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Crystal Structure and Formation Energy of ε-carbide Using First Principles Calculations

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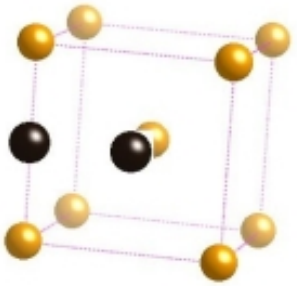


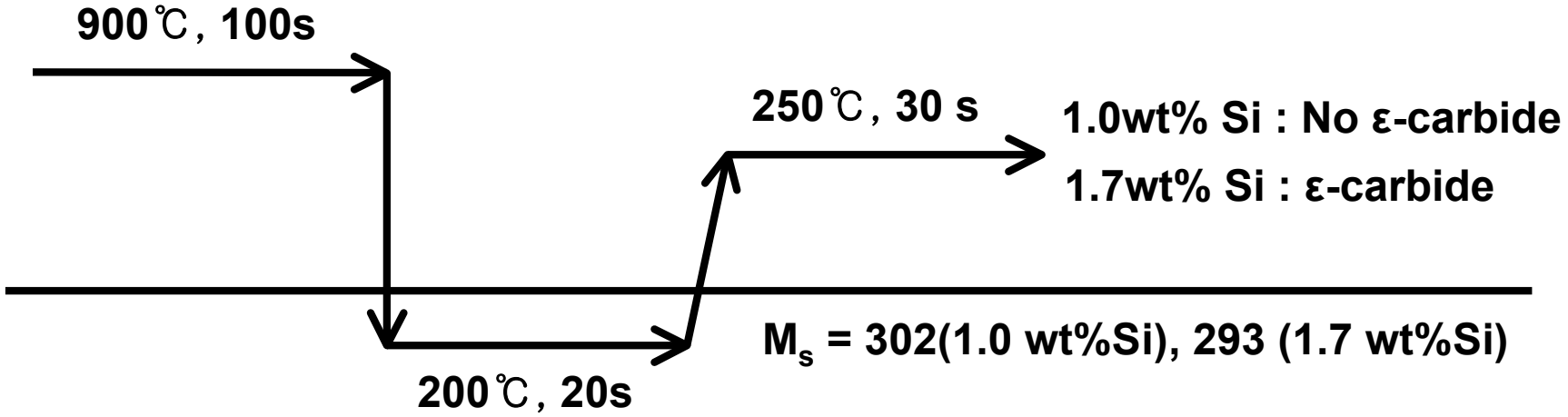
Introduction

- **Martensite (α') → ε-carbide → η-carbide → χ-carbide → Cementite (θ)**

  $Fe_{2.4}C$ Fe_2C $Fe_{2.5}C$ Fe_3C

- **Silicon promotes the formation of ε-carbide below 520 K.**

  S. S. Nayak *et.al*, *Materials Science and Engineering A. 498,* pp.442-456(2008)



- **ε-carbide forms without redistribution of Si.**

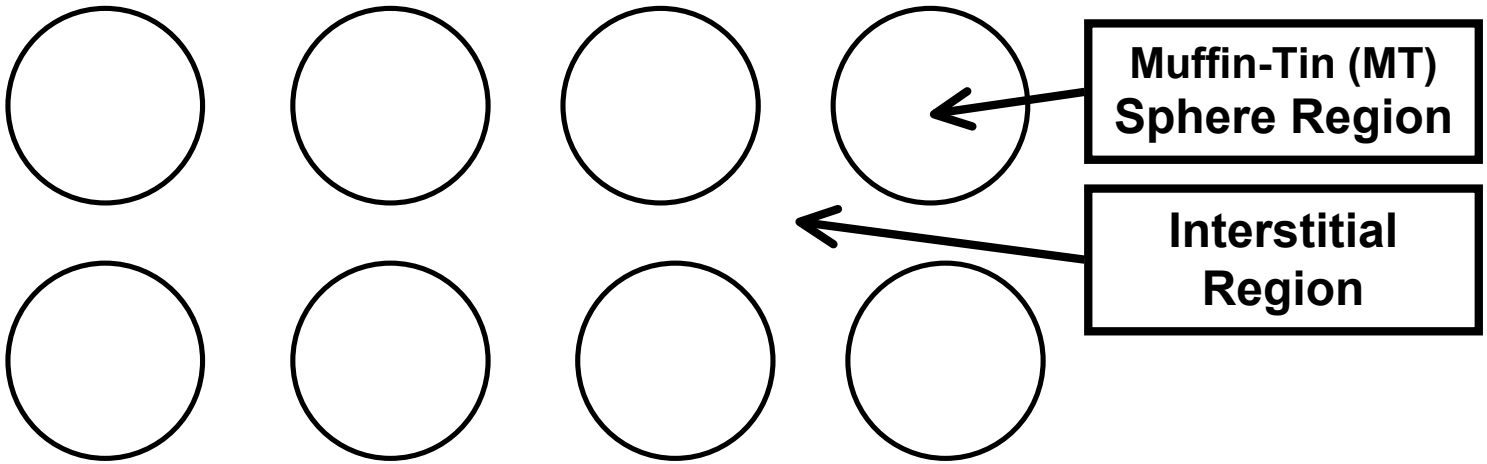
  S. J. Barnard, G. D. W. Smith, *Proceedings of the solid-solid phase transformation.,* pp.881(1981)

- **No initial partitioning of Si between ε, θ and martensite**

  S. S. Babu, K. Hono, T. Sakurai, *Metal Mater. Trans.* **25A** (1994) p. 499

FLAPW method

E. Wimmer, H. Krakauer, M. Weinert, and A. J. Freeman, *Phys. Rev. B* **28**, 864 (1981) and references therein.
M. Weinert, E. Wimmer, and A. J. Freeman, *Phys. Rev. B* **26**, 4571 (1982).



Wave Function Expansion $\psi_{\mathbf{k},v}(\mathbf{r}) = \sum_{|\mathbf{k}+\mathbf{G}|\le \mathbf{K}max} c^{\mathbf{G}}_{\mathbf{k},v}\varphi_{\mathbf{G}}(\mathbf{K},\mathbf{r})$

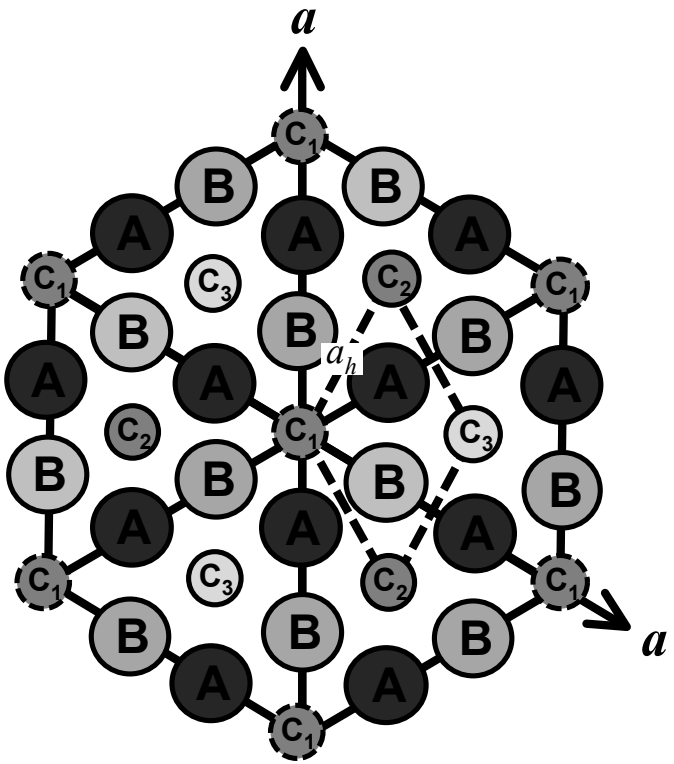
$$\varphi_{\mathbf{G}}(\mathbf{k},\mathbf{r}) = \begin{cases} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} & ,\mathbf{r}\in \text{Interstitial} \\ \sum_{lm}[A^{v}_{lm}u_l(r) + B^{v}_{lm}\dot{u}_l(r)]\times Y_{lm}(\theta,\varphi) & ,\mathbf{r}\in \text{MT sphere } v \end{cases}$$

Calculation Parameters

E. Wimmer, H. Krakauer, M. Weinert, and A. J. Freeman, *Phys. Rev. B* **28**, 864 (1981) and references therein.
M. Weinert, E. Wimmer, and A. J. Freeman, *Phys. Rev. B* **26**, 4571 (1982).
Perdew, J. P., Burke, K., Ernzerhof, M., *Phys. Rev. Let.* **77**,3865 (1996)

- **All-electron Full-potential LAPW method**
- **Generalized Gradient Approximation for Exchange-Correlation Potential**
- **Plane-Wave Cutoff : 21 Ry**
- **Star-Function Cutoff : 340 Ry**
- **k-points : 88 – $Fe_{2.4}C$, 365 – $(Fe_{11}M)C_5$**
- **Muffin-tin Sphere : Fe, Si, Al , Mn (2.04 a.u.), C (1.30 a.u.)**
- **Mixing Method : Broyden**

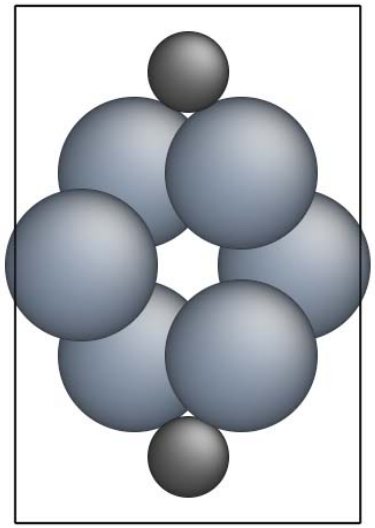
Epsilon Carbide



Formula Unit	$Fe_{2.4}C(Fe_2C{\sim}Fe_3C)$
Structure	hexagonal
Space group	*$P6_322$ or $P6_3/mmc$*
a	4.767 Å
c	4.354 Å
c/a	0.913

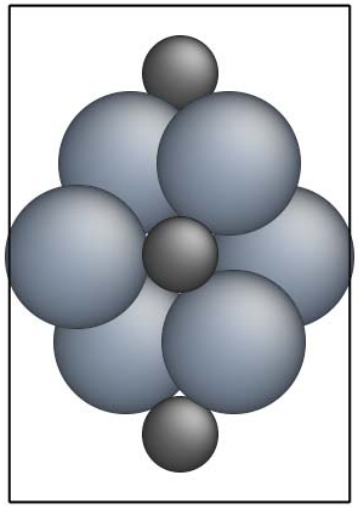
S. Nakagura, *J. Phys. Soc. Jpn*, **14** (1959) 186.

Fe_3C and Fe_2C (ε-carbide)



a	4.661 Å (−2.3%)
c	4.294 Å (−1.4%)
c/a	0.9213
x	0.3190

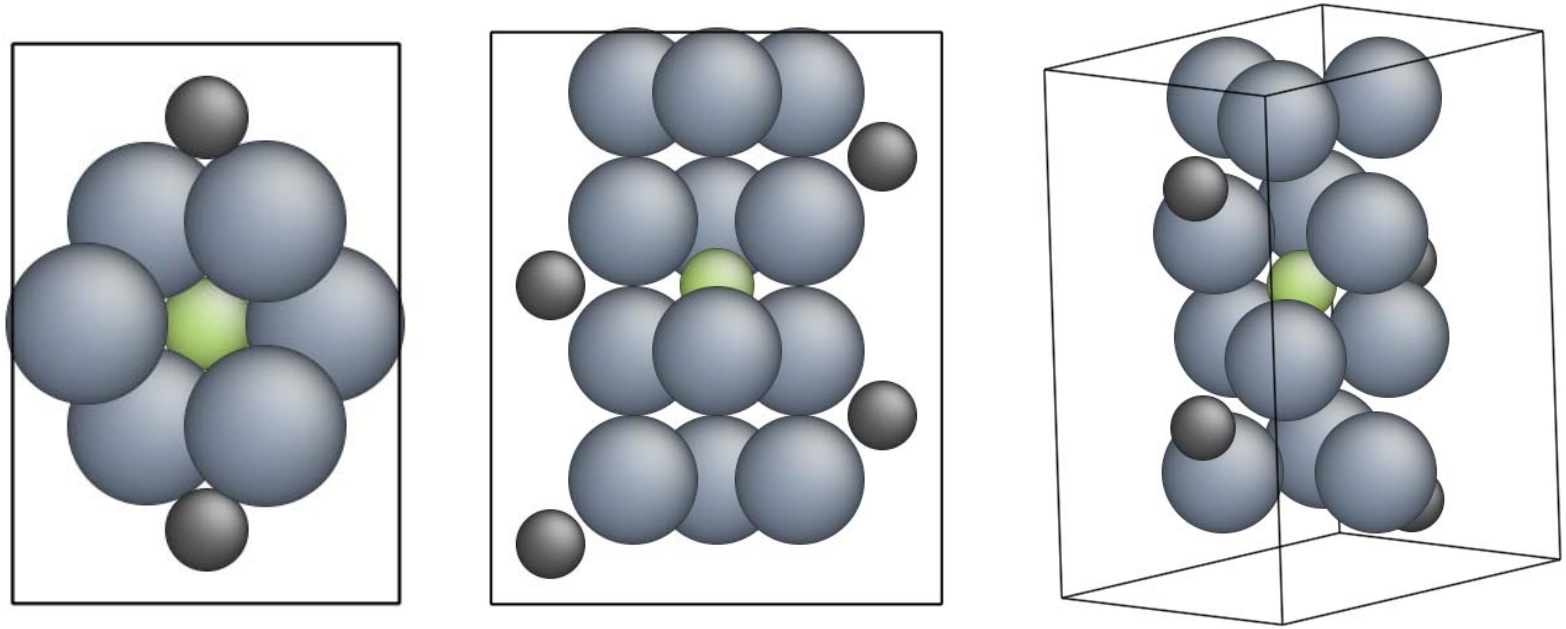
$$\Delta E = \frac{E(\mathrm{Fe_6C_2}) - 6\times E(\mathrm{Fe}) - 2\times E(\mathrm{C})}{8} = 5.09\mathrm{kJ/mol}$$



a	4.785 Å (+0.3%)
c	4.321 Å (−0.8%)
c/a	0.903
x	0.3302

$$\Delta E = \frac{E(\mathrm{Fe_6C_3}) - 6\times E(\mathrm{Fe}) - 3\times E(\mathrm{C})}{9} = 7.00\mathrm{kJ/mol}$$

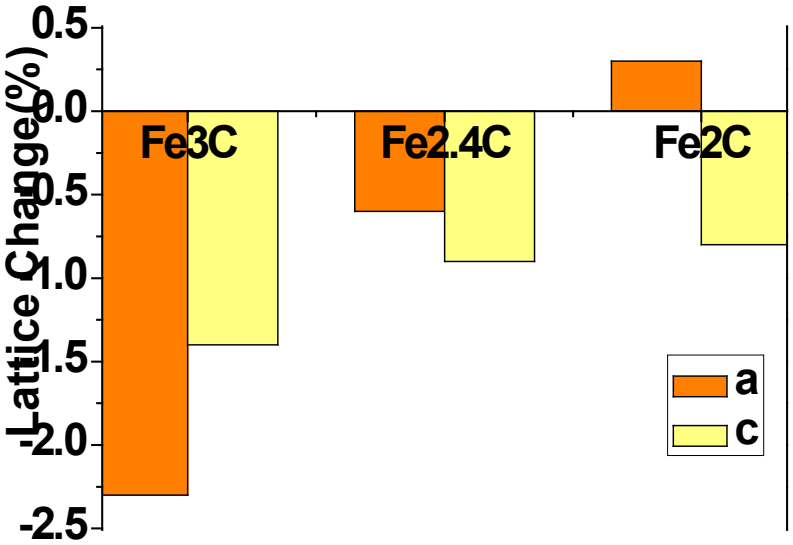
$Fe_{2.4}C$ (ε-carbide)



a	4.740 Å (−0.6%)
c	8.631 Å (−0.9%)

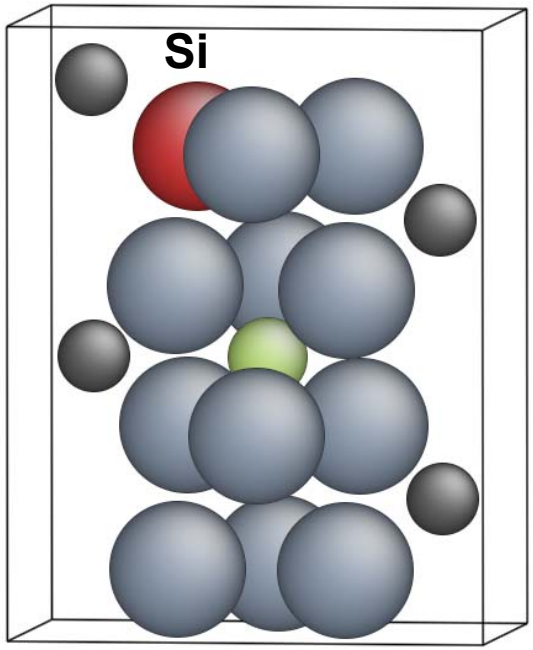
$$\Delta E = \frac{E(\mathrm{Fe_{12}C_5}) - 12 \times E(\mathrm{Fe}) - 5 \times E(\mathrm{C})}{17} = 6.24\mathrm{kJ/mol}$$

Results



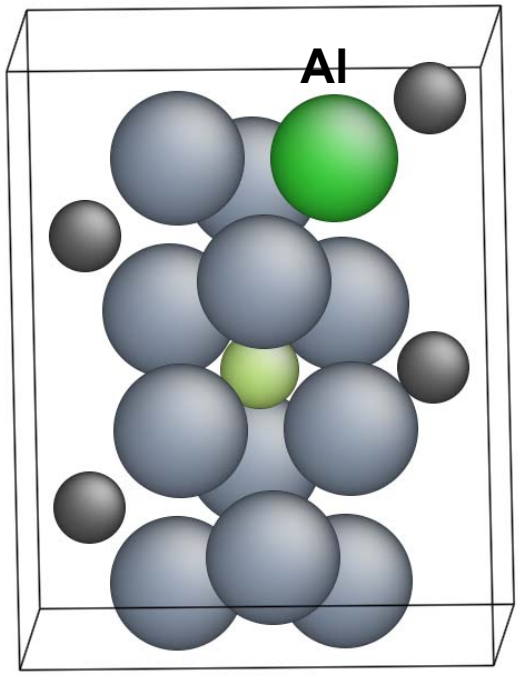
System	a (Å)	c (Å)	c_h/a_h
Measured, ε	4.767	8.708	1.582
Fe_3C	4.661(−2.3%)	8.588 (−1.4%)	1.596
$Fe_{2.4}C$	4.740(−0.6%)	8.631(−0.9%)	1.577
Fe_2C	4.785(+0.3%)	8.642(−0.8%)	1.564

Si, Al and Mn Substitution



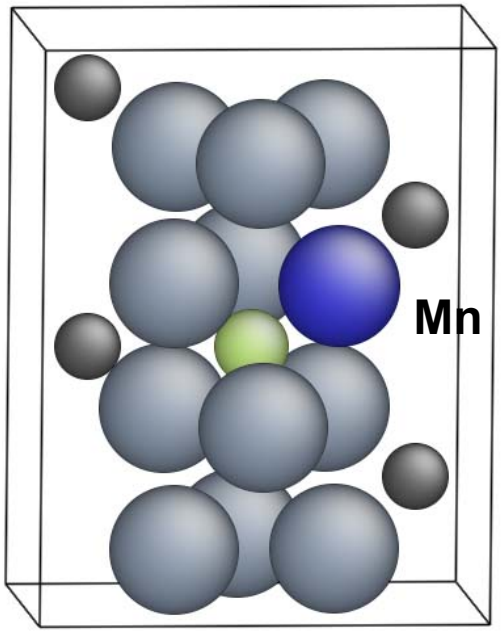
a	4.7303Å (−0.2%)
c	8.5901 Å (−0.5%)

$\Delta E = 9.08\text{kJ/mol}$



a	4.742Å (+0.0%)
c	8.685 Å (+0.6%)

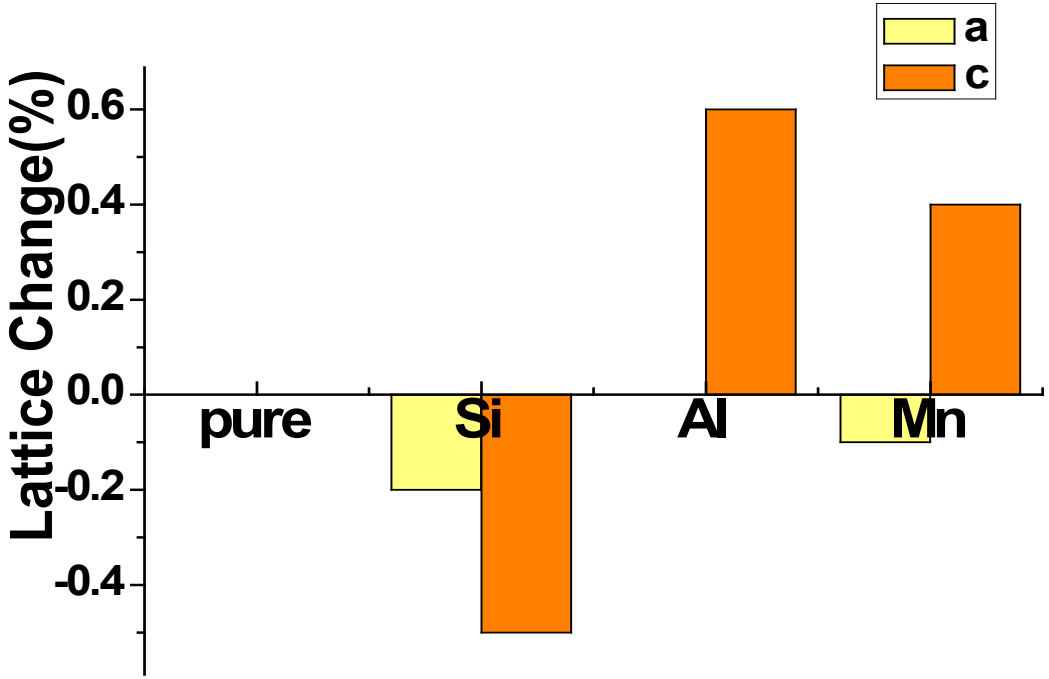
$\Delta E = 4.98\text{kJ/mol}$



a	4.738 Å (−0.1%)
c	8.664 Å (+0.4%)

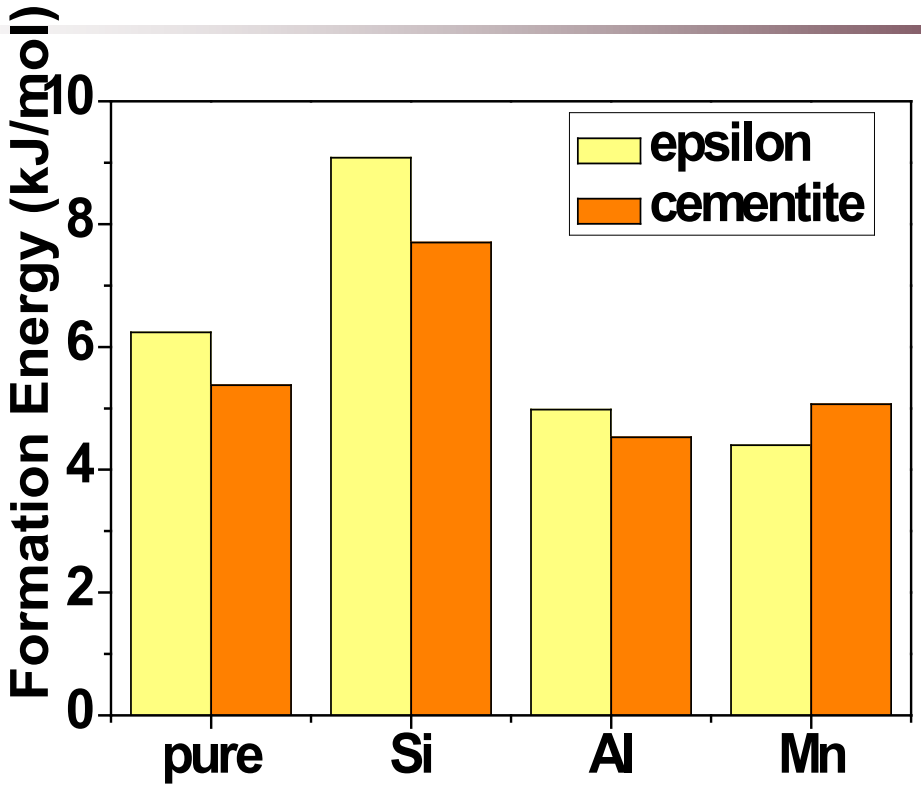
$\Delta E = 4.40\text{kJ/mol}$

Results



System	a (Å)	c (Å)	c_h/a_h
Measured, ε	4.767	8.708	1.582
Calculated, ε	4.740	8.631	1.577
Si substituted	4.730(−0.2%)	8.590(−0.5%)	1.573
Al substituted	4.742(+0.0%)	8.685(+0.6%)	1.586
Mn substituted	4.738(−0.1%)	8.664(+0.4%)	1.584

Results

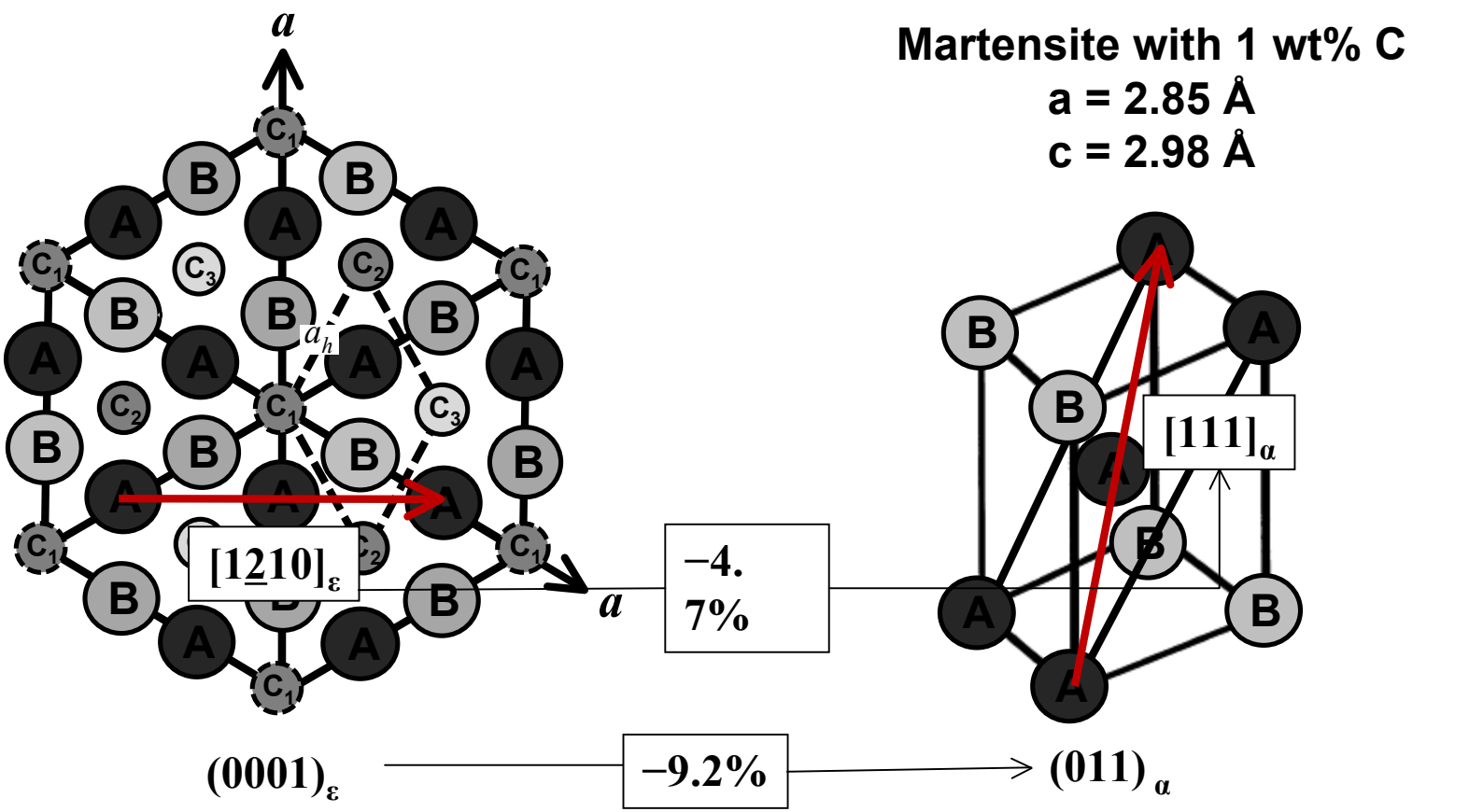


ΔE (kJ/mol)	ε-carbide	cementite
pure-carbide	6.24	5.38
Si substituted	9.08(+2.84)	7.70(+2.32)
Al substituted	4.98(−1.26)	4.53(−0.85)
Mn substituted	4.40(−1.84)	5.07(−0.31)

Orientation Relationship

H. K. D. H. Bhadeshia, *Bainite* (1992)

$(101)_{\alpha'} \| (10\underline{1}1)_{\varepsilon}$ $(211)_{\alpha'} \| (10\underline{1}0)_{\varepsilon}$ $[011]_{\alpha'} \| [0001]_{\varepsilon}$ $(\underline{1}11)_{\alpha'} \| (1\underline{2}10)_{\varepsilon}$

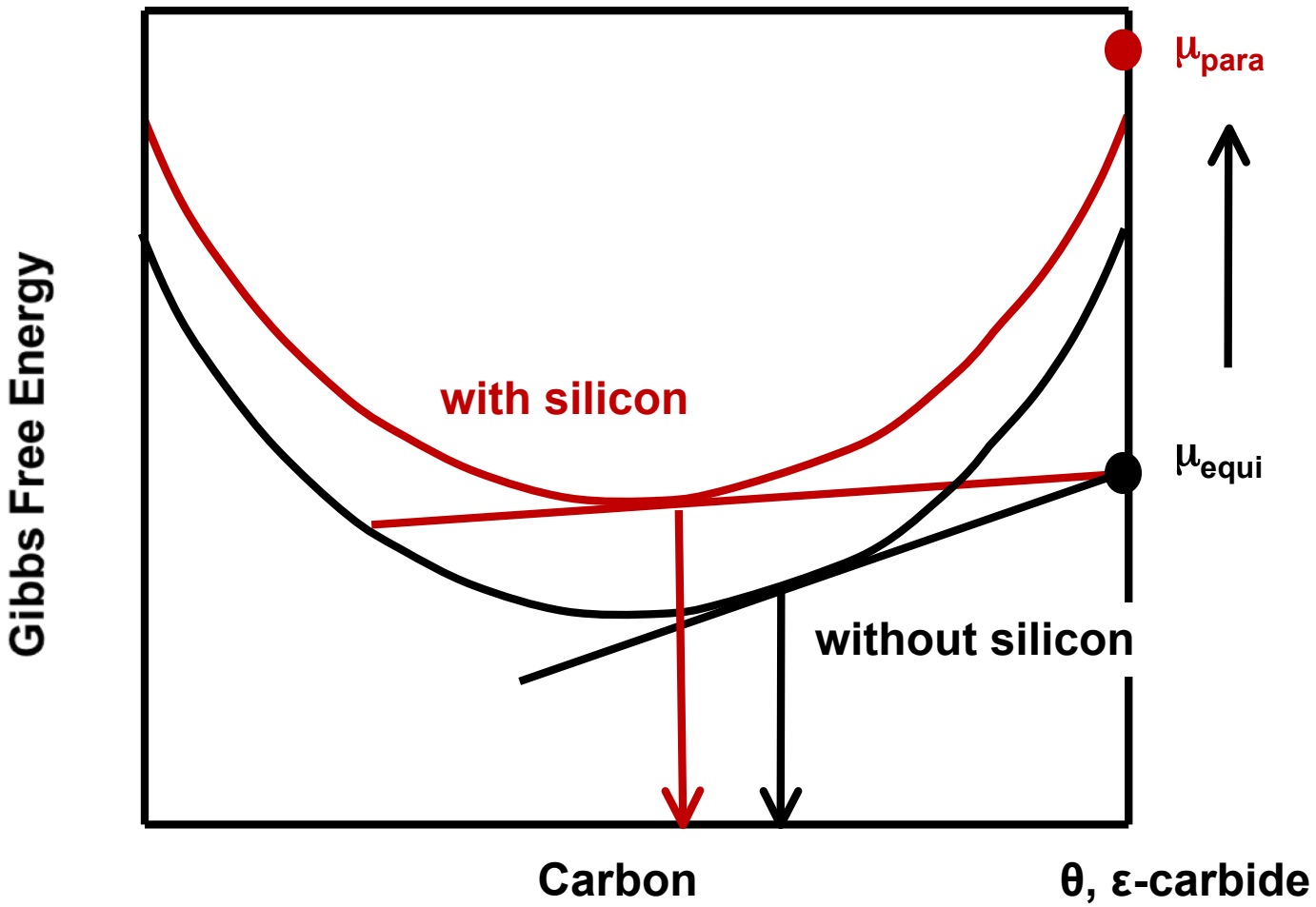


Summary

- First Principles Calculation can be applied for hypothetical crystal structure.
- Si addition increases the formation energy of θ and ε-carbide.
- The formation energy calculation : ε-carbide → θ
- The role of silicon in transition of carbide : Reducing the misfit
- Manganese addition : stable ε-carbide

Thank You !!

Equilibrium Calculation



Appendix A - DFT

• **Hohenberg-Kohn Theorem : The ground state property is a functional of electron density.**

$$E[n] = \int V_{\text{ext}}(\mathbf{r}) \cdot n(\mathbf{r}) d\mathbf{r} + \langle \psi | T + V_{ee} | \psi \rangle$$

$$E[n] \geq E_{GS}, E[n_{GS}] = E_{GS}$$

• **Kohn-Sham Equation : Introducing the non-interacting fictitious particle.**

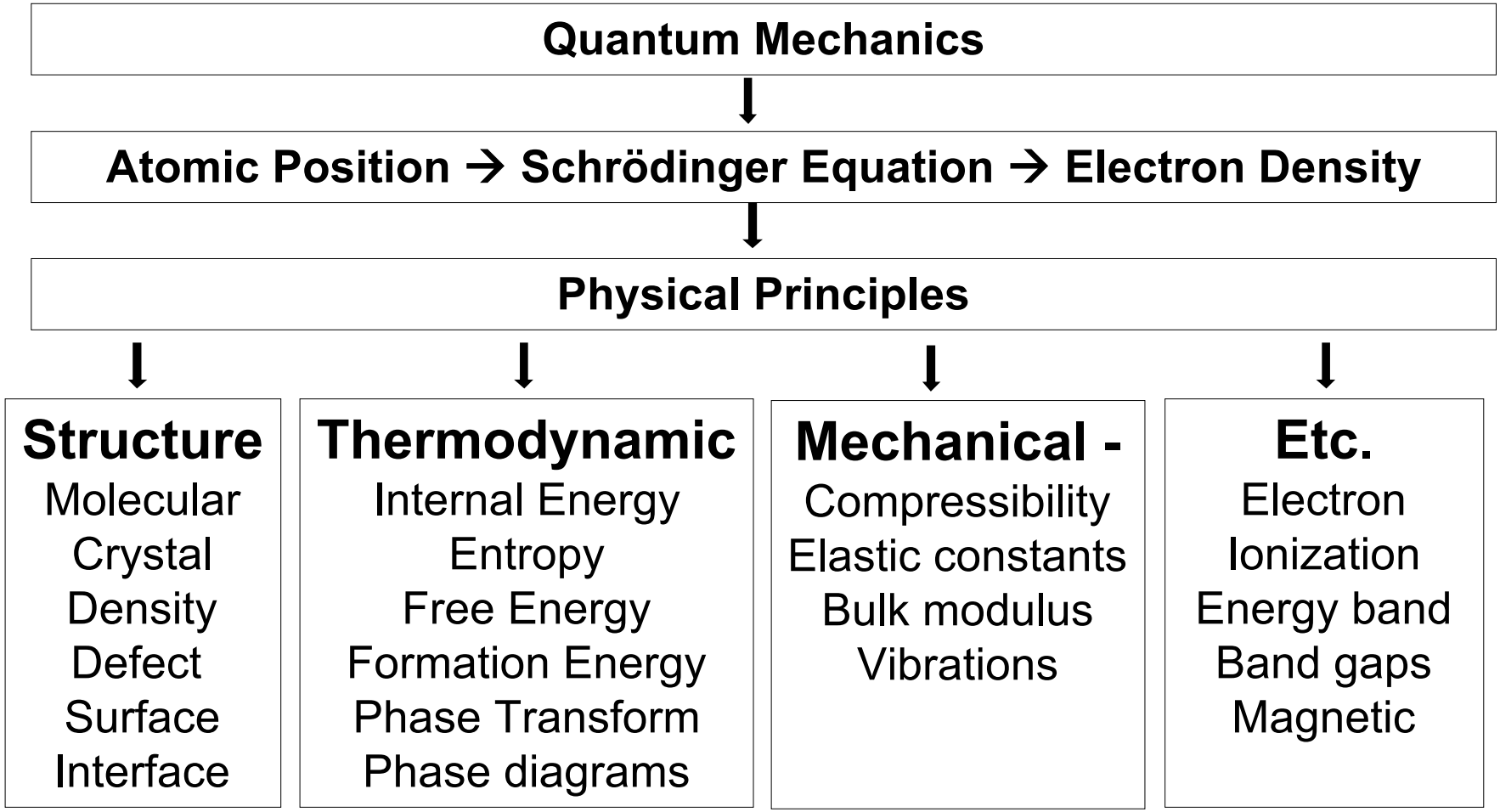
$$E[n] = \int V_{\text{ext}}(\mathbf{r}) \cdot n(\mathbf{r}) d\mathbf{r} + T[n] + \frac{1}{2} \int V_{\text{C}}(\mathbf{r}) \cdot n(\mathbf{r}) d\mathbf{r} + E_{xc}[n]$$

$$\frac{\delta E[n]}{\delta n} = V_{\text{ext}}(\mathbf{r}) + \frac{\delta T[n]}{\delta n} + V_C(\mathbf{r}) + \frac{\delta E_{\text{xc}}[n]}{\delta n} = \mu$$

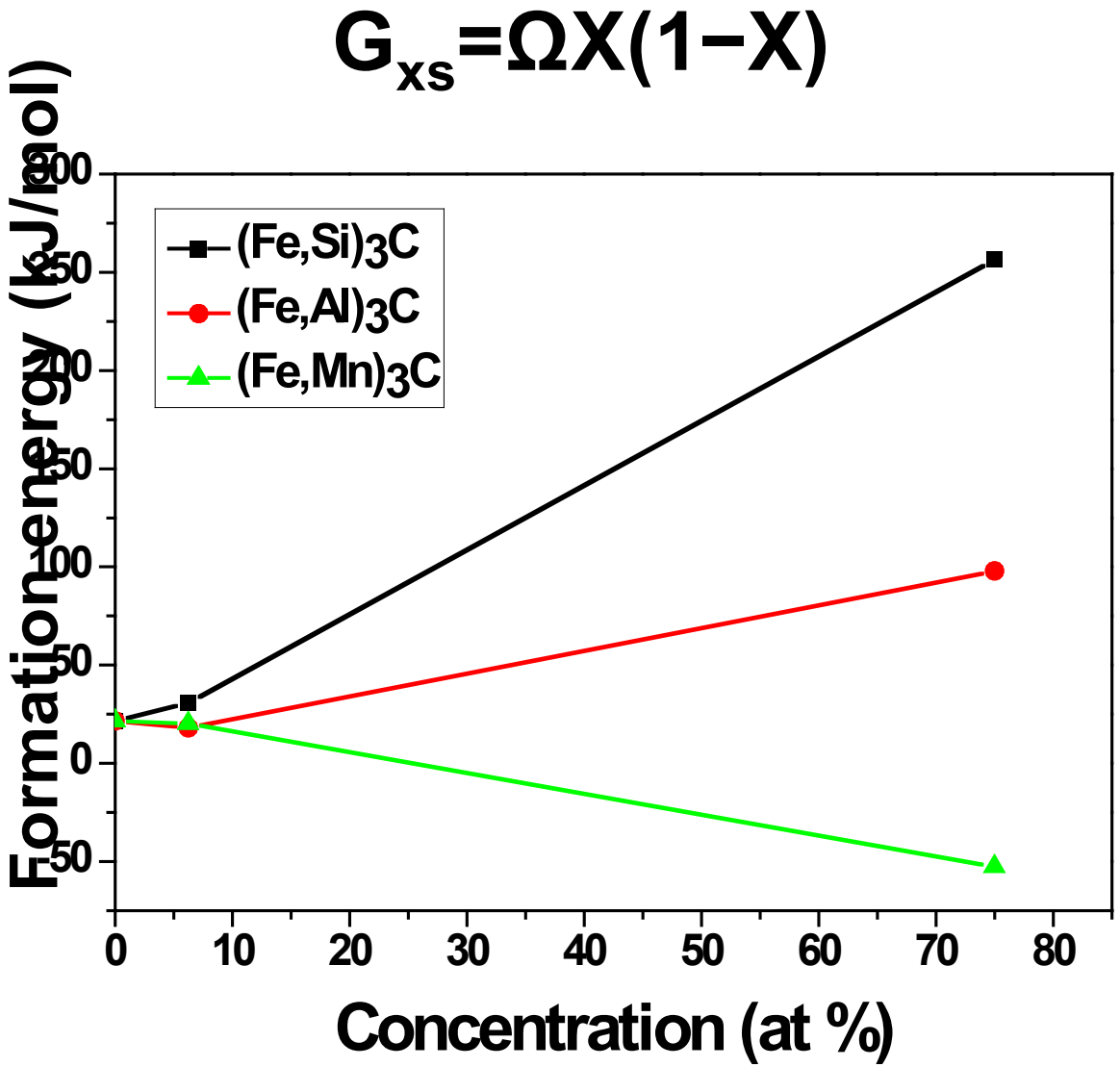
$$\frac{\delta E[n]}{\delta n} = \frac{\delta T[n]}{\delta n} + v_{\text{eff}}(\mathbf{r}) = \mu \qquad v_{\text{eff}}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + V_C(\mathbf{r}) + \frac{\delta E_{\text{xc}}[n]}{\delta n}$$

$$\left[-\frac{1}{2} \nabla^2 + v_{\text{eff}}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}) \qquad n(\mathbf{r}) = \sum_{i=1}^{N} |\psi_i(\mathbf{r})|^2$$

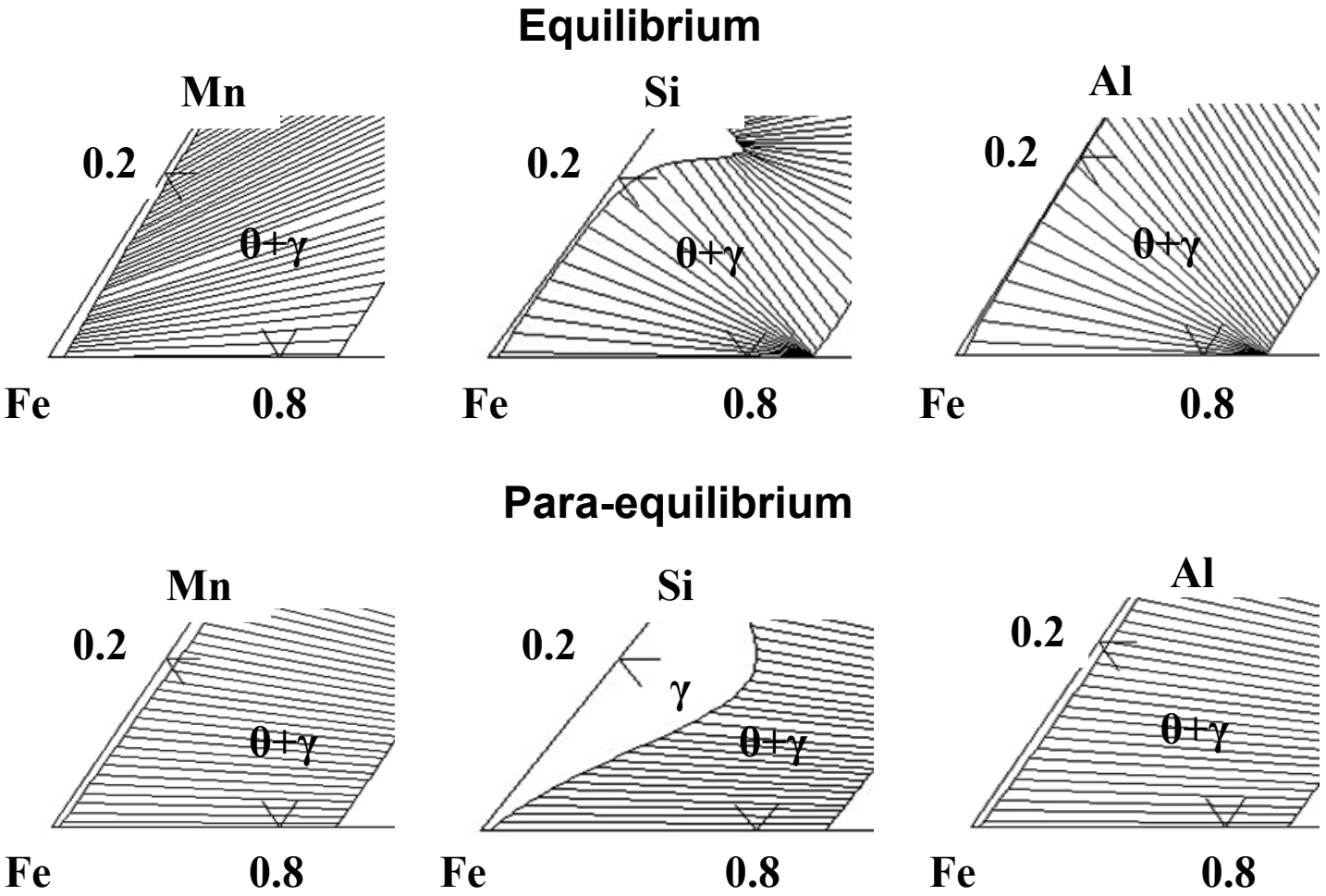
First-Principles Calculation



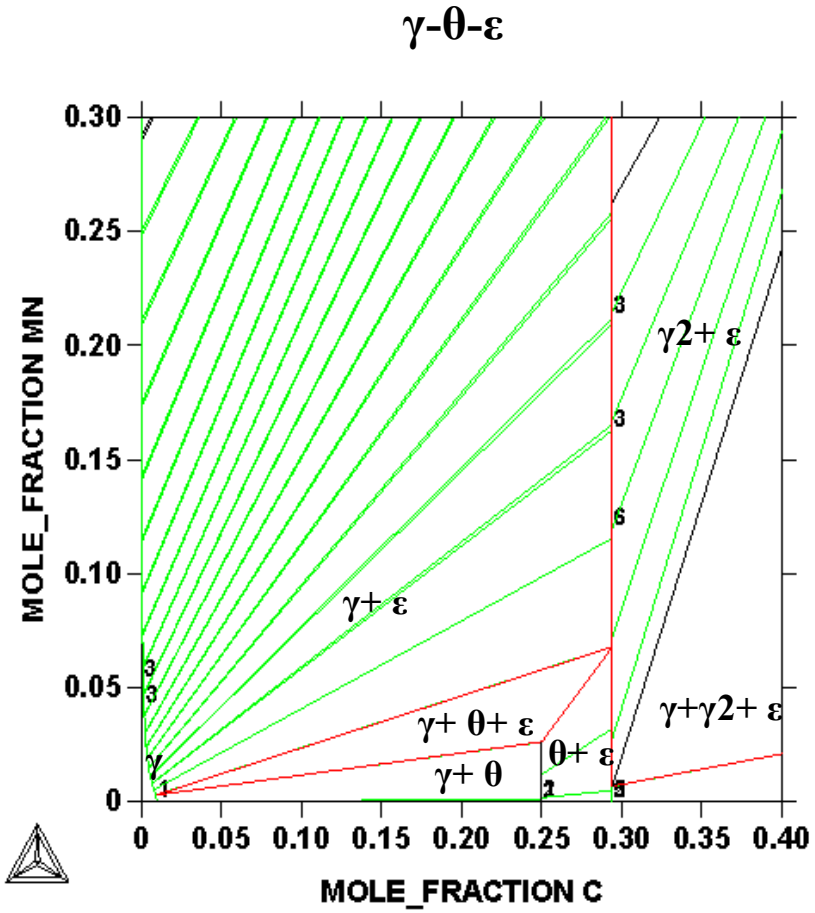
Formation Energy

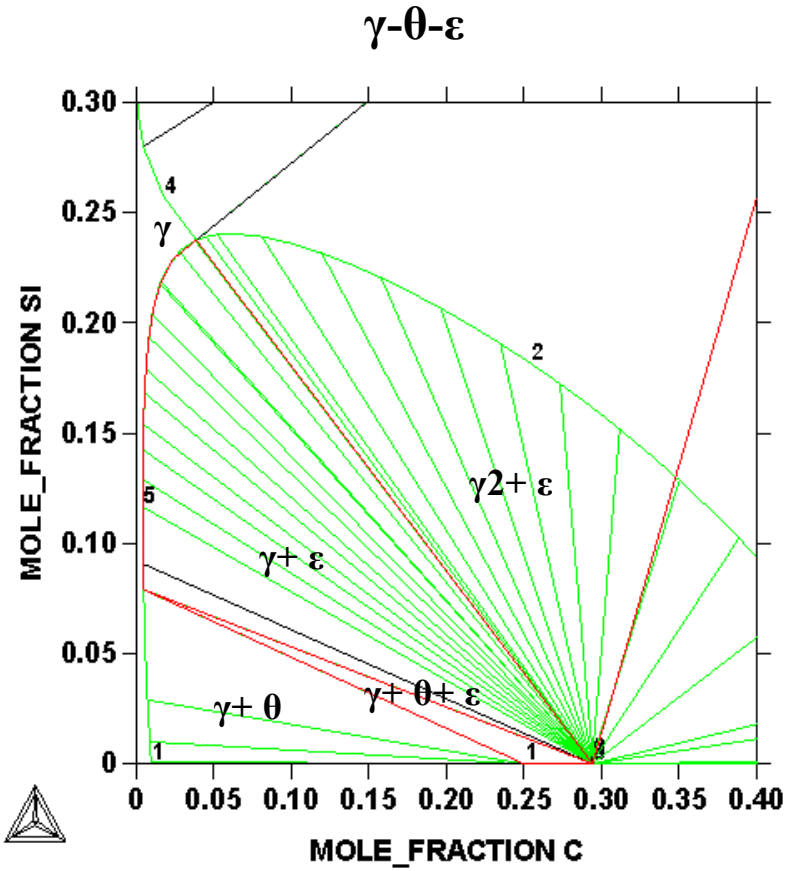


Ternary Phase Diagram at 773K

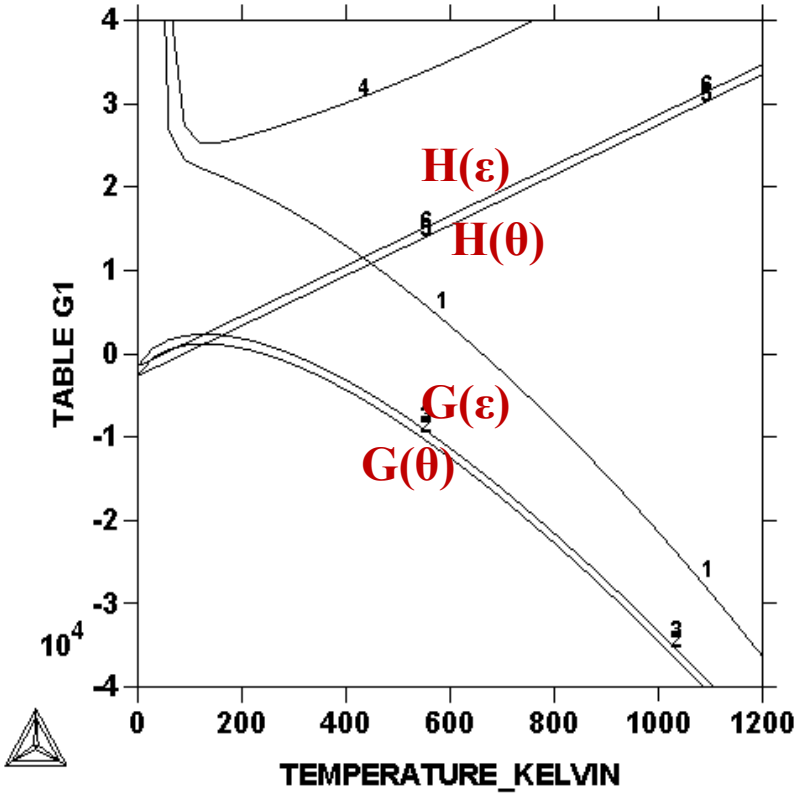


Equilibrium Phase Diagram at 723K

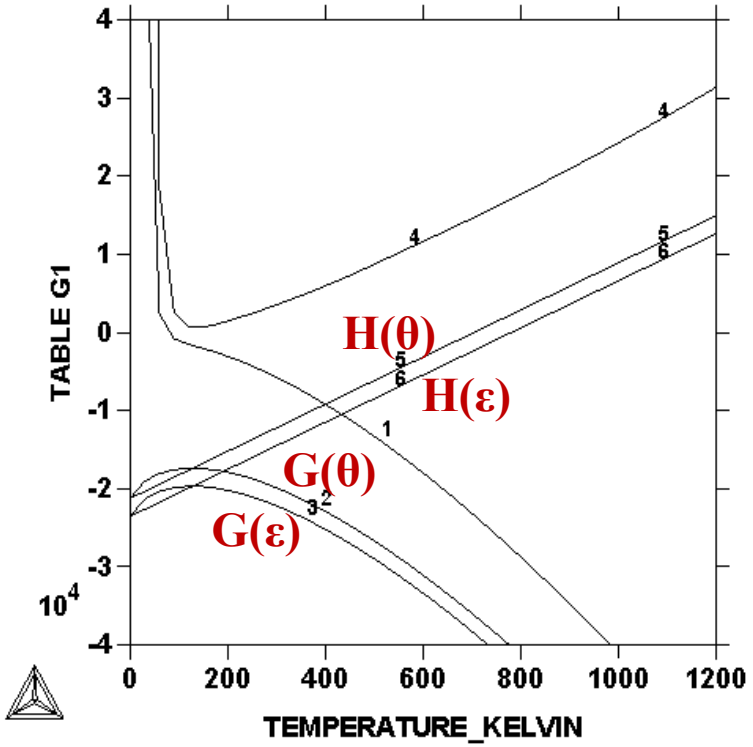




Gibbs Free Energy of Carbide

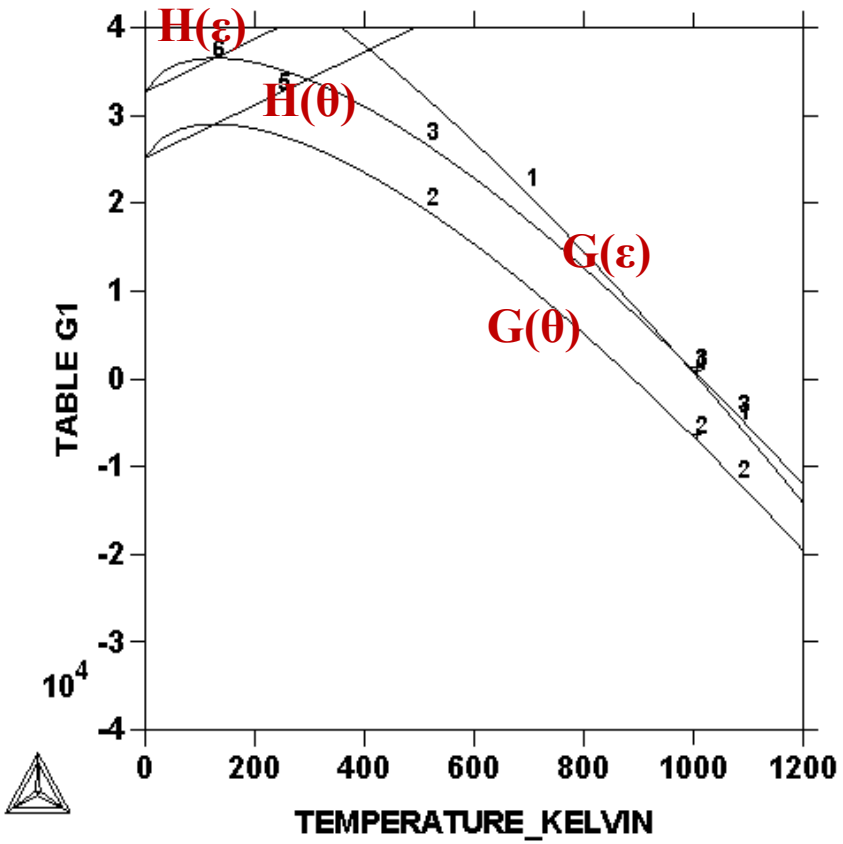


Fe-C System

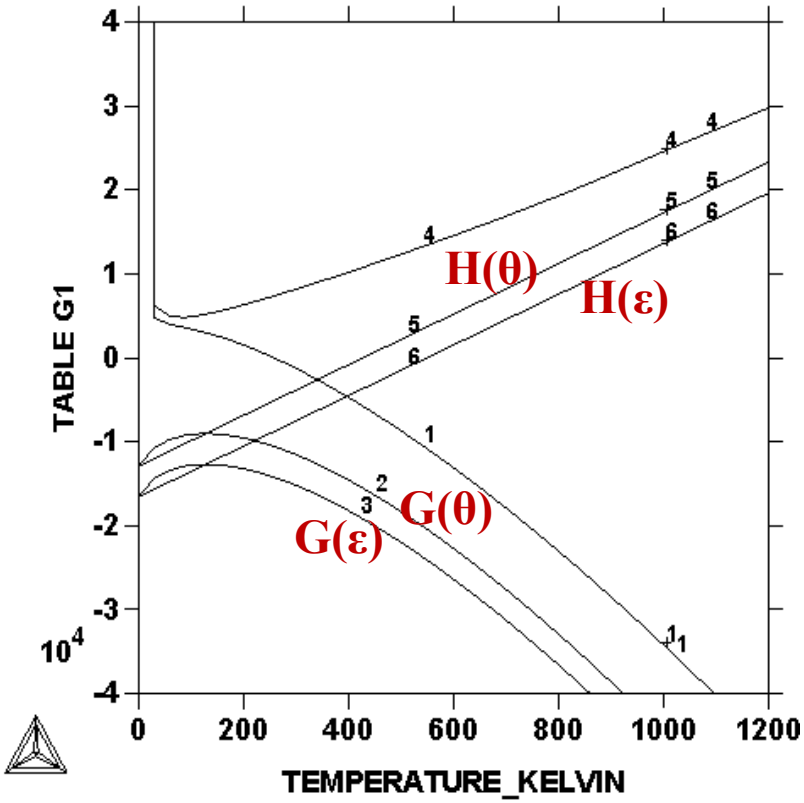


Mn-C System

Gibbs Free Energy of Al-carbide

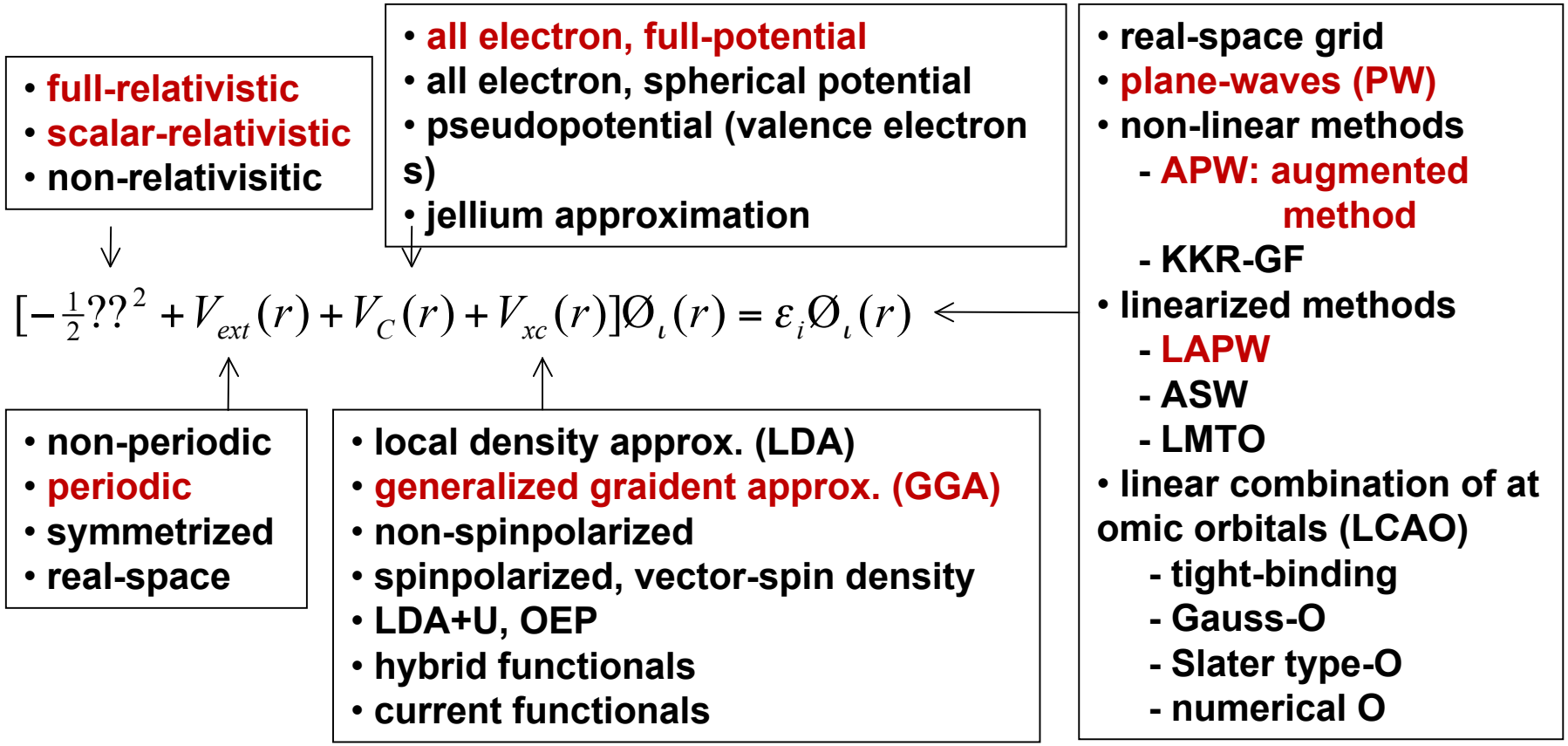


Si-C System



Al-C System

Density Functional Theory



Blugel, S. Bihlmayer, G., *Computational nanoscience: Do it yourself*, 31:85-129 (2006)