Reliable *ab initio* methods

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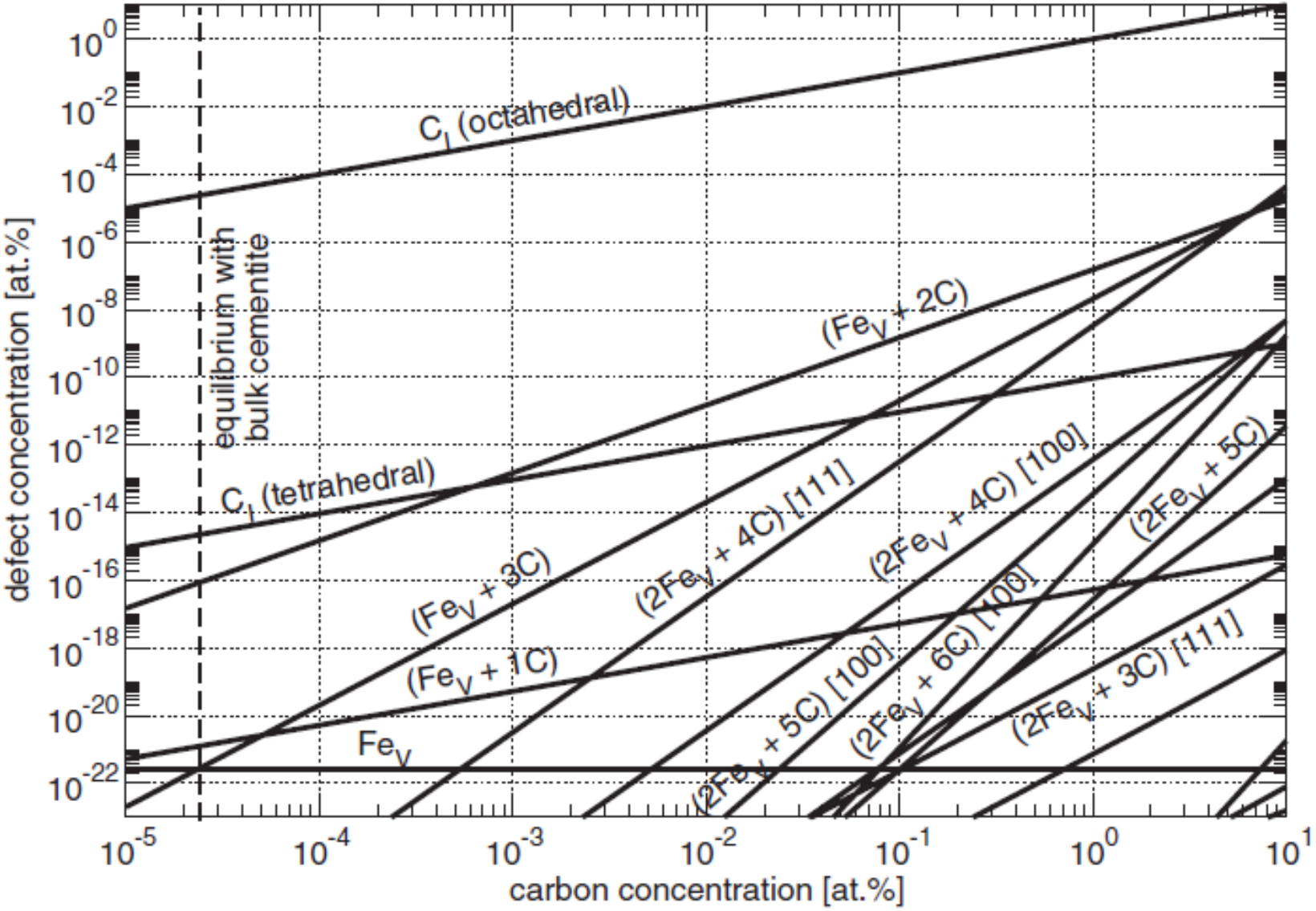
24th July 2013

Outline

- Density functional theory and tight binding
- Pure iron
- Carbon in iron
- Hydrogen in iron



Foerst et al., Phys. Rev. Lett., 96, 175501 (2006)

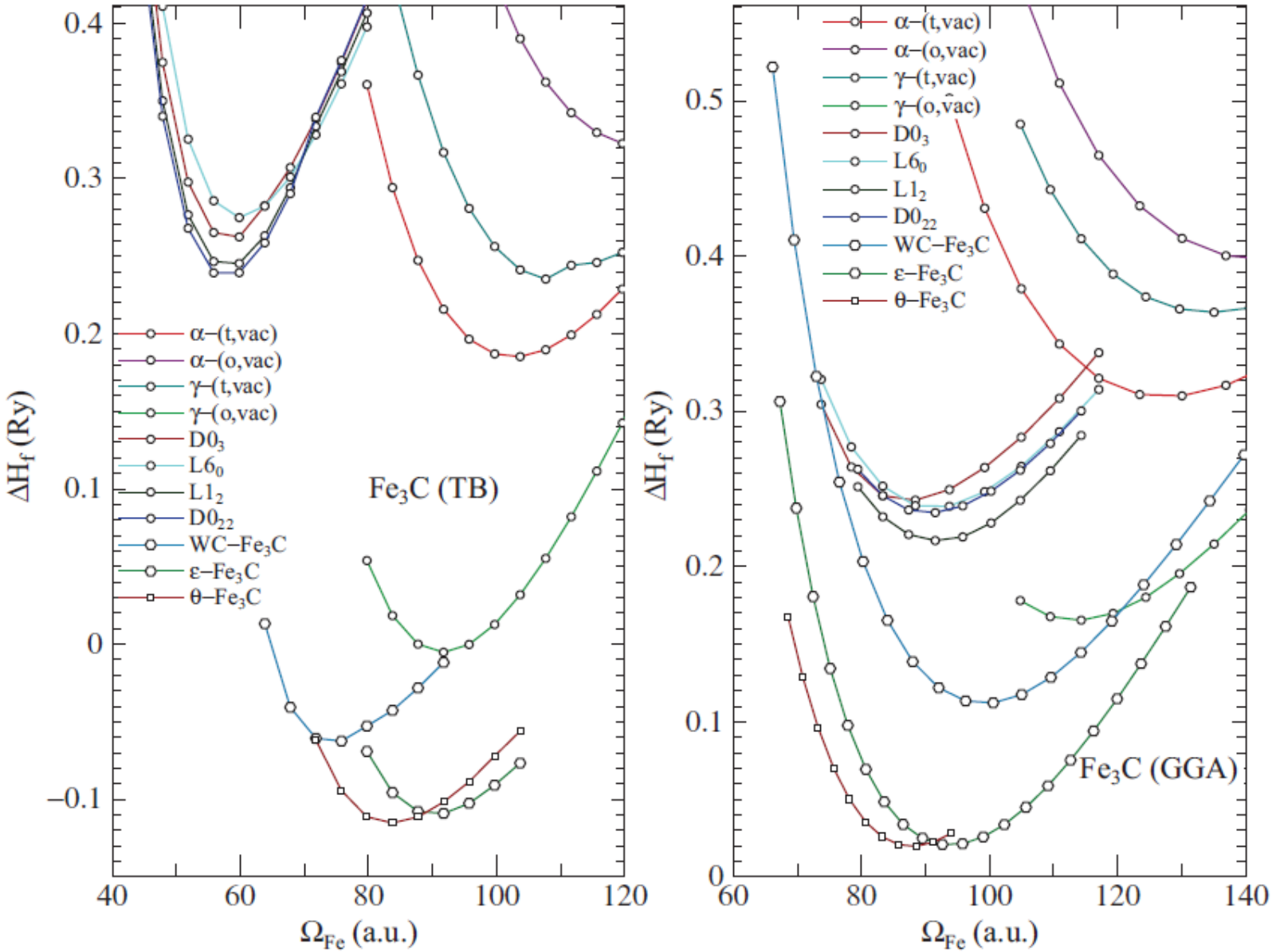
Tight binding models

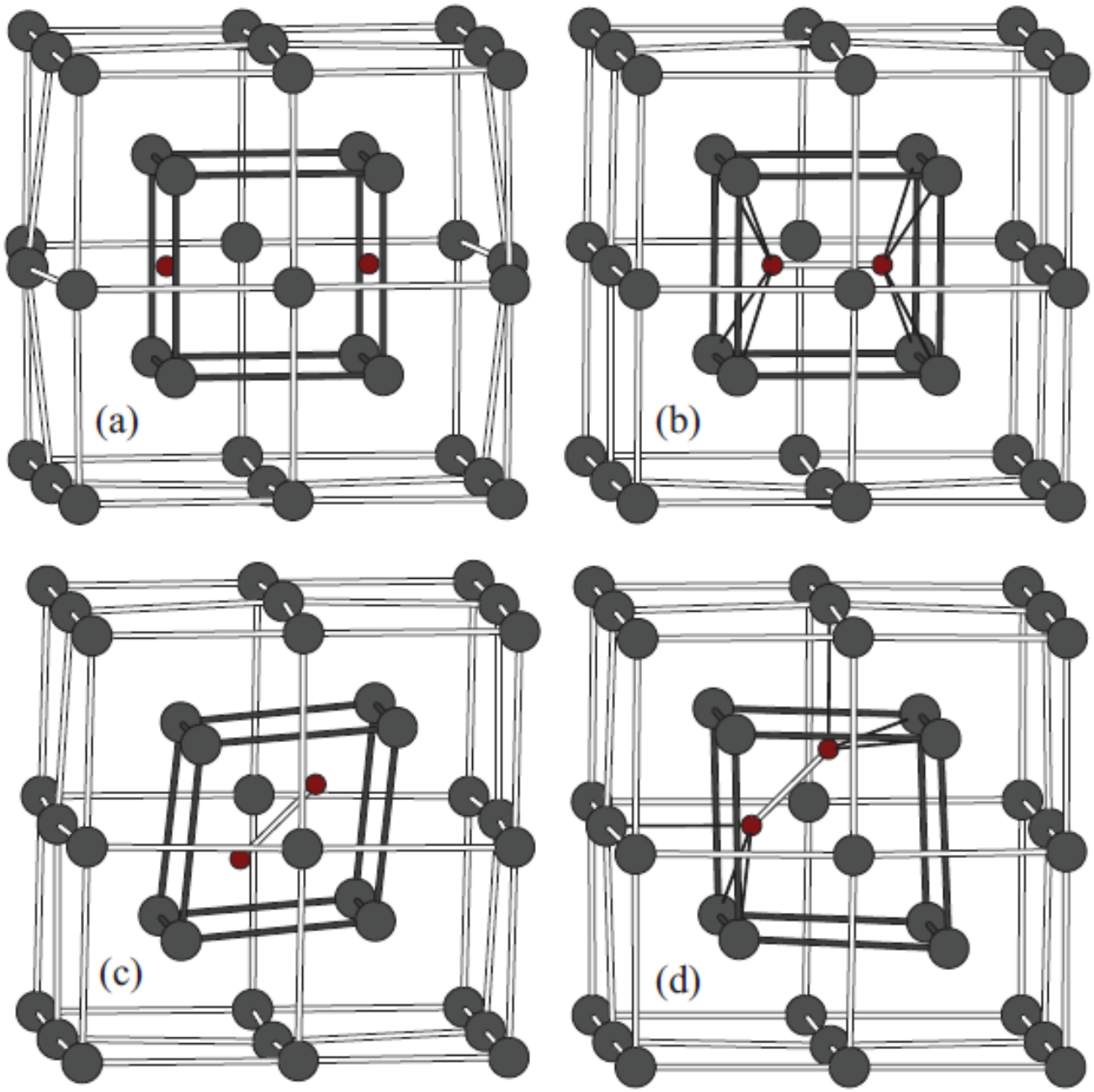
	d-sc	*d*-fx	*sd*-sc	*sd*-fx	Target	
K (Gpa)	161	174	185	192	168	(Expt.)
C' (GPa)	50	50	55	45	53	(Expt.)
c_{44} (Gpa)	118	117	106	100	122	(Expt.)
$\Delta E_{\text{hcp-bcc}}$ (mRy)	8	6	6	6	15	(LSDA-GGA)
$H^{\text{F}}_{\text{Vac.}}$ (eV)	2.0		1.6		1.61–1.75	(Expt.)
					2.0	(LSDA-GGA)
$H^{\text{M}}_{\text{Vac.}}$ (eV)	1.16		0.81		1.12–1.34	(Expt.)
					0.65–0.75	(LSDA-GGA)

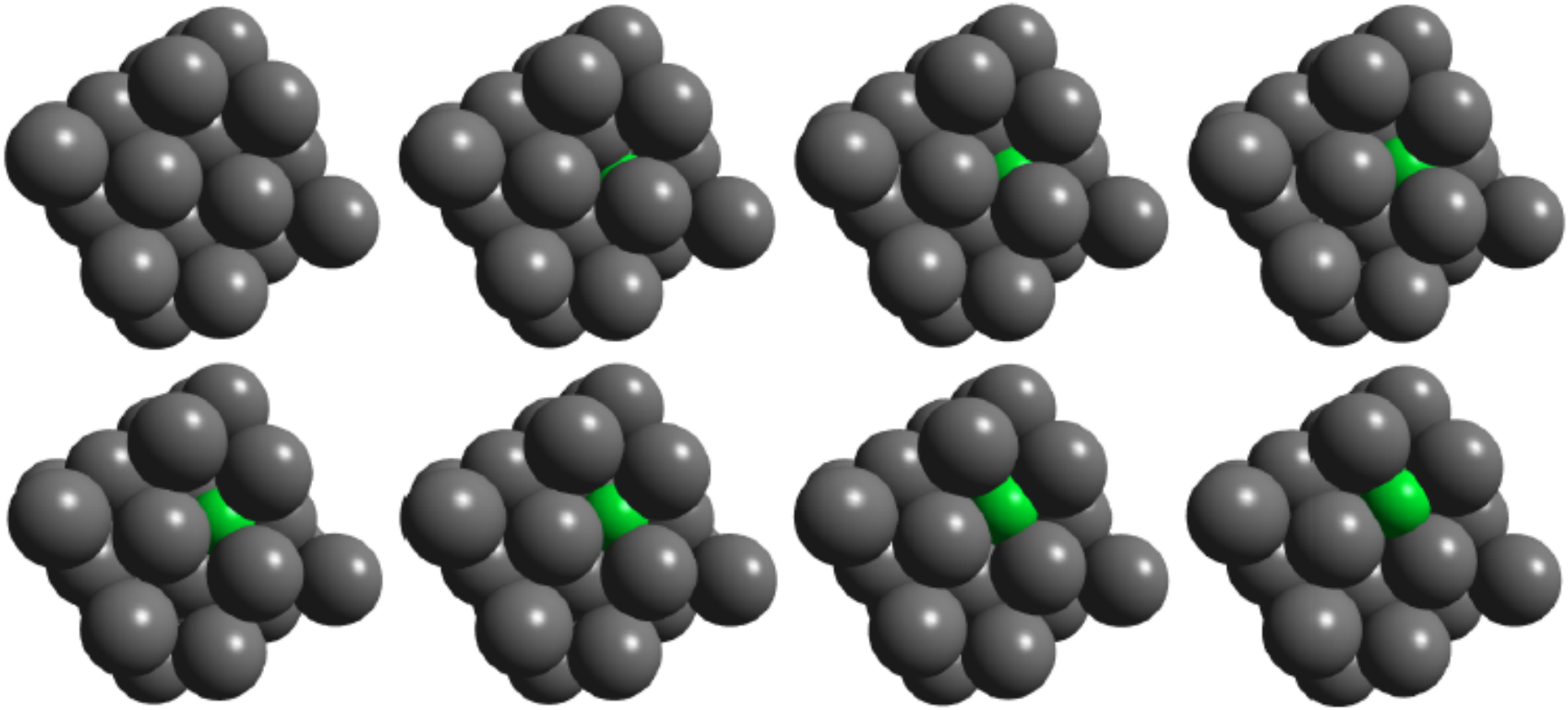
		a	b	c	b/a	c/a	V/V_{exp}
θ-Fe_3C	TB	4.95	6.79	4.42	1.37	0.89	0.96
	LSDA-GGA	5.13	6.65	4.46	1.30	0.86	0.98
	Expt.	5.09	6.74	4.52	1.32	0.89	
ϵ-Fe_3C	TB	4.63		8.64		1.87	0.93
	LSDA-GGA	4.74		8.63		1.82	0.98
	Expt.	4.77		8.71		1.83	

	$H_C^{M_\alpha}$	$E_B(1)$	$E_B(2k)$	$H_C^{M_\gamma}$ (tet)	$H_C^{M_\gamma}$ (d)
LSDA-GGA	0.87	0.47	1.50	1.48	1.00
TB	0.81	0.35	1.55	2.11	0.63

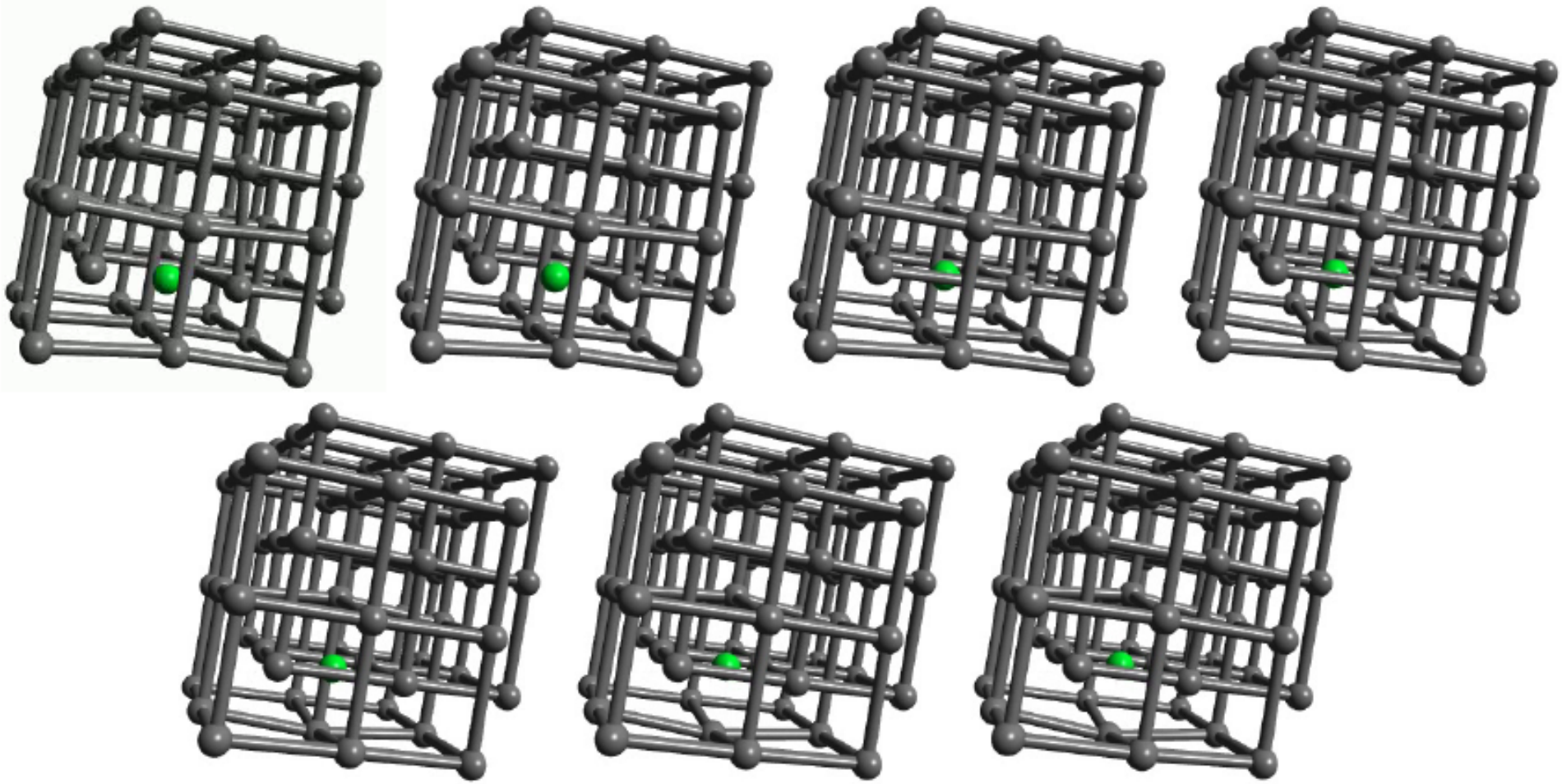
Iron carbides



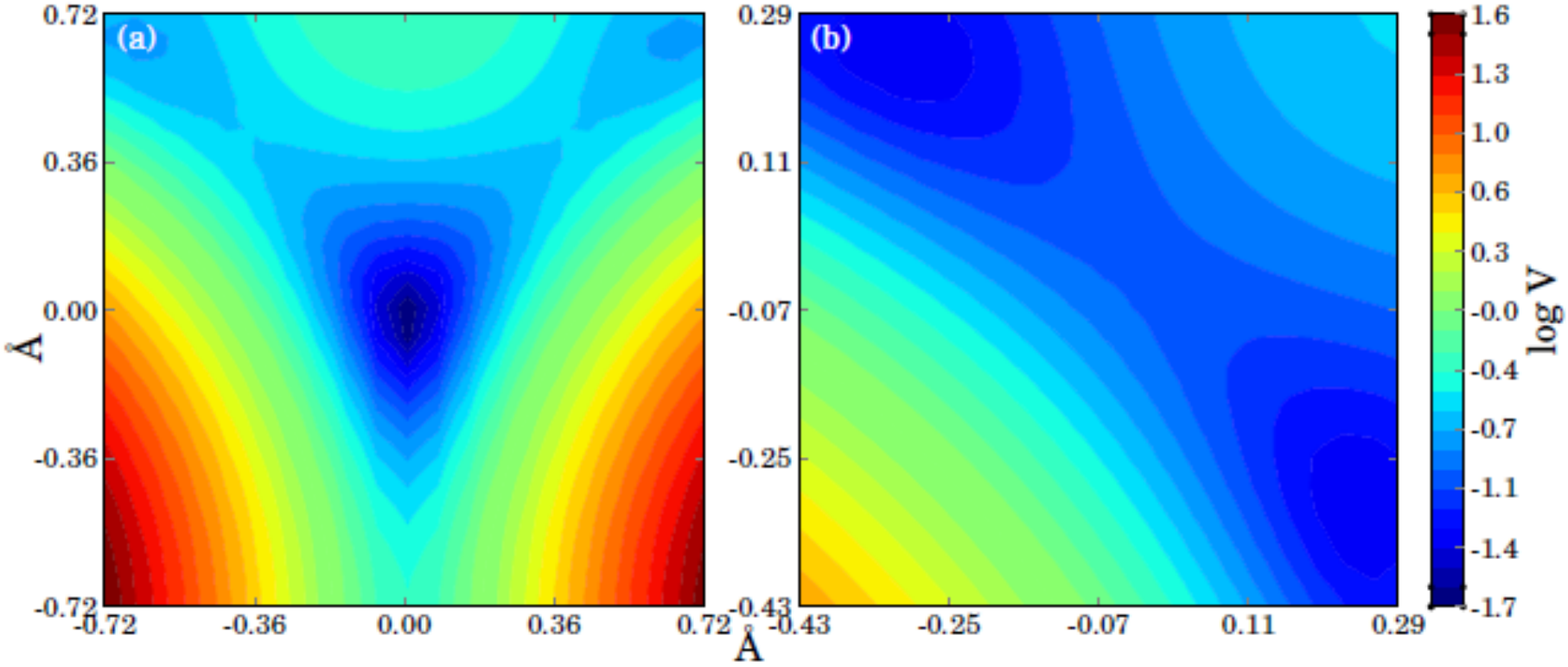

(a)
(b)
(c)
(d)



Carbon diffusion in austenite



Carbon diffusion in ferrite


(a)
(b)
0.72
0.36
0.00
-0.36
-0.72
Å
-0.72
-0.36
0.00
0.36
0.72
Å
0.29
0.11
-0.07
-0.25
-0.43
-0.43
-0.25
-0.07
0.11
0.29
1.6
1.3
1.0
0.6
0.3
-0.0
-0.4
-0.7
-1.1
-1.4
-1.7
log V

$$\text{P.P.D.} = \rho(x, x, T)/Z \qquad F = -kT \log Z$$

$$Z = \sum_i e^{-E_i/kT} = \int \mathrm{d}x\, \rho(x, x, T)$$

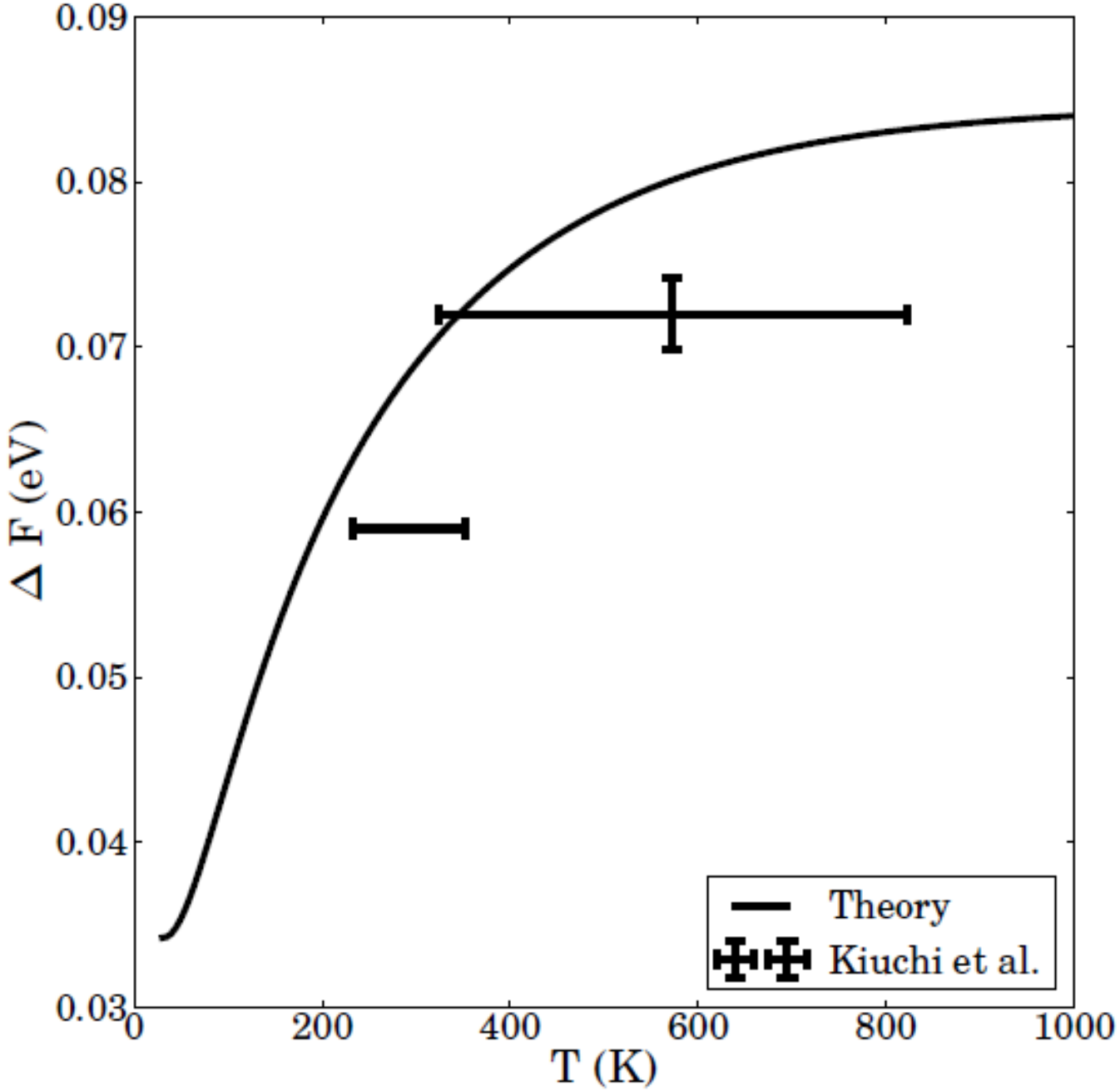
$$\approx \left(\frac{mNkT}{2\pi\hbar^2}\right)^{N/2} \int \mathrm{d}x_1 \ldots \mathrm{d}x_N$$

$$\times \exp\left(-\sum_{s=1}^{N}\left[N\,kT\frac{m}{2\hbar^2}\left(x_{s+1} - x_s\right)^2 + \frac{1}{kT}\frac{V(x_s)}{N}\right]\right)$$

Exact in the limit $N \to \infty$

$$Z = \int \mathcal{D}x(u)\, e^{-S/\hbar}$$

$$S[x(u)] = \int_0^{\beta\hbar} \mathrm{d}u \left[\frac{1}{2}m\dot{x}^2(u) + V(x(u))\right]$$

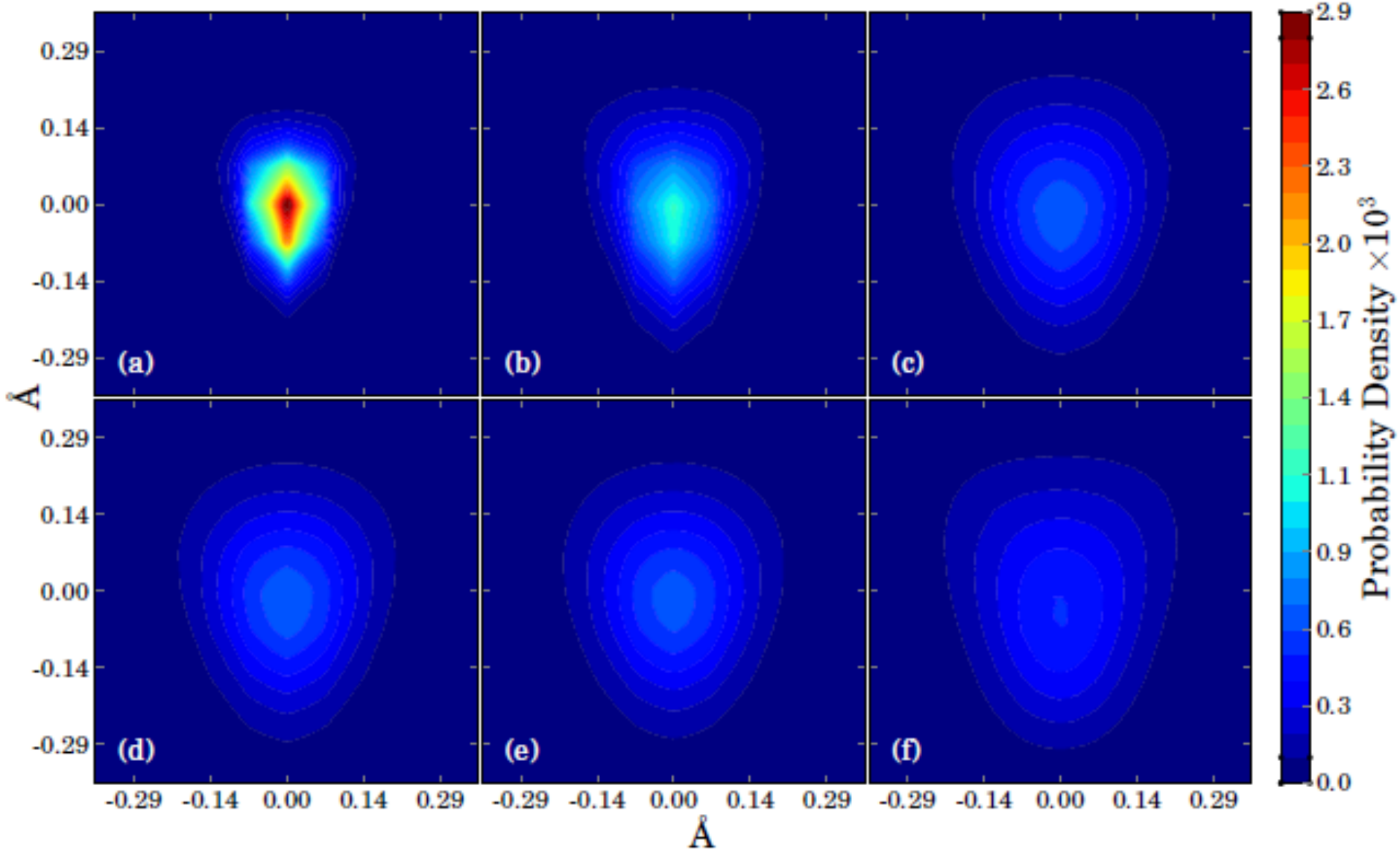

0.09
0.08
0.07
0.06
0.05
0.04
0.03
Δ F (eV)
0
200
400
600
800
1000
T (K)
Theory
Kiuchi et al.

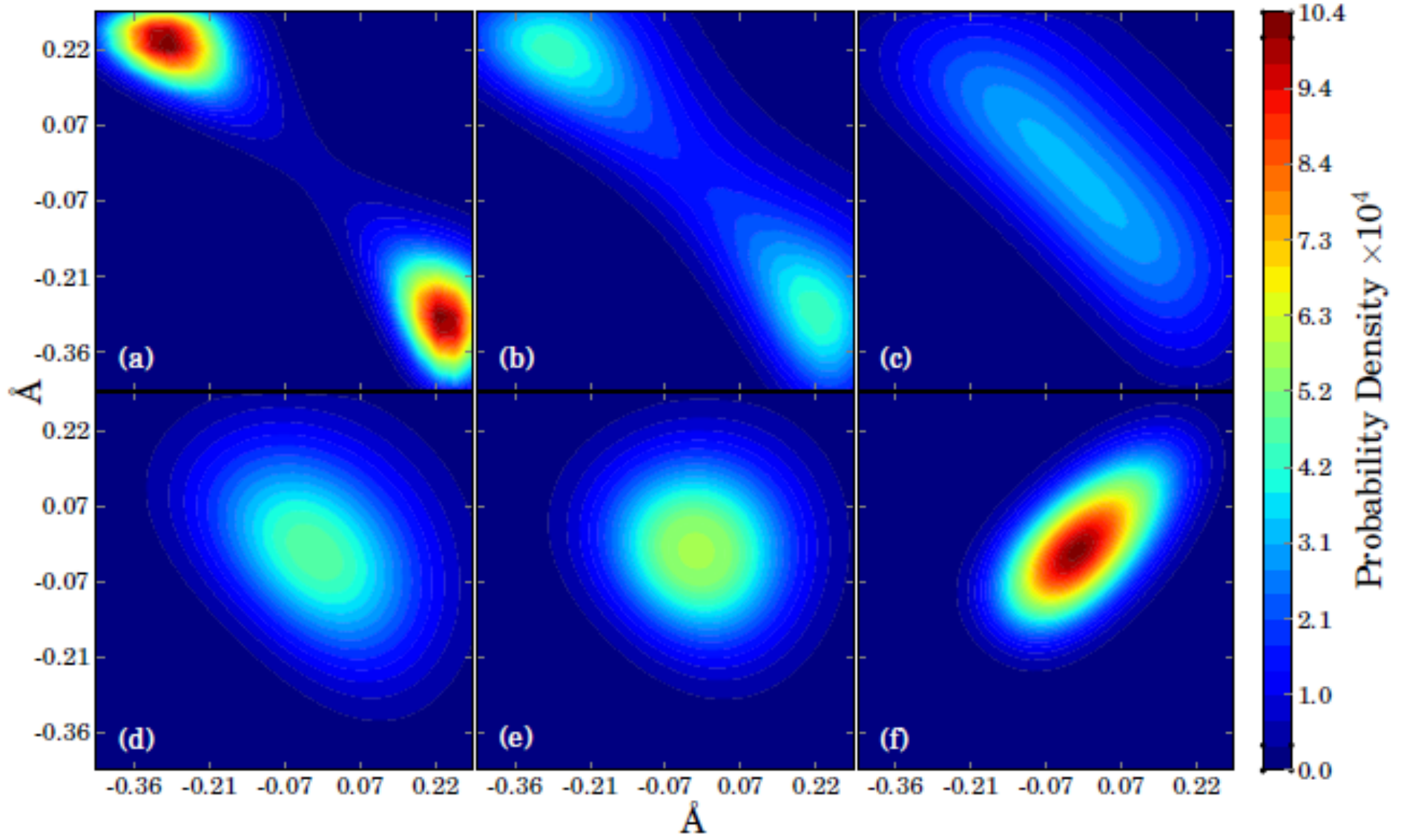
$$\rho_c(q_c, \mathbf{r}_c) = \int \mathcal{D}q(u)\mathcal{D}\mathbf{r}(u)\delta(q_c - q_0)\delta(\mathbf{r}_c - \mathbf{r}_0)\exp\{-S[q(u), \mathbf{r}(u)]/\hbar\}$$

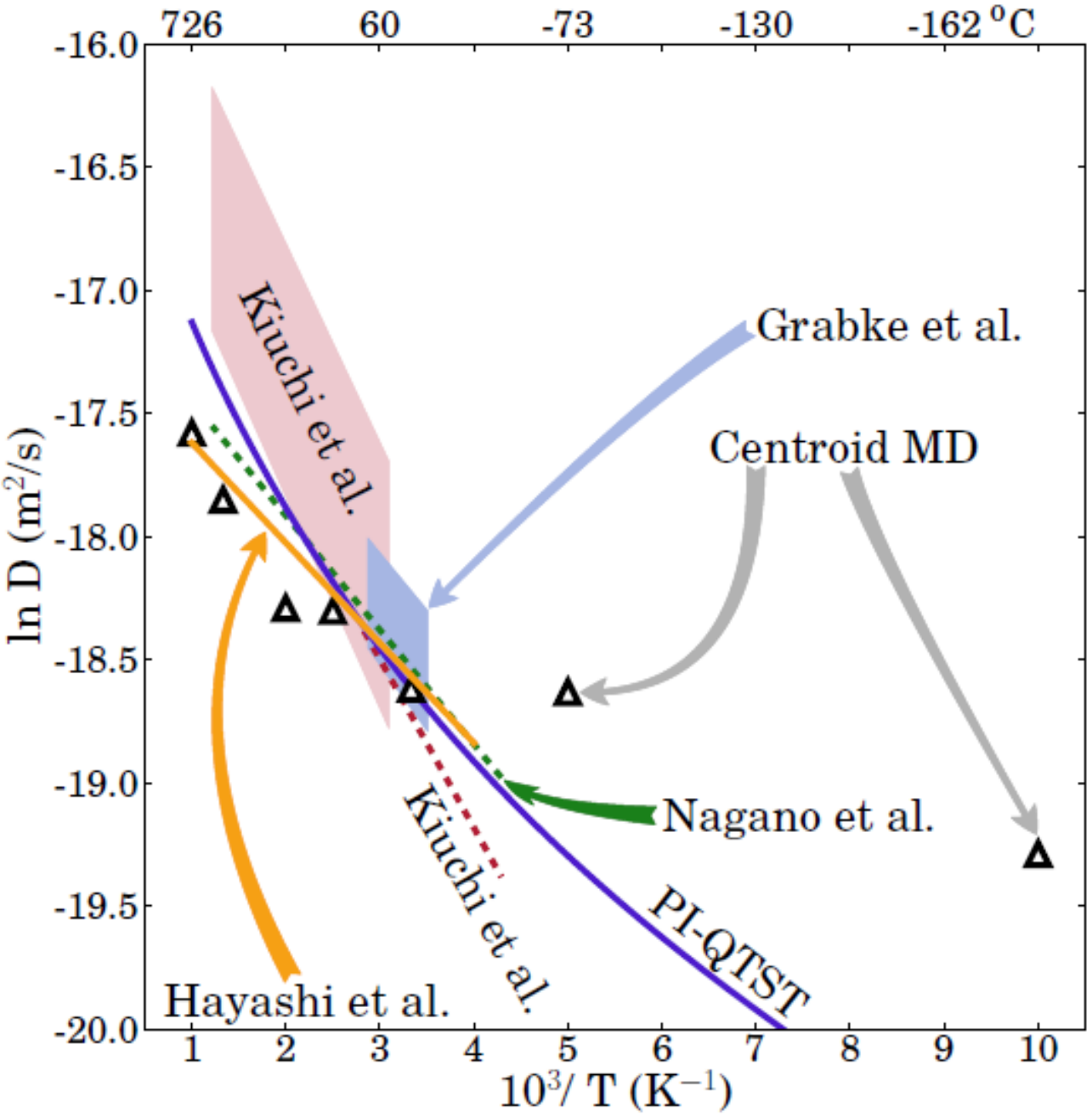
$$Z_c(q_c) = \int d\,\mathbf{r}_c\,\rho(q_c, \mathbf{r}_c)$$

$$\kappa^{\mathrm{QTST}} = \frac{\bar{v}}{2}\frac{Z_c(q^*)}{Z_c(q_R)}$$

$$\bar{v}_{FP} = \left(\frac{2}{\pi m \beta}\right)^{\frac{1}{2}}$$


(a)
(b)
(c)
(d)
(e)
(f)
0.29
0.14
0.00
-0.14
-0.29
Å
Å
Probability Density ×10^3
2.9
2.6
2.3
2.0
1.7
1.4
1.1
0.9
0.6
0.3
0.0


(a)
(b)
(c)
(d)
(e)
(f)
0.22
0.07
-0.07
-0.21
-0.36
Å
-0.36 -0.21 -0.07 0.07 0.22
Å
10.4
9.4
8.4
7.3
6.3
5.2
4.2
3.1
2.1
1.0
0.0
Probability Density ×10^4


726
60
-73
-130
-162 °C
-16.0
-16.5
-17.0
-17.5
-18.0
-18.5
-19.0
-19.5
-20.0
ln D (m²/s)
Kiuchi et al.
Grabke et al.
Centroid MD
Nagano et al.
Kiuchi et al.
PI-QTST
Hayashi et al.
1
2
3
4
5
6
7
8
9
10
10³/ T (K⁻¹)

Conclusions

- Tight binding can be nearly as reliable as density functional theory
- We now have models for C and H in Fe

  Paxton and Elsässer, *Phys. Rev. B*, **82**, 235125 (2010); *ibid*, **87**, 224110 (2013)
- We have a fully quantum mechanical prediction of the diffusivity of H in ferrite