格子欠陥自由エネルギーの非調和性

合金状態図研究会 第4回

2023/12/9 at 小倉

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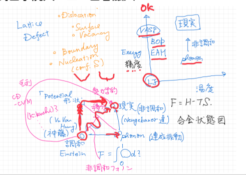
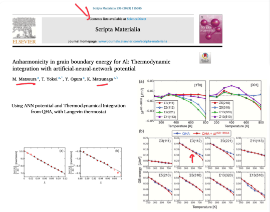
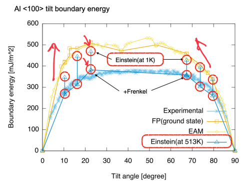


summary

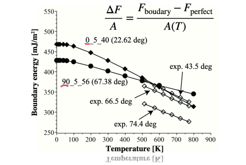
1. Lattice defects free energy
   1. Vacancy, Surface
2. Einstein(Harmonic) + Frenkel-Ladd(Anharmonic)
3. Boundary (Harm. + small Anharm.)
4. Vacancy (Harm.: ?)
5. Perfect (Moment method)
   1. Volume, but …
6. Surface
   1. Harm.:X, Anharm.:?



Al tilt boundary (Eistein)

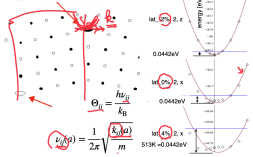


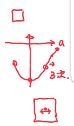
temperature dependency of BE



0_5_40 einstein

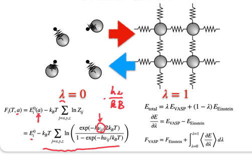
GN dislocation core



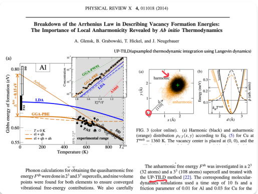


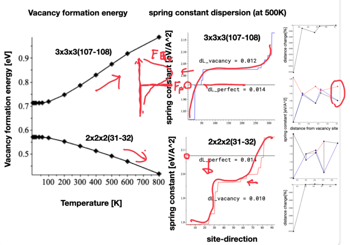
Einstein model　VASP model

Frenkel method



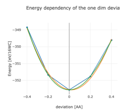
Al Vacancy (Anhramonicity?)





Perfect lattice (Moment + Frenkel-Ladd(MC))

□SMM (Statistical Moment Method) WC



$$E = E_0 + \frac{\partial E}{\partial x_i}dx_i + \frac{\partial^2 E}{\partial x_i^2}dx_i^2 + \frac{\partial^3 E}{\partial x_i^3}dx_i^3 + \frac{\partial^4 E}{\partial x_i^4}dx_i^4$$

0th	-352.5518	-352.5603
1st	-0.8025	-0.0067
2nd	20.7770	21.2321
3rd	0.0	-5.8513
4th	0.0	-2.5690

N. Tan, V. V. Hung, “Investigation of the Thermodynamic Properties of Anharmonic Crystals by the Momentum Method”, Phys. Stat. Sol. (B), vol. 149, pp.511–519, 1988.

$$F_0 + \int_{\lambda=0}^{\lambda=1} \frac{\partial F}{\partial \lambda} d\lambda$$

$$F_{\rm anharm} \approx E_0 + F_{\rm harm} + 3\left\{\frac{\theta^2}{k^2}\left[\gamma_2 x^2 \coth^2 x - \frac{2\gamma_1}{3}\left(1+\frac{x\coth x}{2}\right)\right] + \frac{2\theta^3}{k^4}\left[\frac{4}{3}\gamma_2^2 x\coth x\left(1+\frac{x\coth x}{2}\right) - 2(\gamma_1^2+2\gamma_1\gamma_2)\left(1+\frac{x\coth x}{2}\right)(1+x\coth x)\right]\right\},$$

$\theta = k_B T, x = \frac{\hbar\omega}{2\theta}$

$$E_0 \equiv \sum_j \varphi(|a_j|),$$

$$F_{\rm harm} = \theta[x + \log(1-e^{-2x})],$$

$$k = \frac{1}{2}\sum_j\left(\frac{\partial^2\varphi_{j0}}{\partial u_j^2}\right) = m\omega^2$$

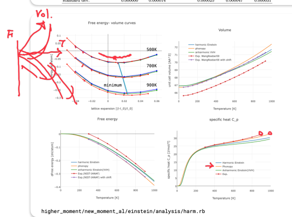
$$\gamma_1 = \frac{1}{48}\sum_j \frac{\partial^4\varphi_{j0}}{\partial u_{j\beta}^4}, \gamma_2 = \frac{6}{48}\sum_j \frac{\partial^4\varphi_{j0}}{\partial u_{j\alpha}^2 \partial u_{j\beta}^2}$$

$$E_{\rm higher}(l') = E_0(l') + \sum_{[k,l,m]} k_{klm}(l')\delta x^k \times \delta y^l \times \delta z^m$$

eV/Å^3

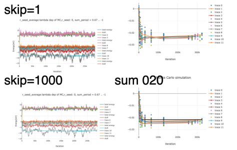
TABLE I. Higher order coefficients of the energy potential.

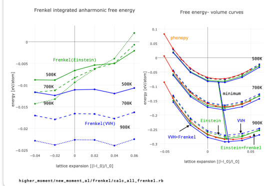
indexes	analytical	numerical p4 dev.=0.04	numerical p4 dev.=0.10	harmonic	VASP(2x2x2) dev.=0.04	VASP(2x2x2) dev.=0.10	VASP(3x3x3) dev.=0.10
0 [0 0 0]	-2.47840	-2.47840	-2.47840	-3.72303	-3.69879	-3.723027	
1 [2 0 0]	6.60522	6.60496	6.60288	6.66320	3.30538	3.37042	4.26487
2 [0 2 0]	6.60522	6.60496	6.60288	6.66320	3.33010	3.35011	4.27330
3 [0 0 2]	6.60522	6.60496	6.60288	6.66320	3.39418	3.35422	4.28811
4 [illegible]		1.720e-12	2.842e-13		0.02135	0.01158	-0.00212
5 [1 1 0]		1.600e-11	-1.125e-12		-0.02505	-0.01058	0.00217
6 [1 0 1]		1.720e-12	8.527e-13		0.03010	0.01165	-0.00154
7 [3 0 0]		-2.852e-09	-1.218e-10		-0.05000	0.00020	0.00054
8 [0 3 0]		-1.158e-09	-5.801e-11		-0.25417	-0.00222	0.00374
9 [0 0 3]		-2.147e-09	2.404e-11		0.25833	-0.00588	0.02284
10 [1 1 1]		-2.224e-26	-8.807e-12		-0.04375	0.00024	0.00056
11 [2 2 0]	29.14519	29.23755	29.34441		53.12500	9.96245	10.62694
12 [2 0 2]	29.14519	29.23755	29.34441		46.30102	9.91347	10.73143
13 [0 2 2]	29.14519	29.23755	29.34441		40.24235	10.46694	10.46041
14 [4 0 0]	6.35142	6.51689	6.84933		-3.54167	0.30400	-0.56800
15 [0 4 0]	6.35142	6.51690	6.84933		-14.47916	2.01067	-1.22133
16 [0 0 4]	6.35142	6.51689	6.84933		-47.29167	1.58400	-2.62133
standard dev.		0.000000	0.000014		0.000025	0.000047	0.000031



LJ-Frenkel

./frenkel/p3_lj/figs

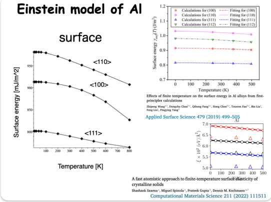




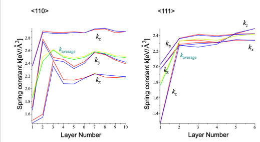
Surface (MC simulations)

Einstein model of Al

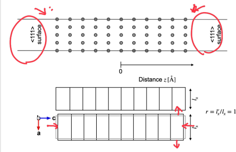
surface

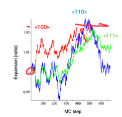


Layer dependency of spring constants



Slab model





Surface expansion during MC simulation.