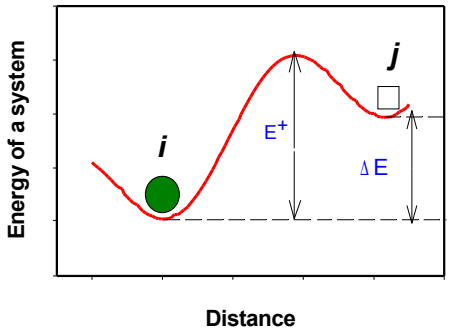
Jump to right position
Moderate E_M

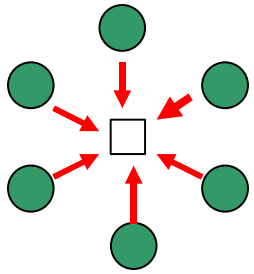
Escape of vacancies
Quite a high E_M

STANDARD MONTE CARLO SIMULATIONS IN BULK:

- A_3B or AB binary system with $L1_2$, $L1_0$ or B2 superstructure,
- $40 \times 40 \times 40$ cubic cells,
- 1 vacancy (*10 vacancies in a piloting study*)

general assumption: vacancy mechanism of atomic migration





Glauber dynamics algorithm:

$$\Pi_{i \to j} = \frac{\exp\left[-\frac{\Delta E}{kT}\right]}{1 + \exp\left[-\frac{\Delta E}{kT}\right]}$$

„Residence-time“ algorithm:

’

$$\Pi_{i \to j} = \Pi_0 \times \exp\left[-\frac{E_i^+ - E_i}{kT}\right]$$

$$\Pi_0 = \left[\sum_l \exp\left(-\frac{E_l^+ - E_l}{kT}\right)\right]^{-1}$$

PROBLEM:

Because of possible correlation between antisite and vacancy concentrations MC simulation with fixed number of vacancies is no longer justified

MODEL: EQUILIBRIUM CONCENTRATION OF THERMAL VACANCIES

W. Schapink, Scr. Metall. 3, 113, (1969).
S. H. Lim, G. E. Murch, W. A. Oates, J. Phys. Chem. Solids 53, 181, (1992)
R. Kozubski, Acta Metall. Mater. 41, 2565, (1993).

Lattice gas:

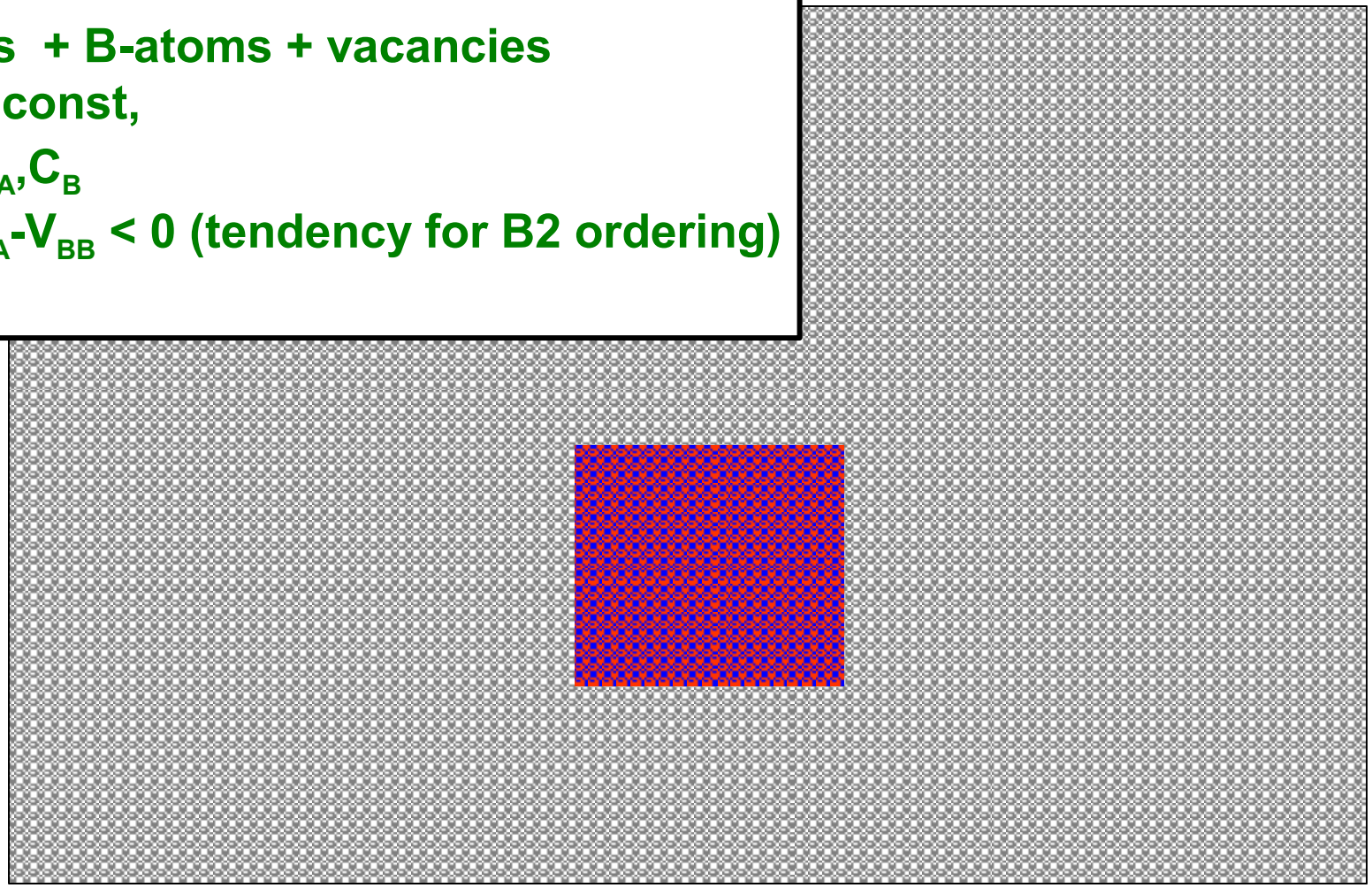
A-atoms + B-atoms + vacancies

C_A/C_B = const,

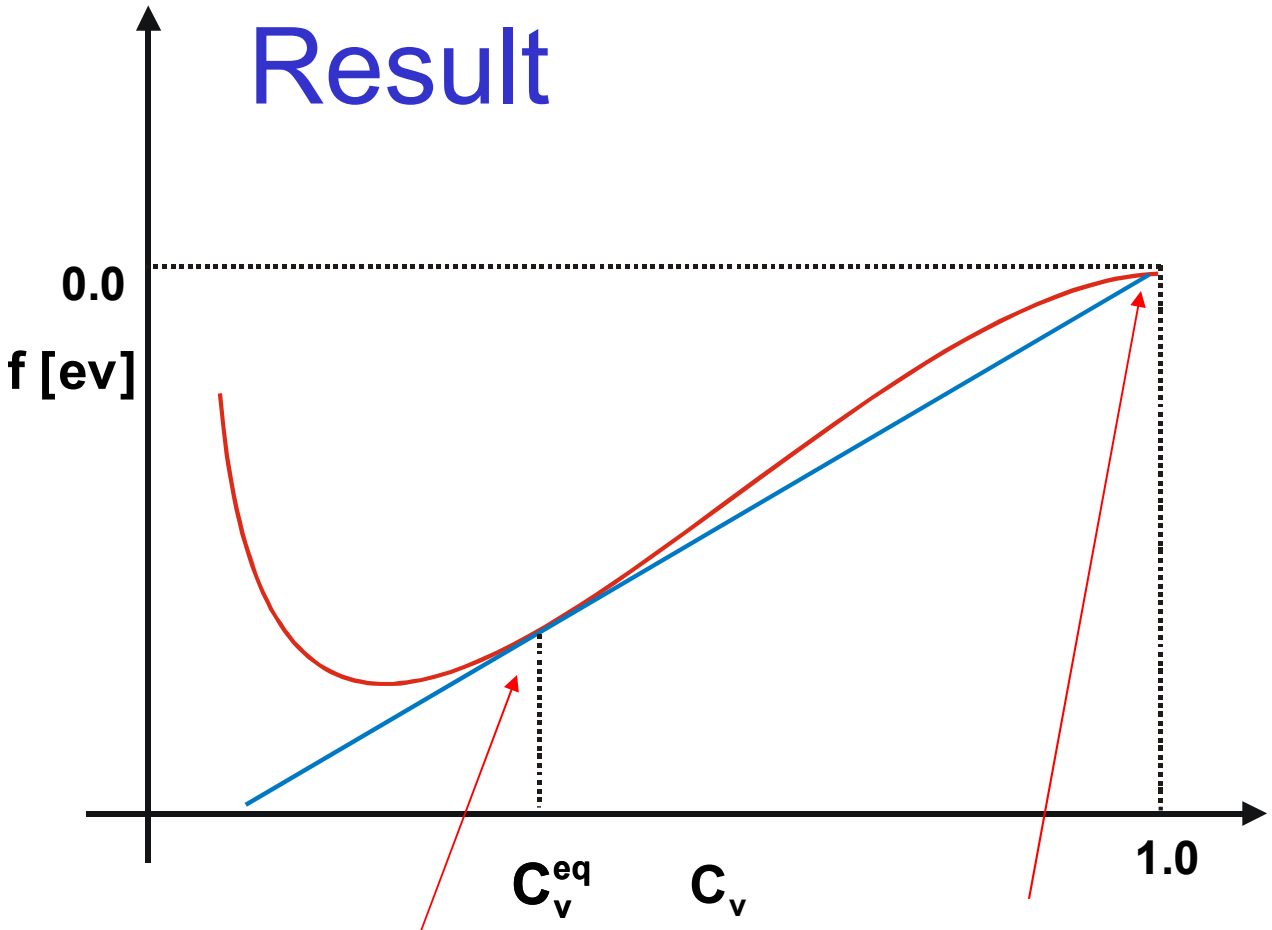
$C_V >> C_A, C_B$

$2V_{AB}-V_{AA}-V_{BB} < 0$ (tendency for B2 ordering)

$V_{VV} = 0$



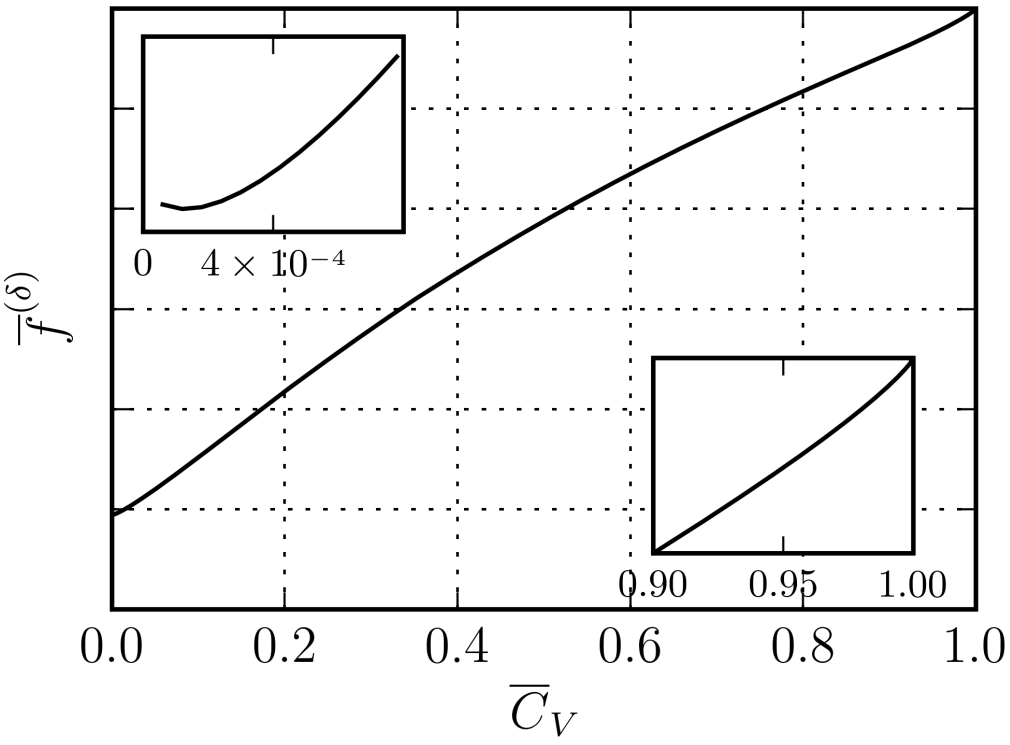
Result

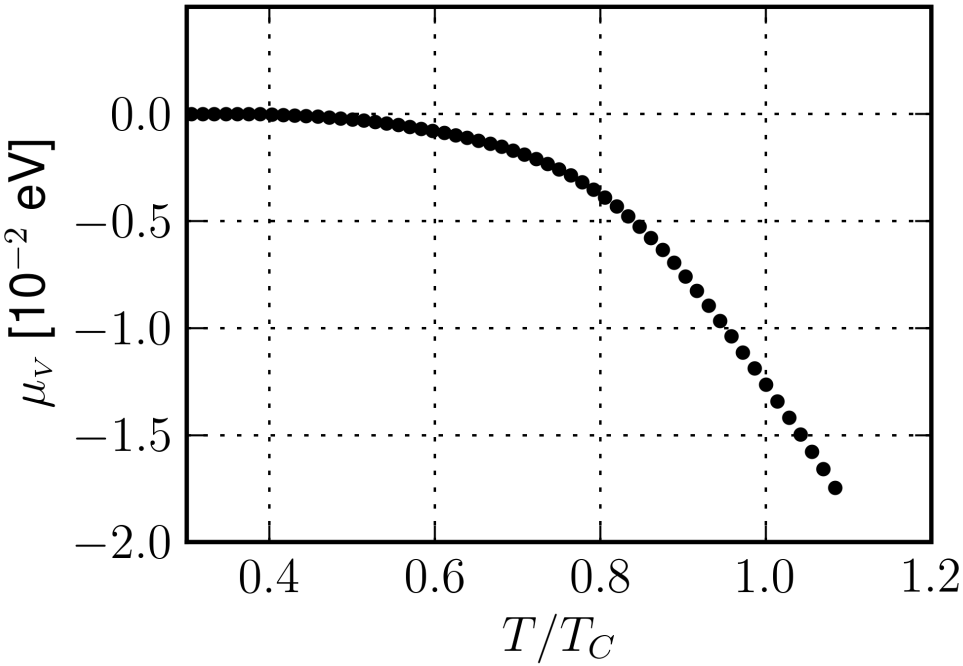


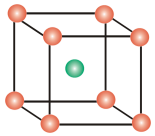
Interpretation: lattice gas decomposes into

Vacancy-poor part: crystal with equilibrium vacancy concentration

Vacancy-rich part


$\overline{f}^{(\delta)}$
0
4×10^{-4}
0.90
0.95
1.00
0.0
0.2
0.4
0.6
0.8
1.0
$\overline{C}_V$


μ_V [10^{-2} eV]
0.0
−0.5
−1.0
−1.5
−2.0
0.4
0.6
0.8
1.0
1.2
T/T_C



Definitions :

$$W = 2V_{AB} - V_{AA} - V_{BB}$$

$$E_{as} = V_{AA} - V_{BB}$$

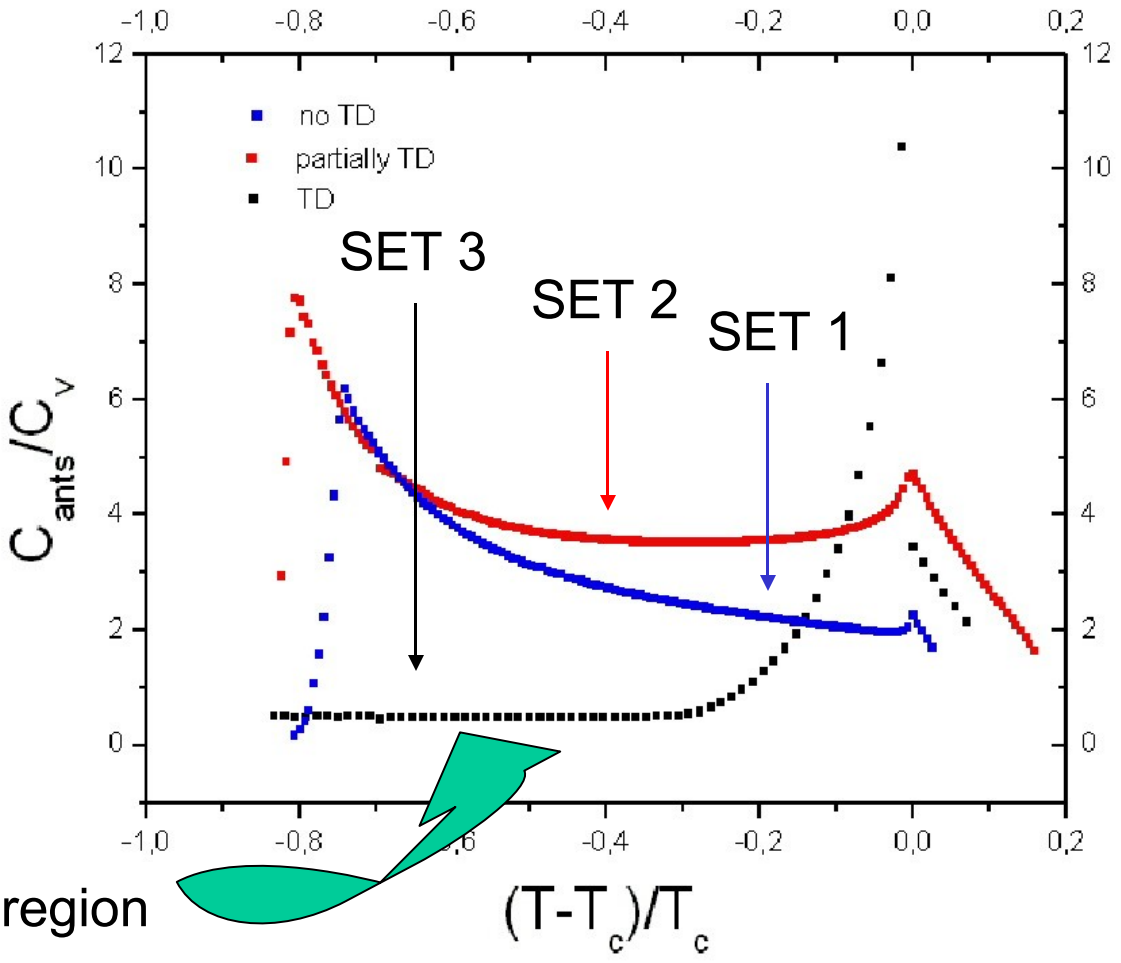
Calculations were made for various sets of energies

	W [eV]	E_{as} [eV]	V_{BB} [eV]	V_{AV} [eV]	V_{BV} [eV]	Structural vacancies	Plateau
SET1	-0,08	-0,03	-0,05	0,0	0,0	No	No
SET2	-0,08	-0,07	-0,05	0,0	0,0	No	Partially
SET3	-0,08	-0,07	-0,05	0,051	-0,051	Yes	Yes

STOICHIOMETRIC BINARY SYSTEM

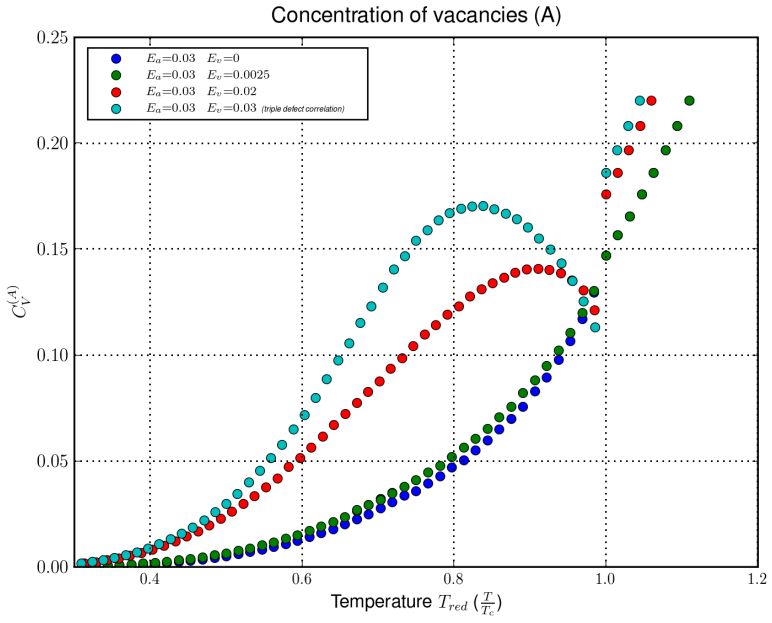
$A_{50}B_{50}$

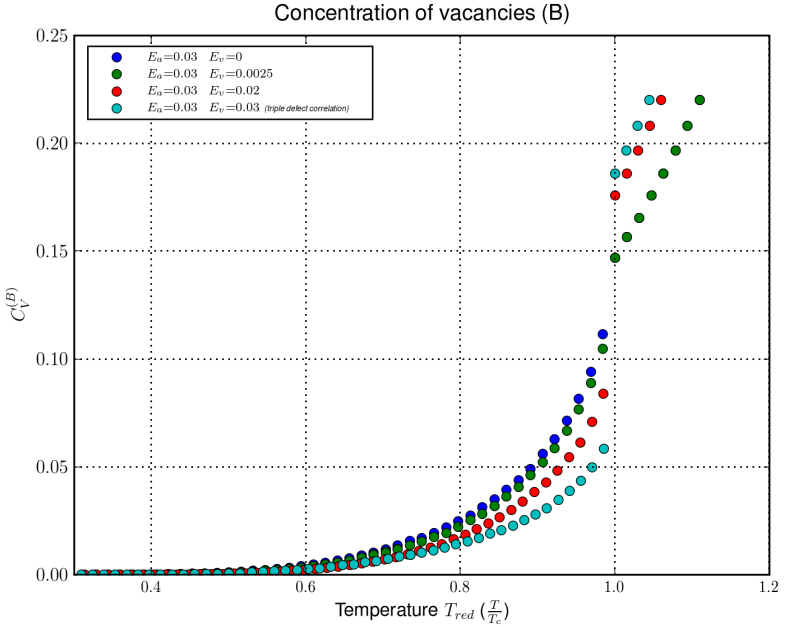
MAIN RESULT (from Bragg-Williams calculations)

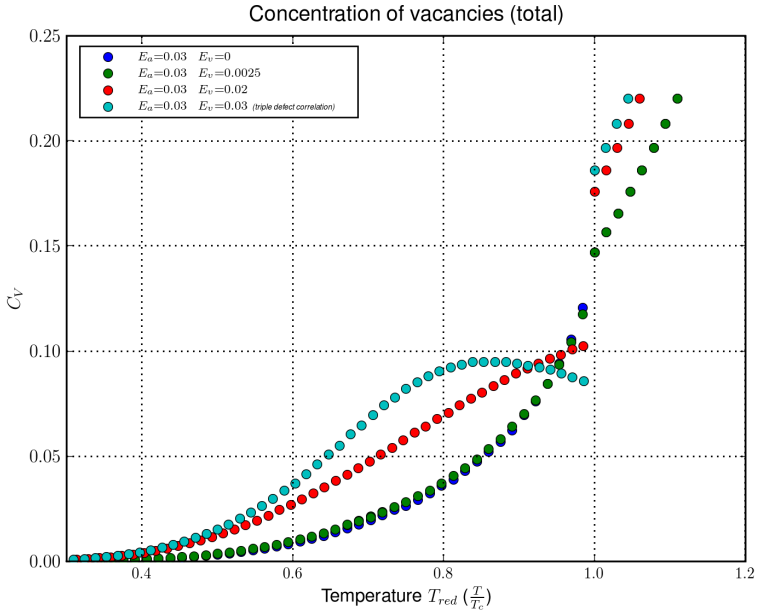


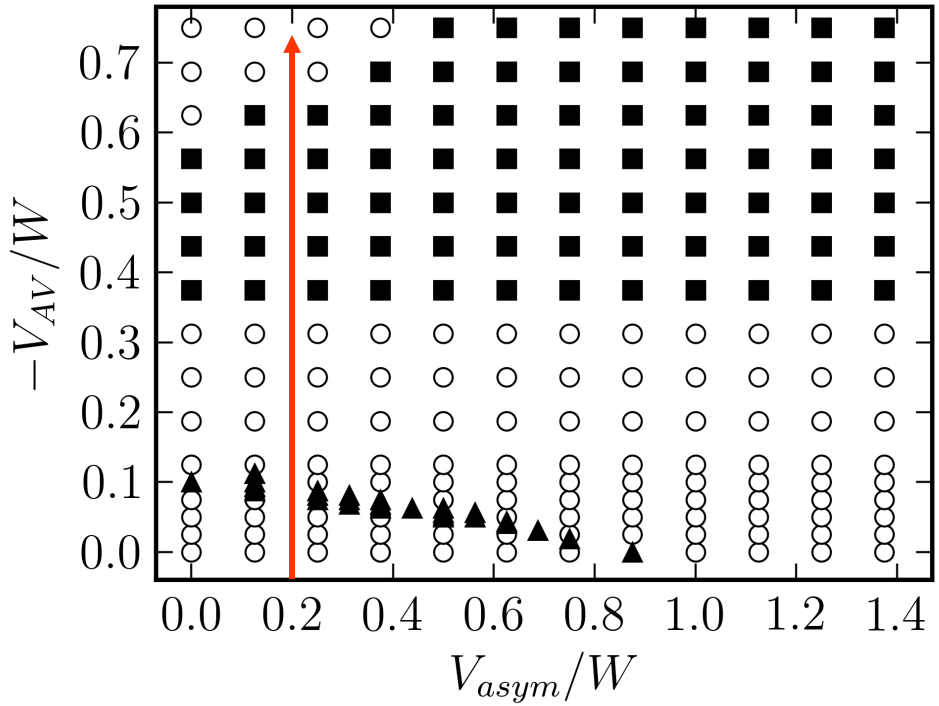
Triple Defect region

IN PROGRESS: MC on Grand Canonical Ensemble


Concentration of vacancies (A)
E_a=0.03 E_v=0
E_a=0.03 E_v=0.0025
E_a=0.03 E_v=0.02
E_a=0.03 E_v=0.03 (triple defect correlation)
$C_V^{(A)}$
Temperature T_{red} ($\frac{T}{T_c}$)

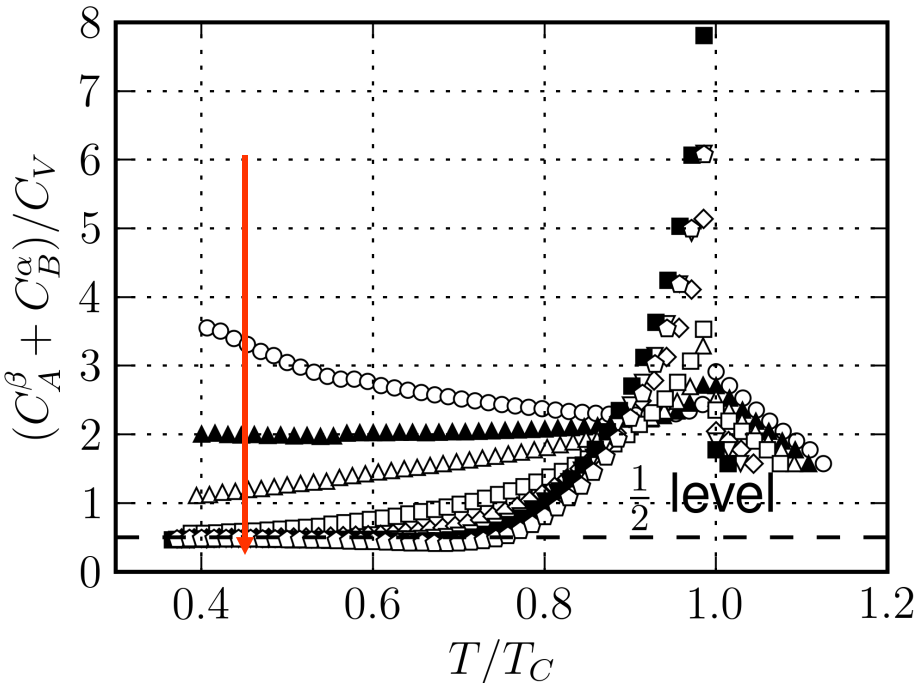

Concentration of vacancies (B)
E_a=0.03 E_v=0
E_a=0.03 E_v=0.0025
E_a=0.03 E_v=0.02
E_a=0.03 E_v=0.03 (triple defect correlation)
$C_V^{(B)}$
Temperature T_{red} ($\frac{T}{T_c}$)


Concentration of vacancies (total)
E_a=0.03 E_v=0
E_a=0.03 E_v=0.0025
E_a=0.03 E_v=0.02
E_a=0.03 E_v=0.03 (triple defect correlation)
C_V
Temperature T_{red} ($\frac{T}{T_c}$)



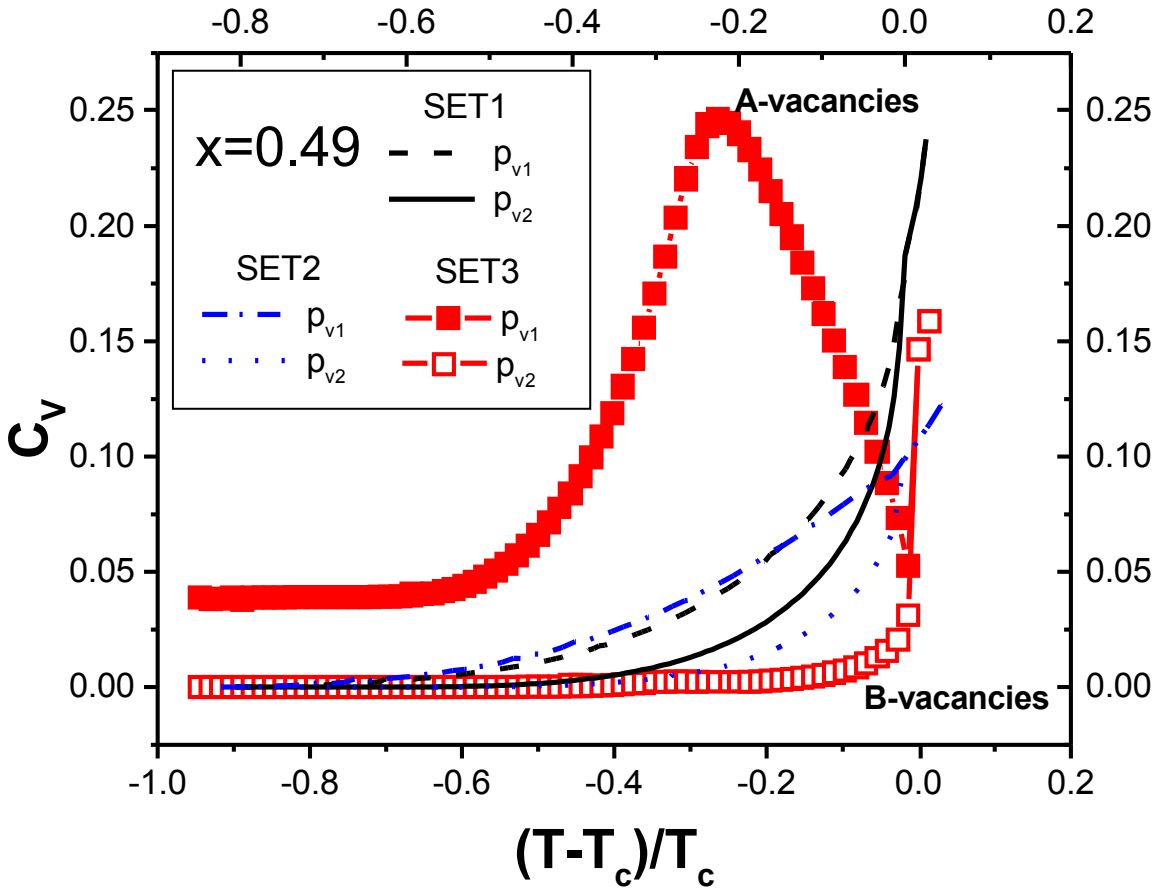
SET 3 energetics

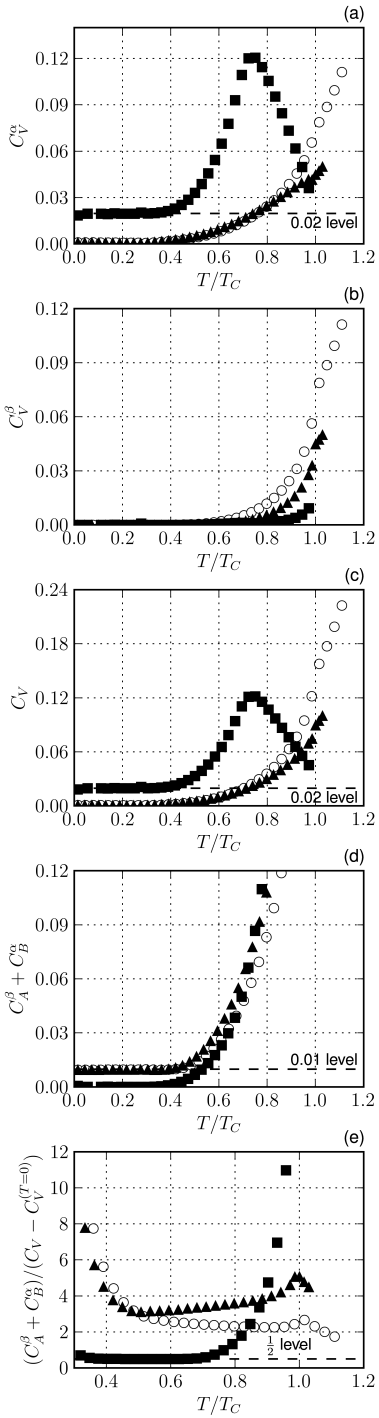
˜ no plateau; □ “higher-level plateau”; ¡ “plateau”.



NON-STOICHIOMETRIC BINARY SYSTEMS

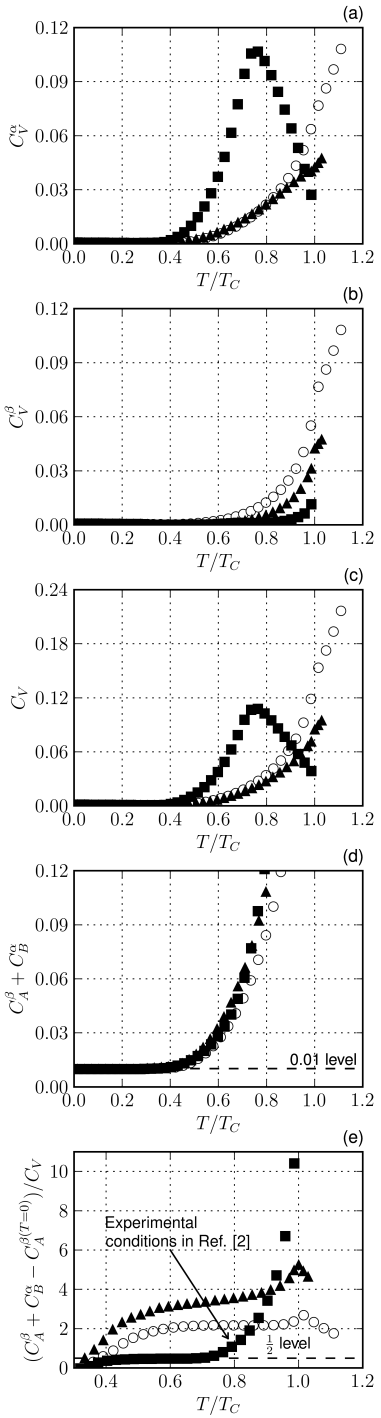
CONSTITUTIONAL VACANCIES IN $A_{0.49}B_{0.51}$



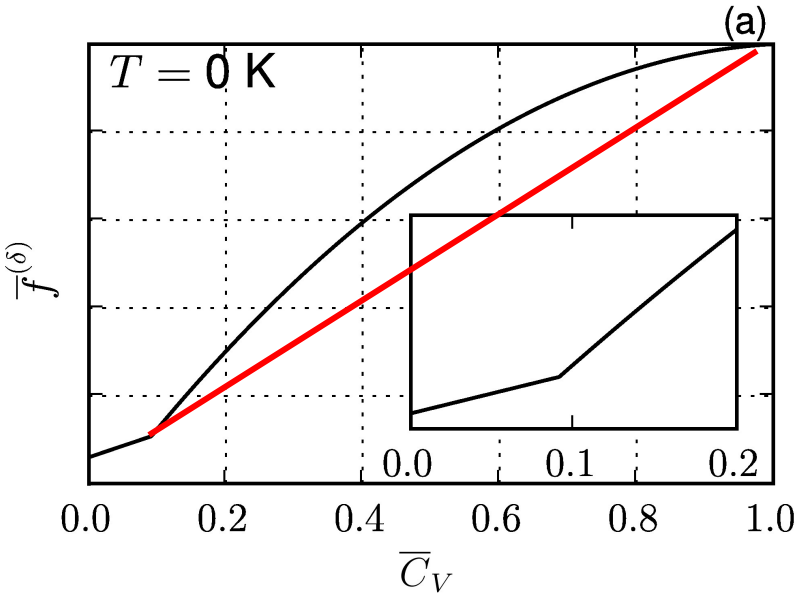


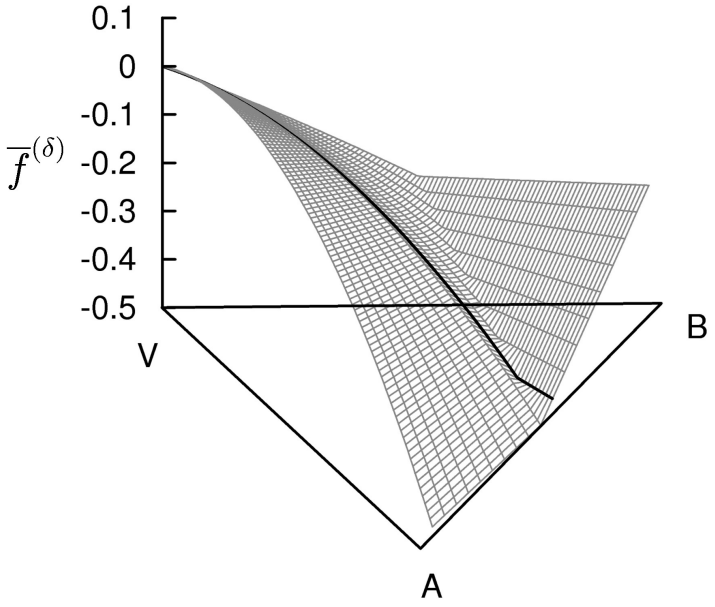
$A_{49}B_{51}$

$A_{51}B_{49}$

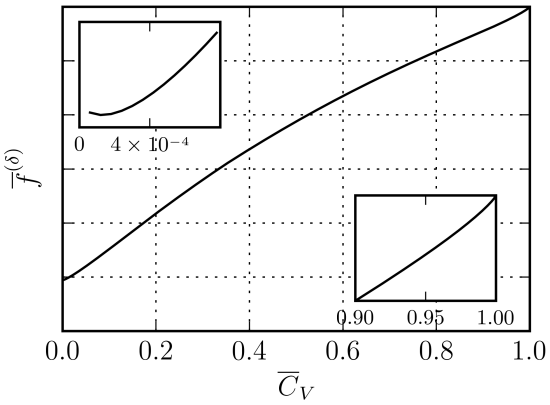


GENERATION OF CONSTITUTIONAL VACANCIES:

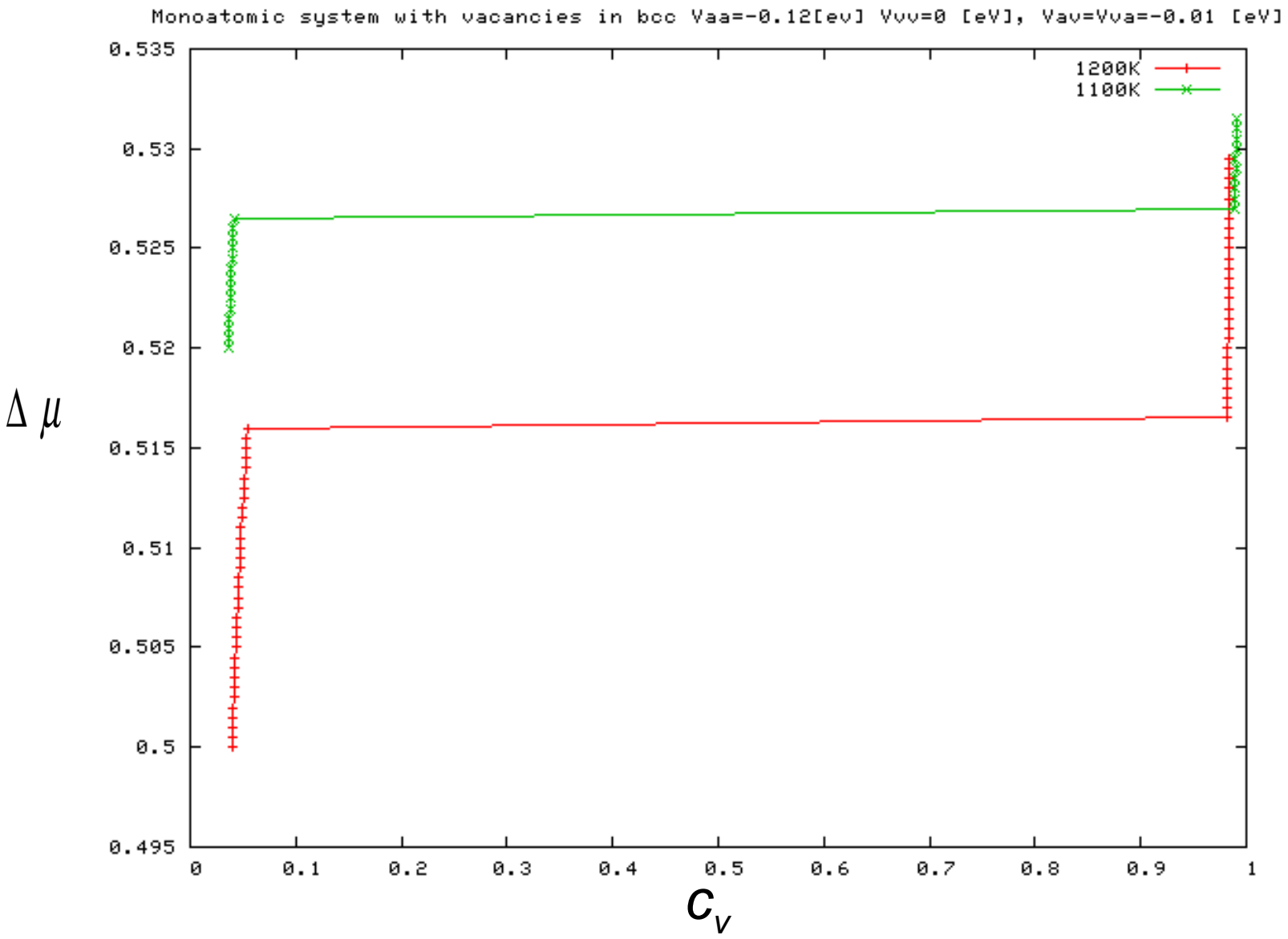


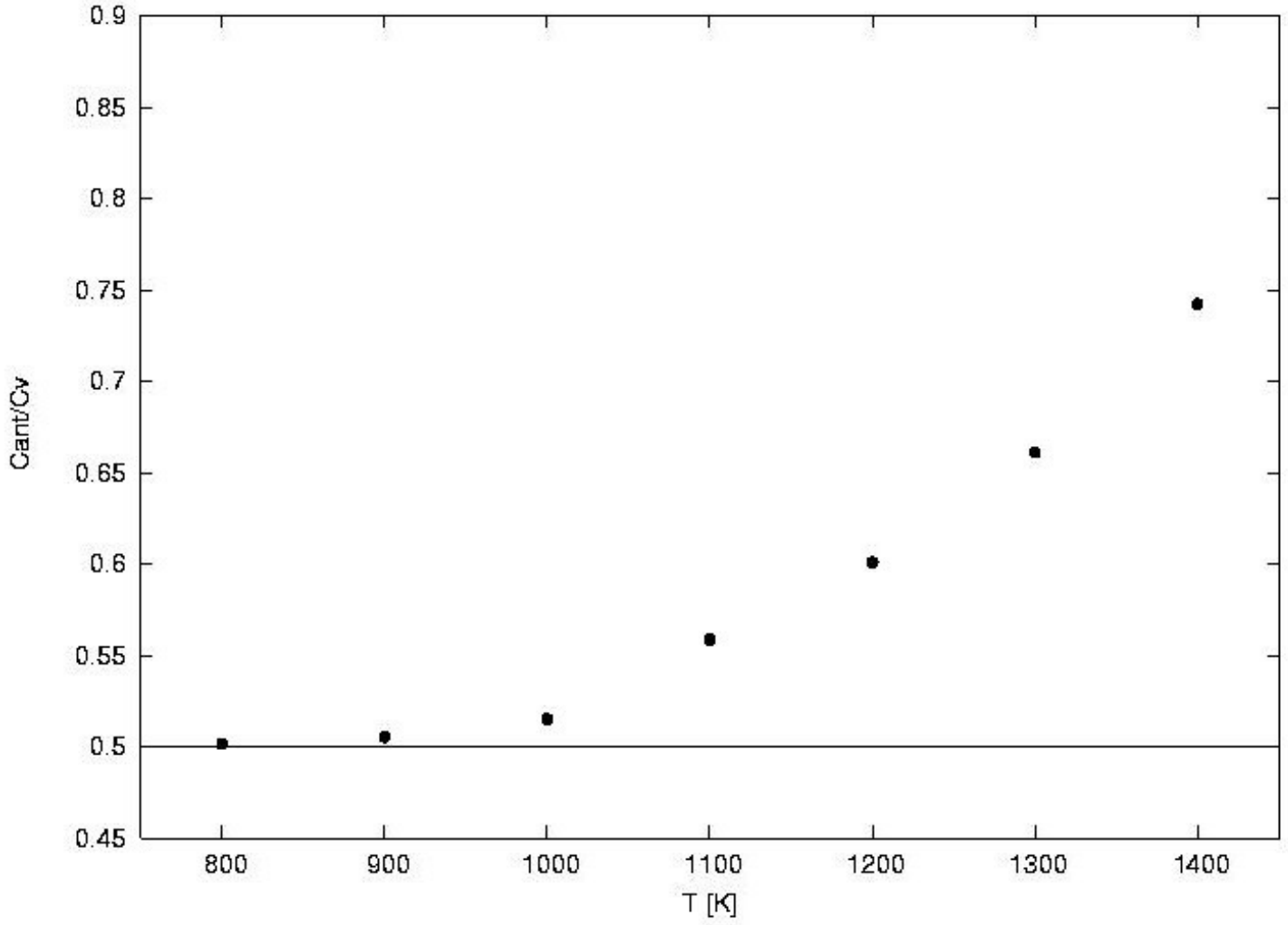


T > 0 K

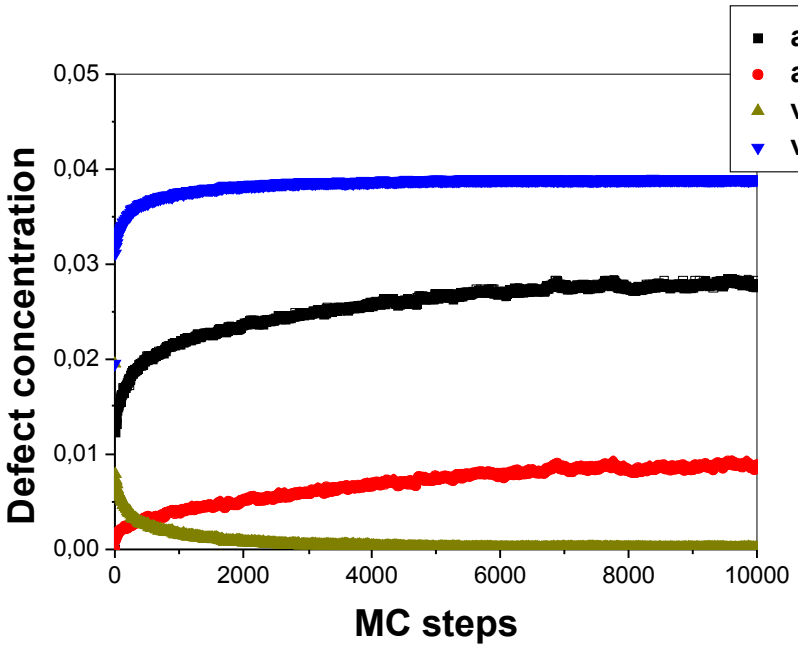


Two phases decomposition in SGCMC



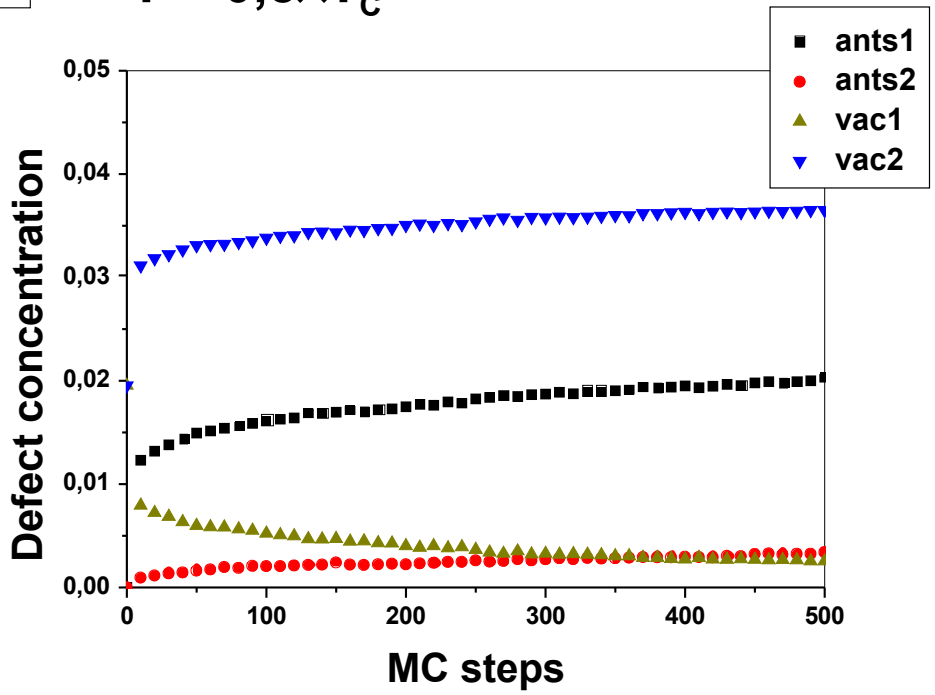

0.9
0.85
0.8
0.75
0.7
0.65
0.6
0.55
0.5
0.45
Cant/Cv
800
900
1000
1100
1200
1300
1400
T [K]

FIRST MC SIMULATIONS OF DISORDERING KINETICS



SET 3 of pair-interaction energies

$T = 0{,}5 \times T_C$



Conclusions:

Initial stage: fast creation of triple defects (only A-antisites)

Continuation: very slow generation of A- and B-antisites

CONCLUSIONS:

- Triple-defect-type correlation between antisite and vacancy concentrations in B2-ordering AB binary follows from a Bragg-Williams model of atom-vacancy lattice gas

- Vacancy trapping by triple defects results in substantial slowing-down of „order-order" relaxations in B2 intermetallics showing very high vacancy concentration