Ab initio calculation of variable saddle point energies for atom jumps in $L1_2$ ordered Ni_3Al

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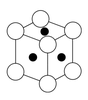
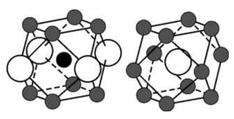
Monte-Carlo simulation: How sensitive is saddle point energy to atom environment?

The 4-atom window and the single atom jump

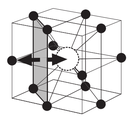
Geometric relations in the $L1_2$ structure:



$L1_2$ structure

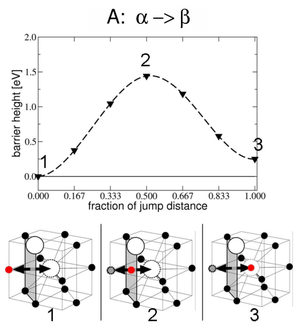


Environment of sublattices



4-atom window

The single atom jump:



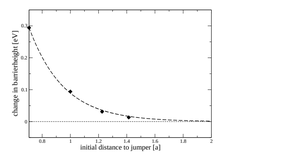
•Vacancy mechanism

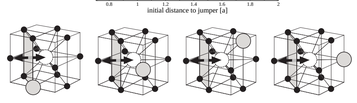
•Main stages of the jump: 1. Initial equilibrium position.
2. Saddle point state.
3. Final equilibrium position.

•Transition state theory: $\Gamma_{ij} = \Gamma_0 \quad exp\left(-\frac{\Delta E_{is}}{k_B T}\right)$

Grey: 4-atom window of common nearest neighbors.

The importance of the 4-atom window:



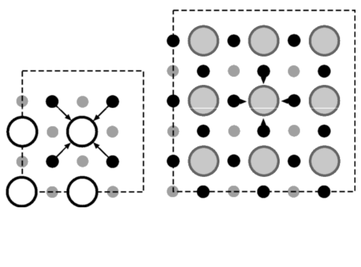


Variation of distance of one antisite to jumping atom

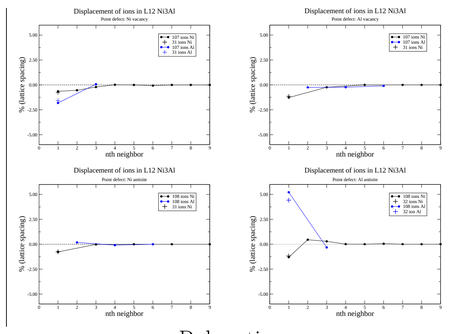
Details of VASP calculations

General settings:
- GGA (PW91), ENCUT 350 eV
- **2x2x2** and **3x3x3** supercells (6x6x6 and 4x4x4 k points, respectively)
- Nudged elastic band (**NEB**) method was used where necessary
- atoms located on the surface of the supercell are fixed

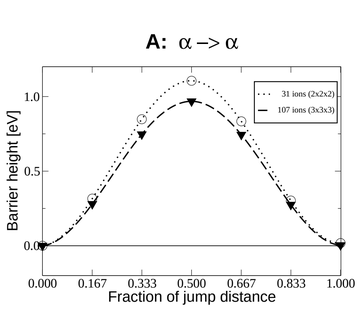
Comparison of 3x3x3 and 2x2x2 supercells



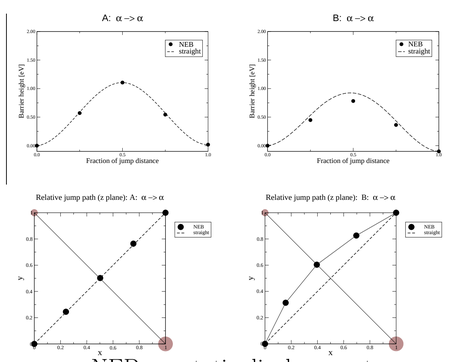
Residual Forces



Relaxation



Barrier height



NEB vs. static displacement

Classification and results

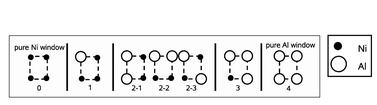
Classification

Jump types

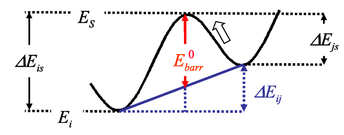
order-preserving: A: $\alpha \to \alpha$, B: $\alpha \to \alpha$

ordering-disordering: A: $\alpha \to \beta$, B: $\beta \to \alpha$

Window types



Results for E^0_{barr}



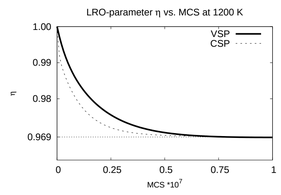
$E^0_{barr} = E_{is} - \frac{1}{2}\Delta E_{ij}$

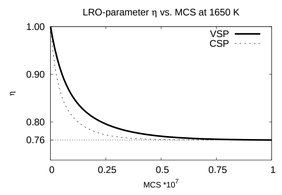
window configuration	E^0_{barr}	window configuration	E^0_{barr}		
A: $\alpha \to \alpha$	2x2x2	3x3x3	**A:** $\alpha \to \beta$	2x2x2	3x3x3
0	1.02	**0.97**	0	1.03	**0.95**
1	1.00	**0.94**	1	1.32	**1.18**
2-1	1.10	**0.97**	2-1	1.54	**1.39**
2-2	1.03	**0.97**	2-2	1.28	**1.15**
2-3	1.17	**1.06**	2-3	1.64	**1.40**
3	1.09	**0.97**	3	1.53	**1.36**
4	1.09	**0.93**	4	1.48	**1.34**
B: $\alpha \to \alpha$	2x2x2	3x3x3	**B:** $\beta \to \alpha$	2x2x2	3x3x3
0	0.29	**0.29**	0	0.72	**0.58**
1	0.55	**0.49**	1	1.20	**0.96**
2-1	0.83	**0.75**	2-1	1.77	**1.45**
2-2	0.83	**0.77**	2-2	1.60	**1.26**
2-3	0.99	**0.86**	2-3	1.96	**1.49**
3	1.28	**1.12**	3	2.35	**1.85**
4	1.76	**1.52**	4	2.92	**2.25**

Results of Kinetic Monte-Carlo Simulations

Computational details:
- Residence time algorithm
- 50x50x50 atoms in simulation cell, containing 1 vacancy
- Periodic boundary conditions in all directions
- Initial state of perfect order, 2 final temperatures (1200K and 1650K)
- E_i, E_j via pair interaction Hamiltonian (up to NNN) from P. Oramus et al., Phys. Rev. B **63** 174109 (2001)

Long range order parameter





VSP ... Variable saddle point, CSP ... Constant saddle point

$\eta(t) = A \exp\left(-\frac{t}{\tau_1}\right) + (1 - A) \exp\left(-\frac{t}{\tau_2}\right)$

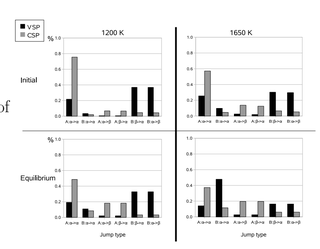
with $0 \leq A \leq 1$; $\tau_2 > \tau_1$

Temperature	model	A	τ_1 [MCS*10^6]	τ_2 [MCS*10^6]
1200 K	CSP	0.25	0.08	1.18
	VSP	0.09	0.22	1.63
1650 K	CSP	0.78	0.41	1.98
	VSP	0.45	0.52	1.81

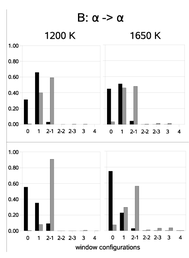
Jump statistics

•shift of relative incumbencies of jump types

•correlation effects (Al jumps)



Window statistics



•shift toward 'cheaper' windows

More details: M. Leitner, D. Vogtenhuber, W. Pfeiler and W. Püschl, Intermetallics **18** 1091 (2010).
M. Leitner, D. Vogtenhuber, W. Pfeiler and W. Püschl, PTM2010 Proceedings, accepted.

Saddle point energies are very sensitive to atomic environment!

Acknowledgements:
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