united nations
educational, scientific
and cultural
organization

international atomic
energy agency

the
abdus salam
international centre for theoretical physics

SMR/1310 - 13

SPRING COLLEGE ON
NUMERICAL METHODS IN ELECTRONIC STRUCTURE THEORY

(7 - 25 May 2001)

"Temperature and composition of the Earth's core from *ab-initio* calculations"

presented by:

D. ALFÈ

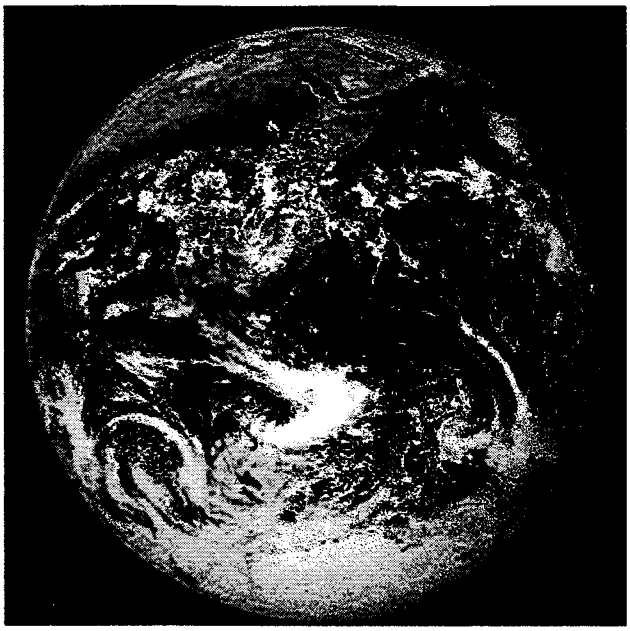
University College London
Department of Geological Sciences
and
Department of Physics and Astronomy
London
United Kingdom

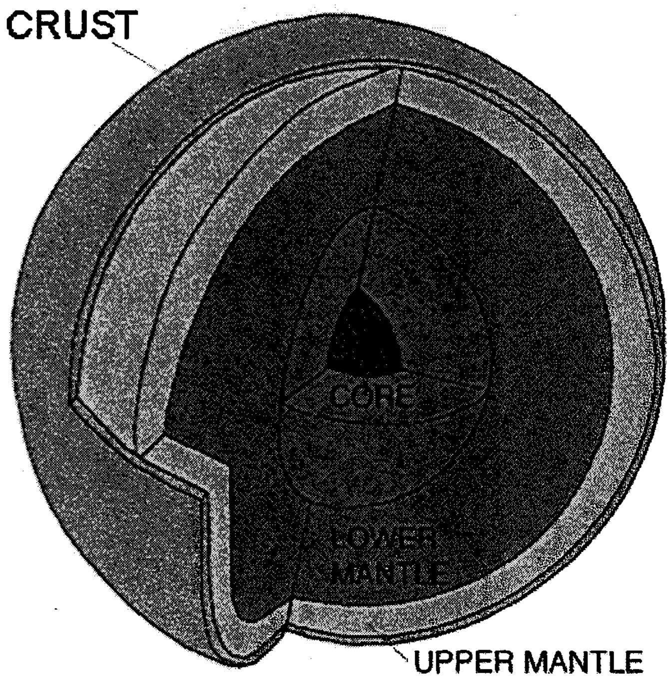
Temperature and Composition of the Earth's core from ab-initio calculations

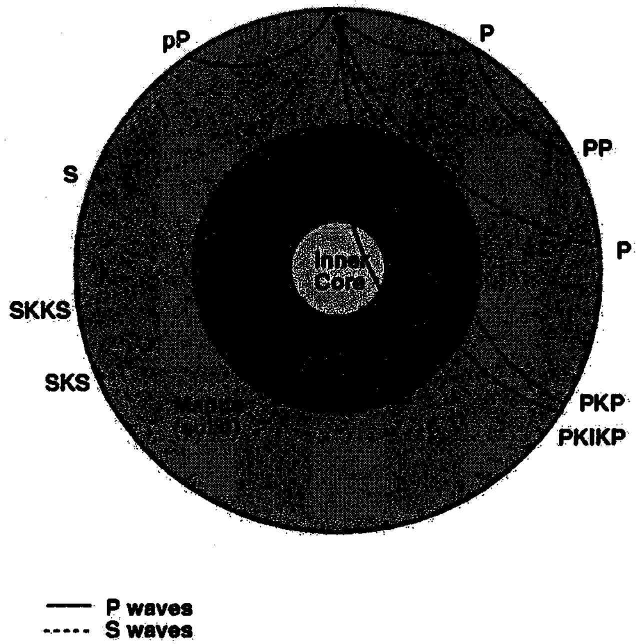
Dario Alfe`

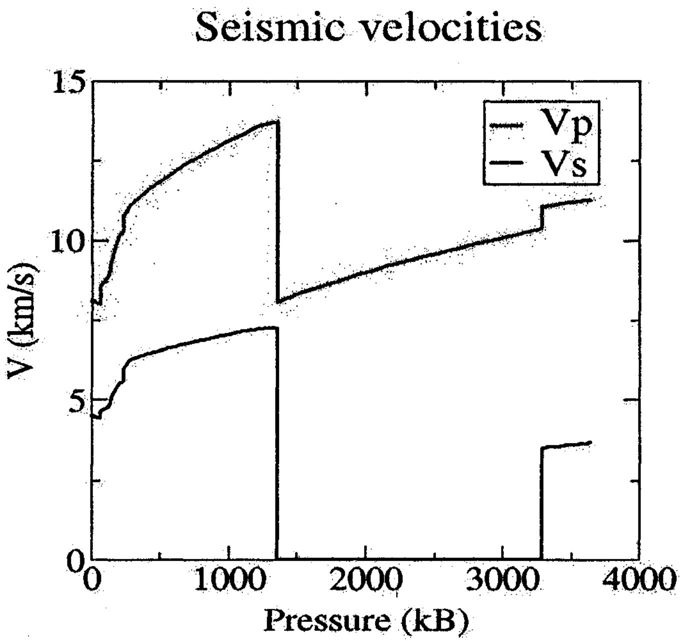
Mike Gillan
David Price

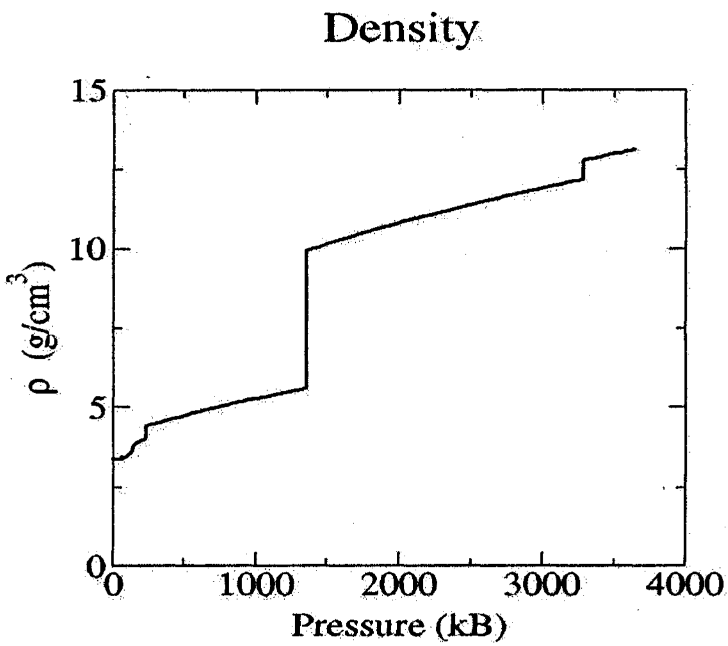
University College London



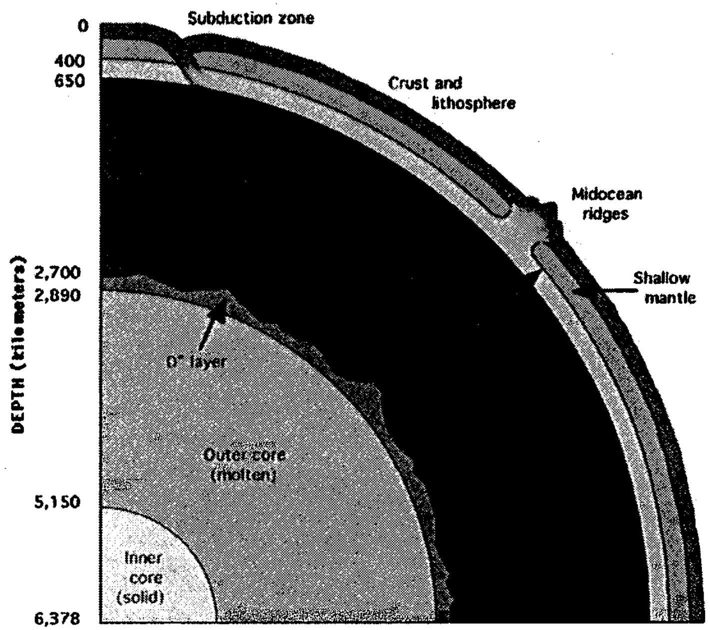

CRUST
CORE
LOWER
MANTLE
UPPER MANTLE


pP
P
PP
P
S
SKKS
SKS
PKP
PKIKP
Inner Core
P waves
S waves


Seismic velocities
Vp
Vs
V (km/s)
Pressure (kB)
0
5
10
15
0
1000
2000
3000
4000


Density
ρ (g/cm3)
Pressure (kB)
0
5
10
15
0
1000
2000
3000
4000

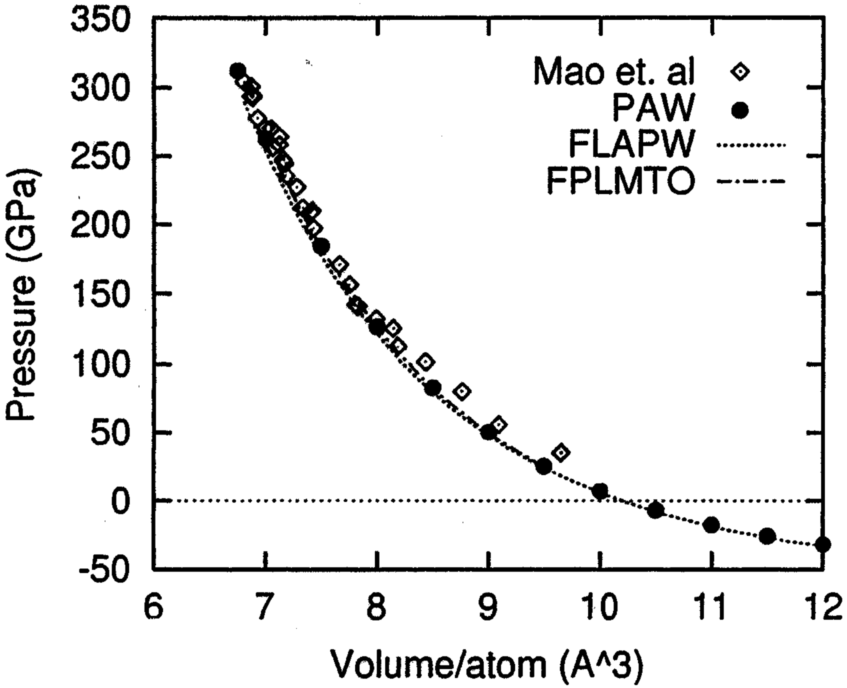
- **Temperature of the Earth's core?**
- **Composition?**

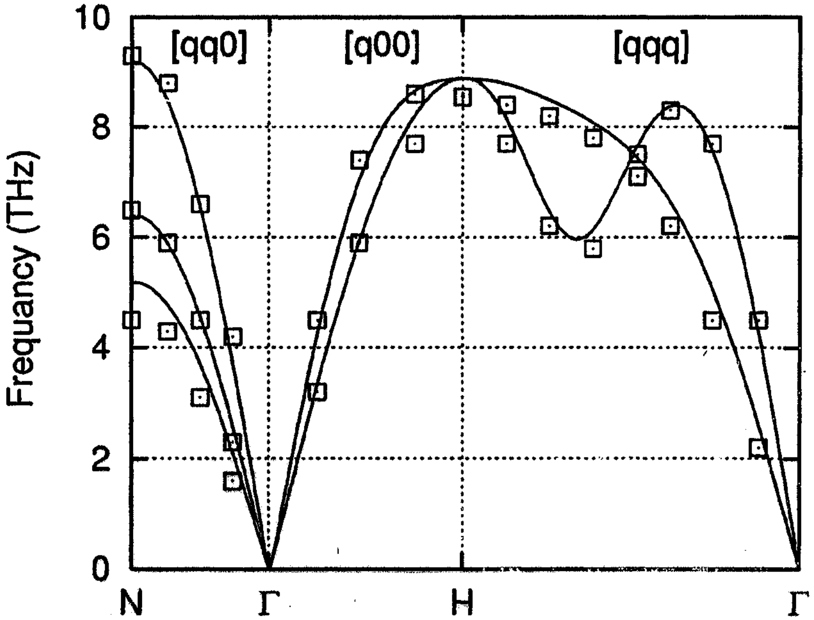


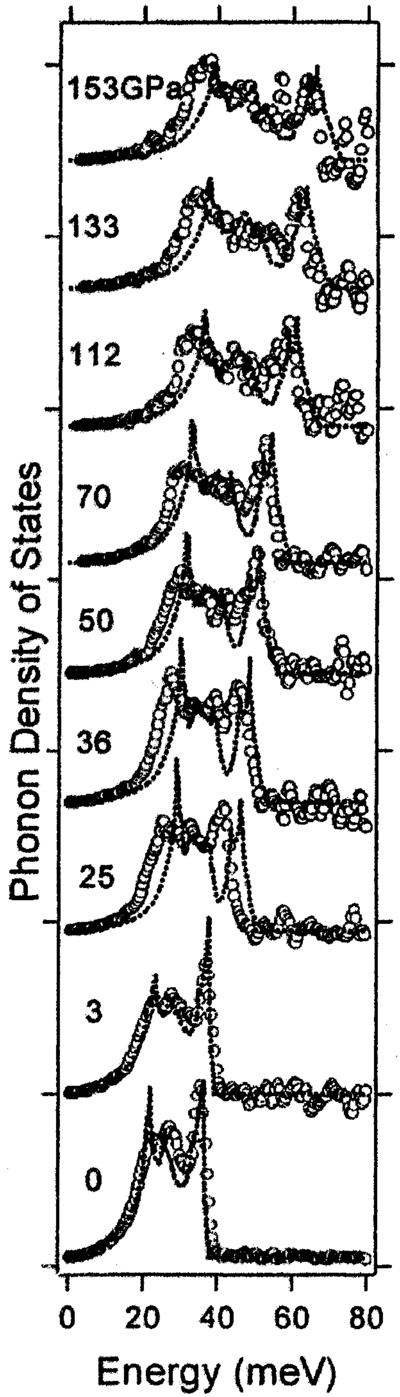
- Properties of pure Fe
  - Melting temperature
  - Density change on melting
  - ……
- Composition
  - Impurities: S, Si, O
  - Binary mixtures Fe/X ? Other possibilities ?
  - Shift of melting temperature

Ab-initio technical details

- Density Functional Theory
- Generalized Gradient Approximation (PW91)
- VASP code (Kresse and Furthmuller, PRB 54, 11169 (1996))
- PAW/USPP
- Finite temperature Fermi smearing
- Kpoints


Mao et. al
PAW
FLAPW
FPLMTO
Pressure (GPa)
Volume/atom (A^3)
350
300
250
200
150
100
50
0
-50
6
7
8
9
10
11
12

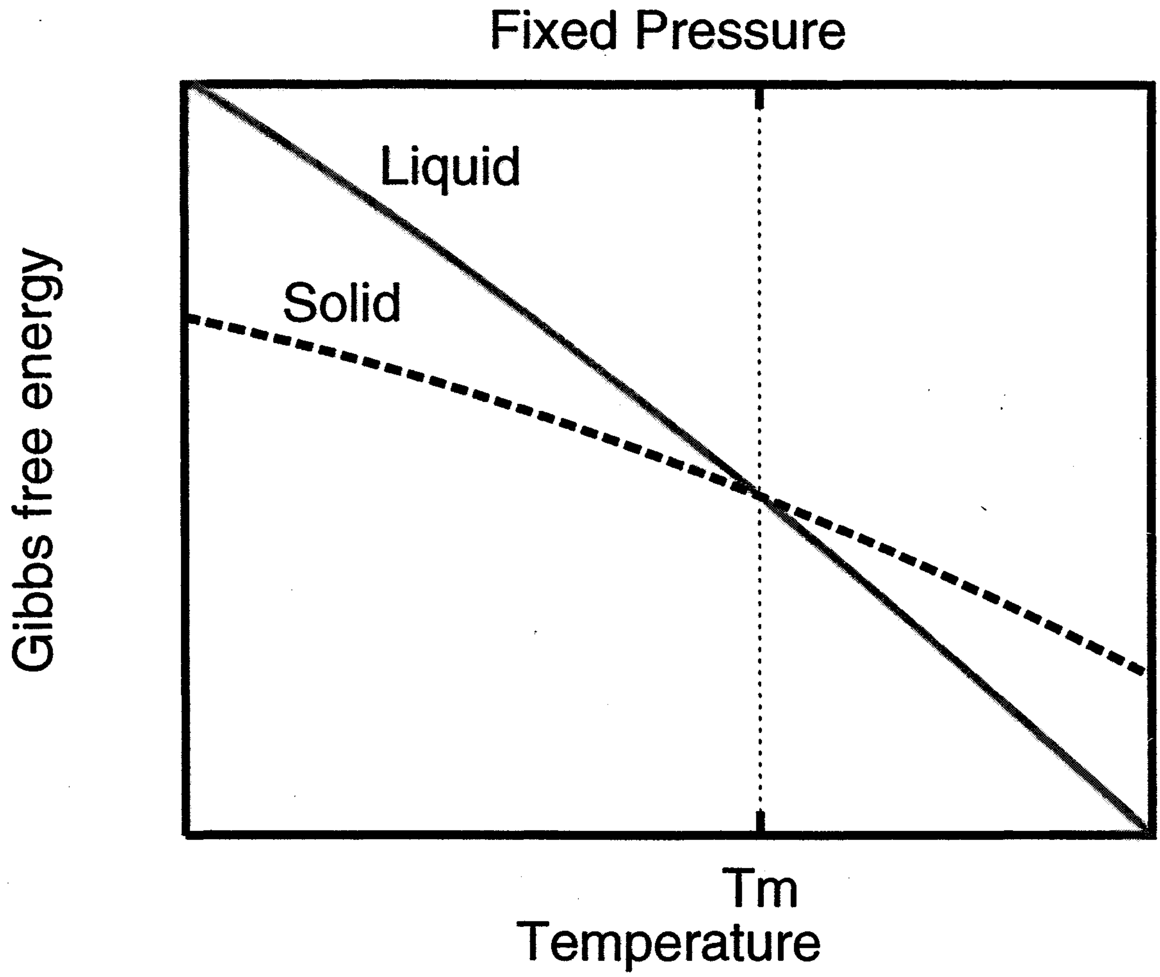

[qq0]
[q00]
[qqq]
Frequancy (THz)
10
8
6
4
2
0
N
Γ
H
Γ


153GPa
133
112
70
50
36
25
3
0
Phonon Density of States
Energy (meV)
0
20
40
60
80

Strategy for Melting

Gibbs free energy calculations:

$$G_{liquid}(P,T) = G_{solid}(P,T)$$



We calculate the Helmholtz free energy: $F(V,T)$
$P = -\partial F(V,T)/\partial V$
$G = F \mp PV$

Liquid Iron

$$F = -k_B T \ln \left\{ \frac{1}{\Lambda^N N!} \int d\mathbf{R}\; e^{-U(\mathbf{R})/k_B T} \right\}$$

Thermodynamic integration:

chose a reference system:

$$U_{ref}(\mathbf{R})$$

define

$$U_\lambda(\mathbf{R})$$

such that

$$U_0(\mathbf{R}) = U_{ref}(\mathbf{R})$$
$$U_1(\mathbf{R}) = U(\mathbf{R})$$

$$F_\lambda = -k_B T \ln \left\{ \frac{1}{\Lambda^N N!} \int d\mathbf{R}\; e^{-U_\lambda(\mathbf{R})/k_B T} \right\}$$

$$F = F_0 + \int_0^1 d\lambda \frac{dF_\lambda}{d\lambda}$$

$$F = F_0 + \int_0^1 d\lambda \langle \frac{\partial U_\lambda}{\partial \lambda} \rangle_\lambda$$

We choose:

$$U_\lambda = \lambda U + (1 - \lambda) U_{ref}$$

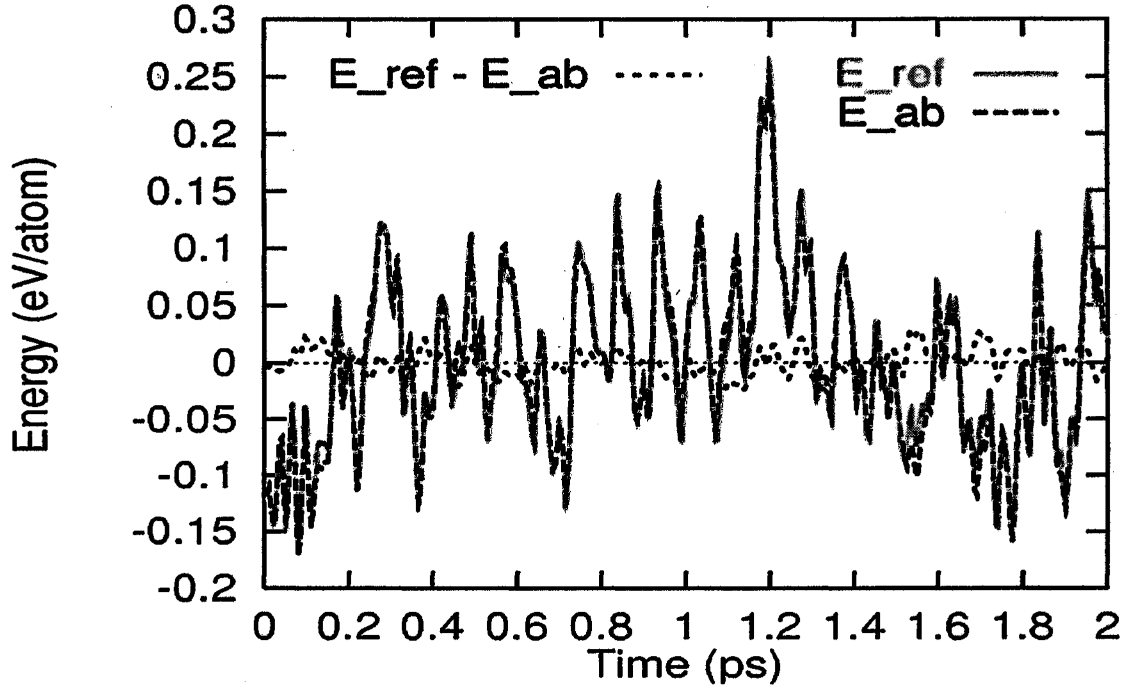
so

$$F = F_0 + \int_0^1 d\lambda \langle U - U_{ref} \rangle_\lambda$$

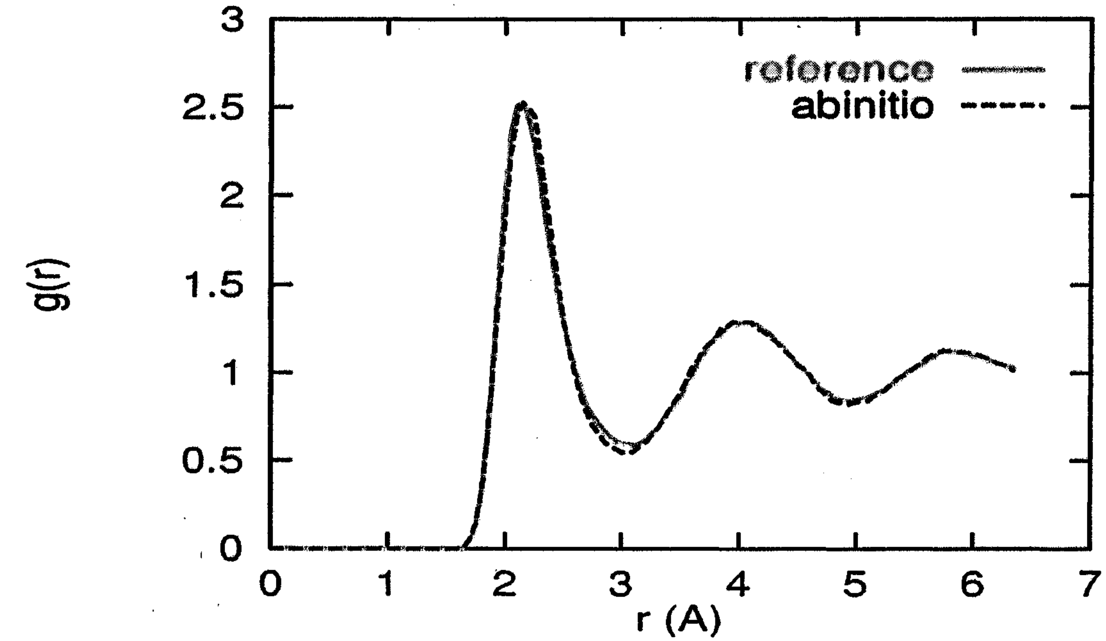
A good U_{ref}:

$$U_{ref}(A, \alpha; \mathbf{r}_1, ..., \mathbf{r}_N) = \frac{1}{2} \sum_{i \neq j} \frac{A}{|\mathbf{r}_i - \mathbf{r}_j|^\alpha}$$

$$(A, \alpha) = \min_{A,\alpha} \langle (U - U_{ref} - \langle U - U_{ref} \rangle)^2 \rangle$$

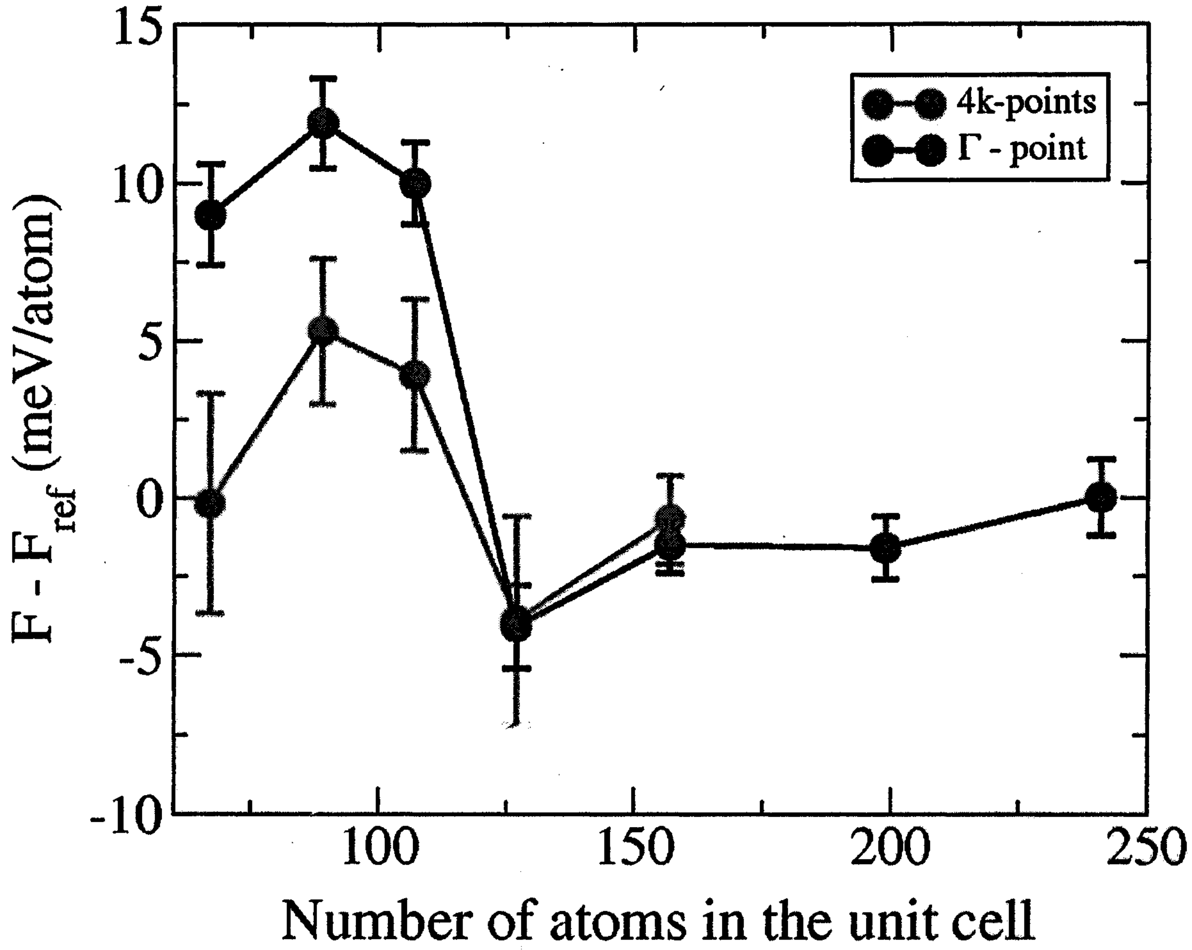


E_ref - E_ab
E_ref
E_ab
Energy (eV/atom)
Time (ps)



reference
abinitio
g(r)
r (A)

Size tests



4k-points
Γ - point
15
10
5
0
-5
-10
F - F_ref (meV/atom)
100
150
200
250
Number of atoms in the unit cell

Solid Iron (h.c.p.)

$$F(V,T) = F_{perf}(V,T) + F_{harm}(V,T) + F_{anharm}(V,T)$$

$$F_{harm}(V,T) = \frac{3k_BT}{N_sN_{\mathbf{q}}}\sum_{s,\mathbf{q}} \ln \frac{\hbar\omega_{s,\mathbf{q}}(V,T)}{k_BT}$$

$$\mathbf{D}(\mathbf{q}) = \frac{1}{M}\sum_{\mathbf{R}} \mathbf{D}(\mathbf{R})e^{i\mathbf{q}\cdot\mathbf{R}}$$

Finite displacements method:

$$F_\alpha(\mathbf{R}) = -\sum_{\mathbf{R}',\beta} D_{\alpha,\beta}(\mathbf{R}'-\mathbf{R})u_\beta(\mathbf{R}')$$

With a supercell $3\times3\times2$ (36 atoms) F_{harm} is converged within 3 meV/atom. Checks up to a $5\times5\times3$ (150 atoms) supercell.

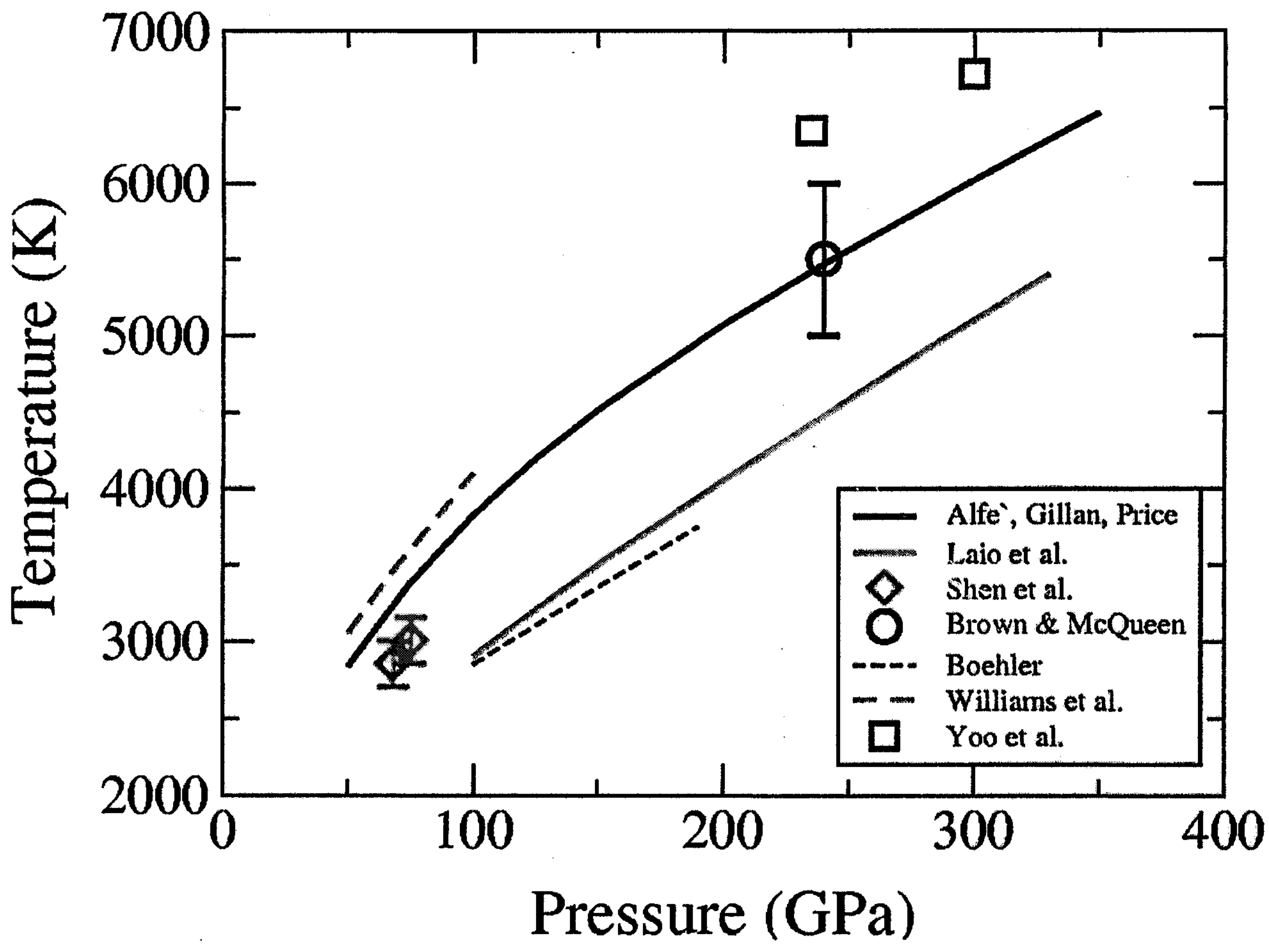
Anharmonicity

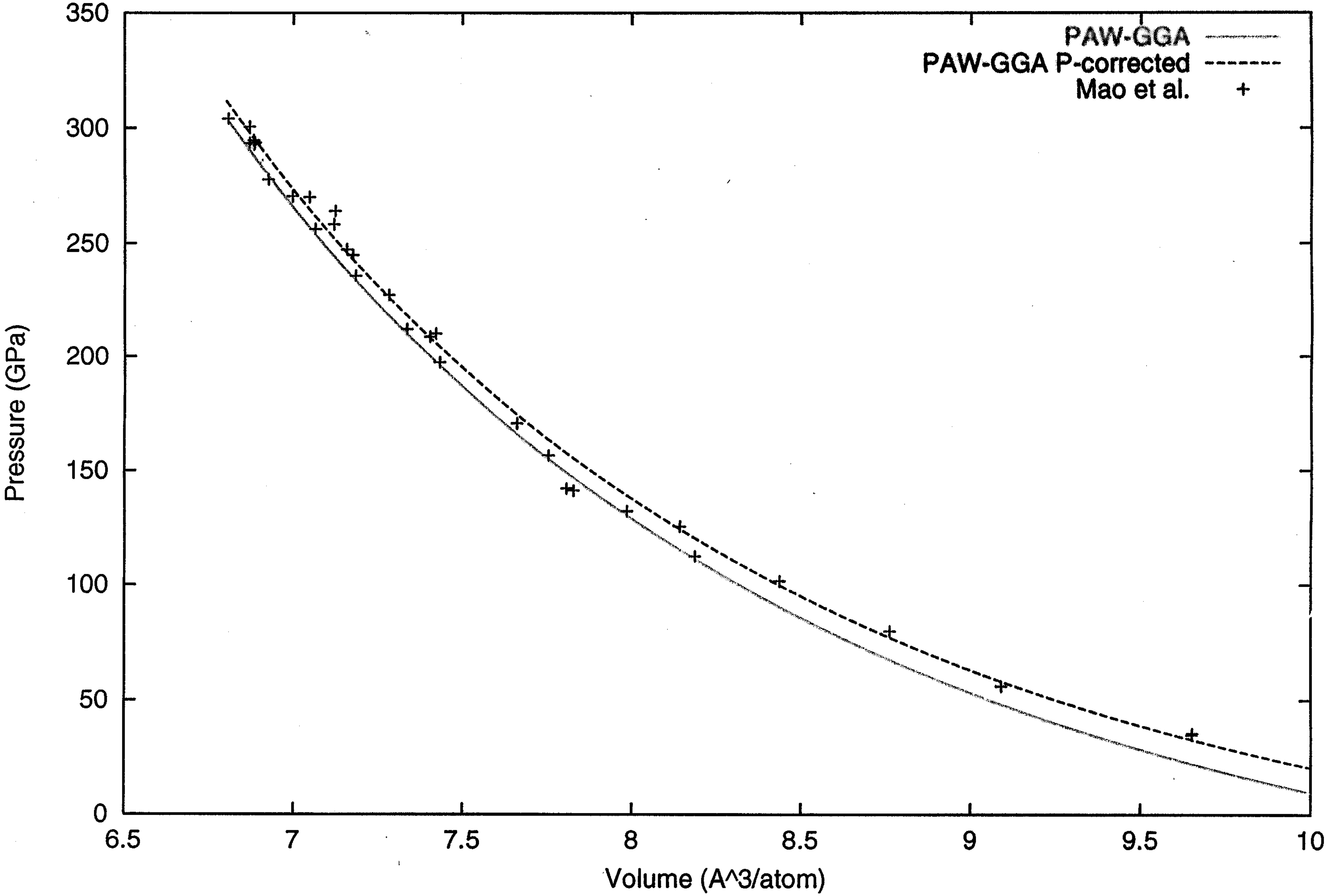
$$F_{anharm} = \int_0^1 d\lambda \, \langle U - U_{ref} \rangle_\lambda + (F_{ref} - F_{harm})$$

$$U_{ref} = c_1 U_{harm} + c_2 U_{IP}$$

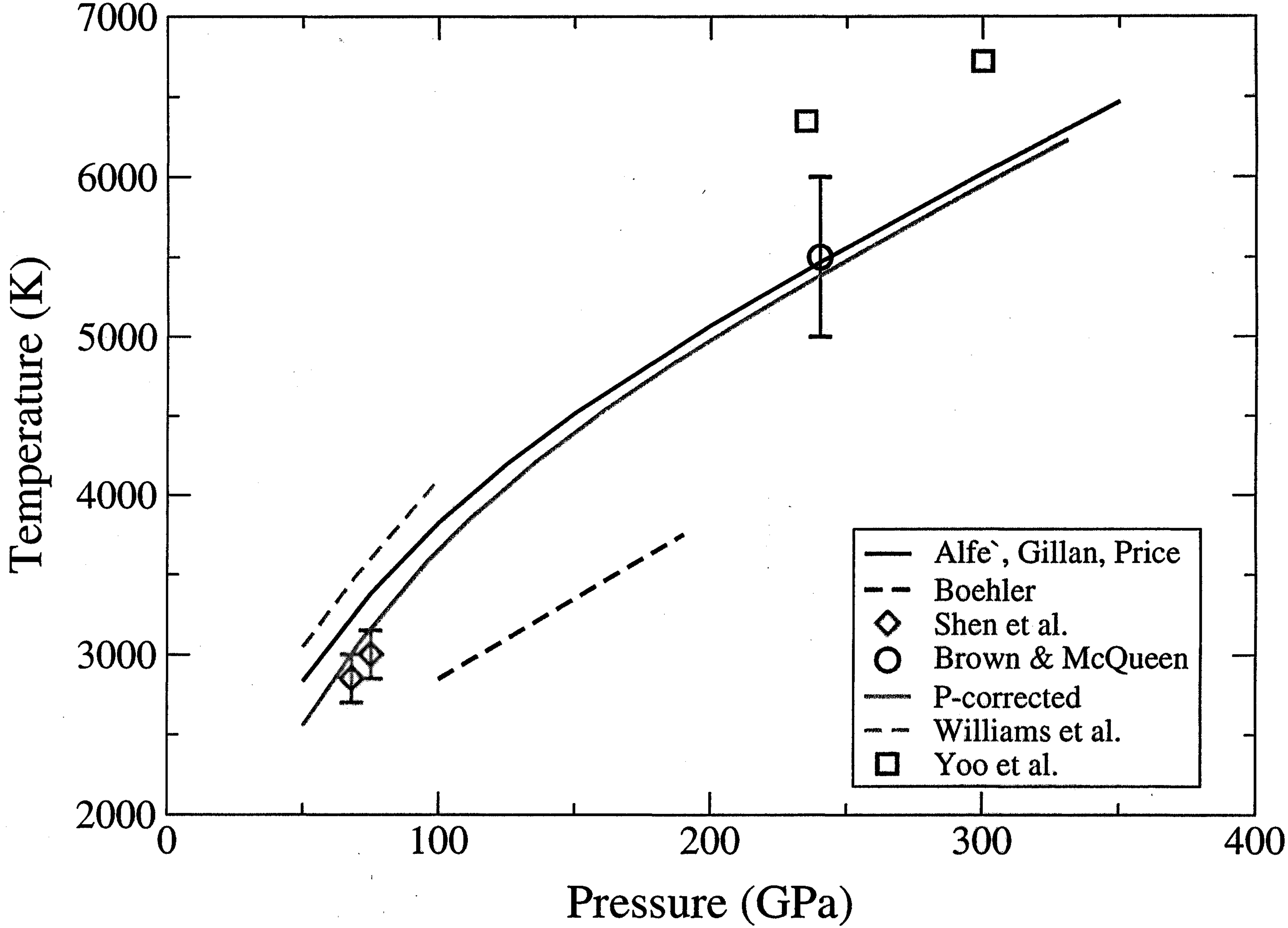
$$U_{harm} = \frac{1}{2} \sum_{i\alpha, j\beta} u_{i\alpha} \Phi_{i\alpha, j\beta} u_{j\beta} \qquad U_{IP} = \frac{1}{2} \sum_{i \neq j} \frac{A}{\left| r_i - r_j \right|^{\alpha}}$$

The melting curve of Fe



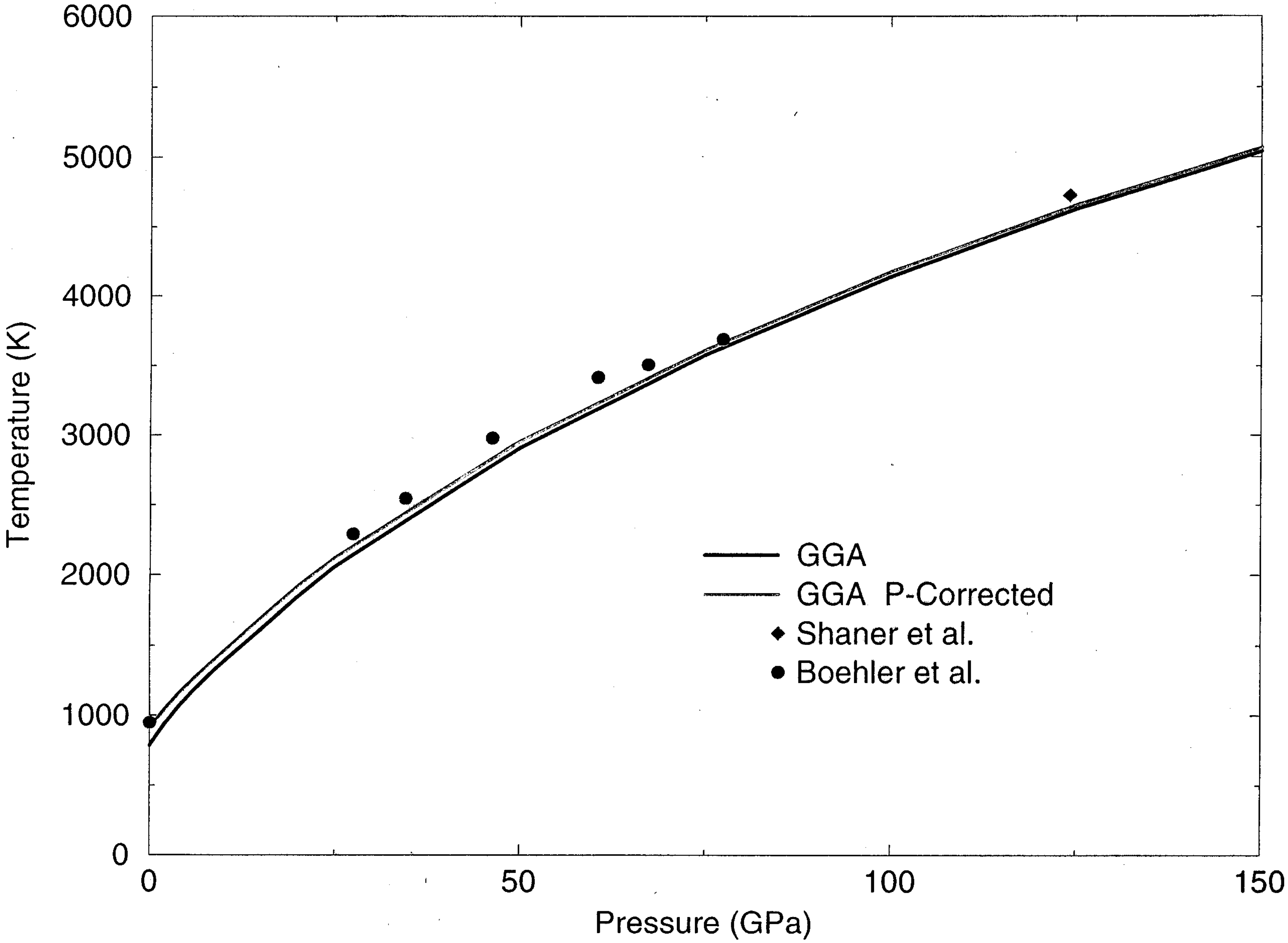


PAW-GGA
PAW-GGA P-corrected
Mao et al.
Pressure (GPa)
Volume (A^3/atom)
350
300
250
200
150
100
50
0
6.5
7
7.5
8
8.5
9
9.5
10



7000
6000
5000
4000
3000
2000
0
100
200
300
400
Temperature (K)
Pressure (GPa)
Alfe`, Gillan, Price
Boehler
Shen et al.
Brown & McQueen
P-corrected
Williams et al.
Yoo et al.

Aluminium melting curve

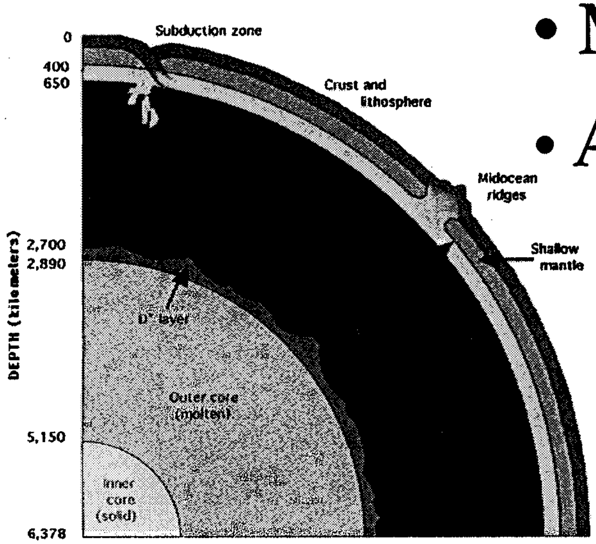


Lidunka Vočadlo
&
Dario Alfè
to be published

Composition of the Earth's Core

- Density change at ICB ~ 5 % (seismological data).
- Density change on melting for Fe ~ 1.7 % (ab-initio calculations).
- ➔ Partitioning of light elements.

Procedure



- Make an hypothesis: binary mixture Fe/X
- At ICB liquid and solid are in equilibrium:

$$\mu^l_X(p,T,c^l_X) = \mu^s_X(p,T,c^s_X)$$

$$\mu_X(p,T,c_X) = k_B T \ln c_X + \tilde{\mu}_X(p,T,c_X)$$

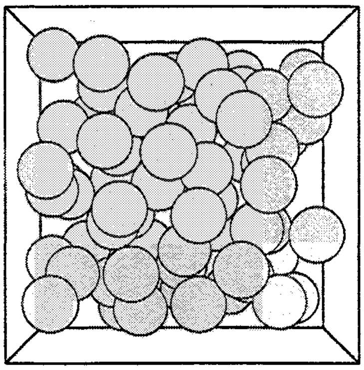
$$c^s_X / c^l_X = \exp\left[(\tilde{\mu}^l_X - \tilde{\mu}^s_X)/k_B T\right]$$

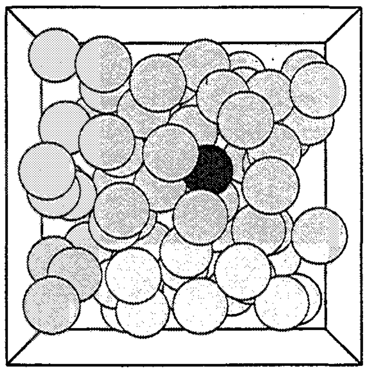
Liquid chemical potential

We transmute 1 Fe atom in S and we calculate ΔF.

Thermodynamic integration:

$$\Delta F = \int_0^1 d\lambda \langle U_{FeS} - U_{Fe} \rangle_\lambda$$
$$U_\lambda = \lambda U_{FeS} + (1-\lambda) U_{Fe}$$





Step 1 U_{Fe}, F_{Fe}	*Step* 1 U_{FeS}, F_{FeS}

$$F_\lambda = \lambda F_{Fe} + (1-\lambda) F_{FeS}$$

Step 2 U_{Fe}, F_{Fe}	*Step* 2 U_{FeS}, F_{FeS}

$$F_\lambda = \lambda F_{Fe} + (1-\lambda) F_{FeS}$$

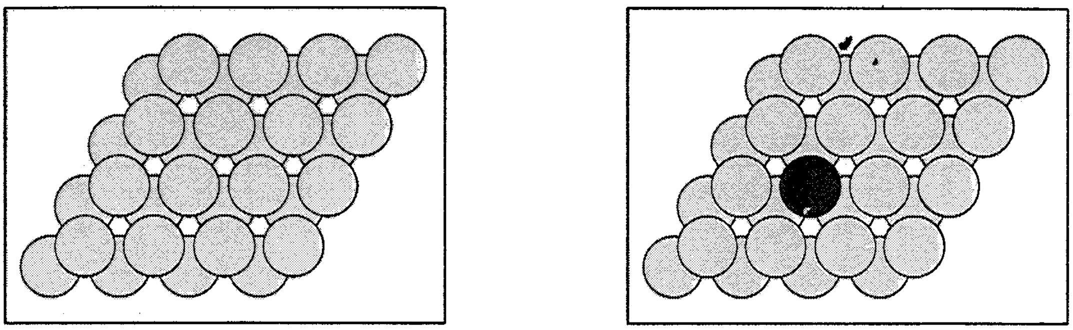
⋮ ⋮

⋮ ⋮

Solid

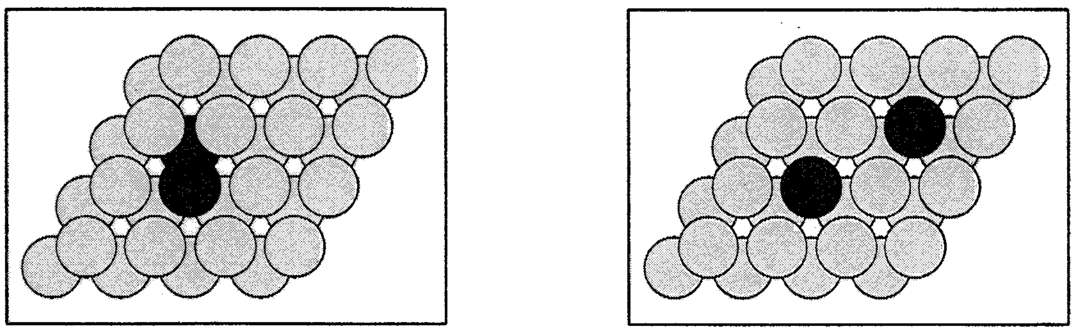
Limit of zero concentration:

$$\Delta F = \Delta F_{perf} + \Delta F_{harm}$$



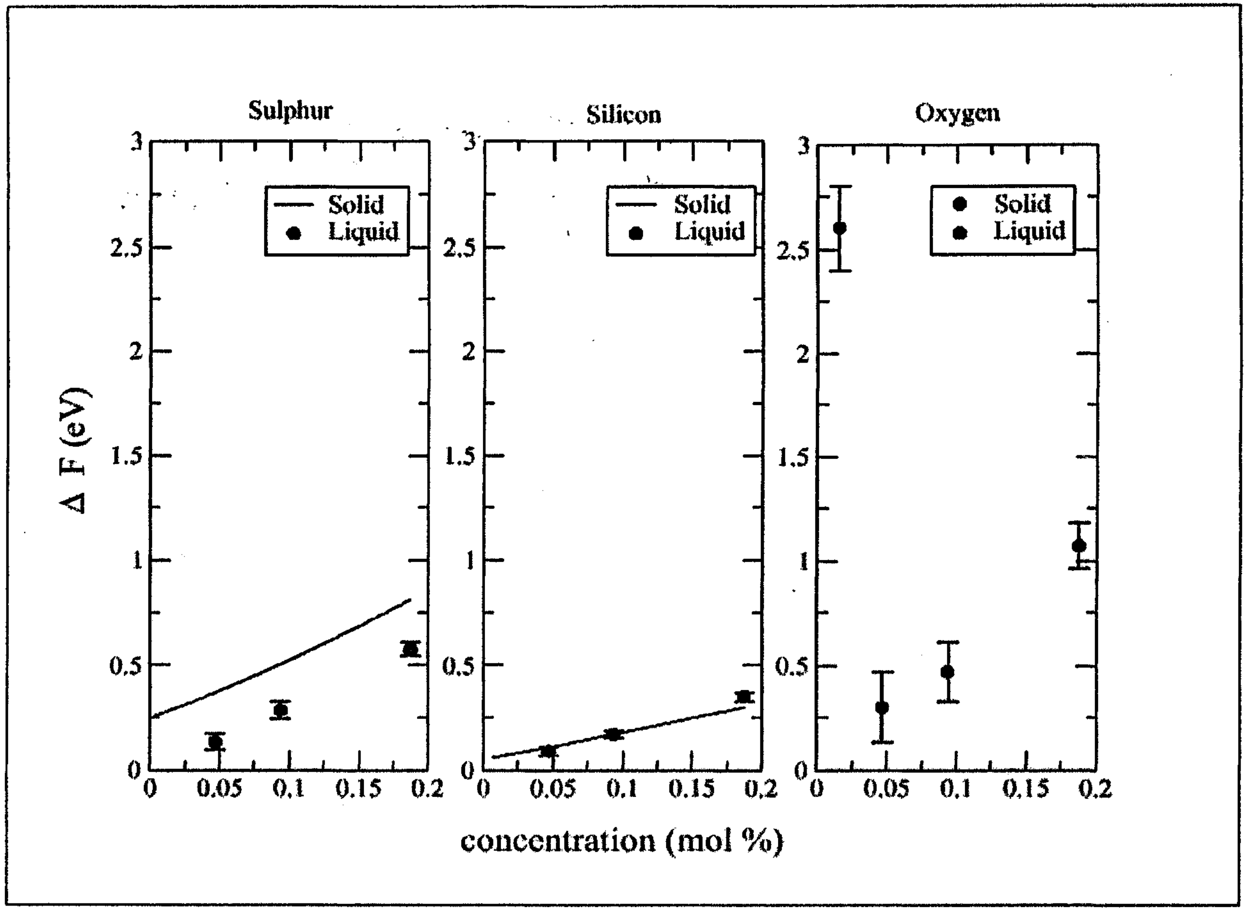
$$\Delta F_{harm} = -k_B T \sum_n [\ln \omega'_n - \ln \omega_n]$$

Dependence on concentration:



- Montecarlo simulation on the h.c.p. lattice gas

Results



$$c_X^s / c_X^l = \exp\left[(\tilde{\mu}_X^l - \tilde{\mu}_X^s) / k_B T \right]$$

Composition:

	Solid	Liquid
S/Si	8.5 +- 2.5%	10 +- 2.5 %
Ox	0.3 +- 0.1 %	8 +- 2.5 %

Shift of melting temperature:

$$\Delta T \simeq 600 - 700K$$

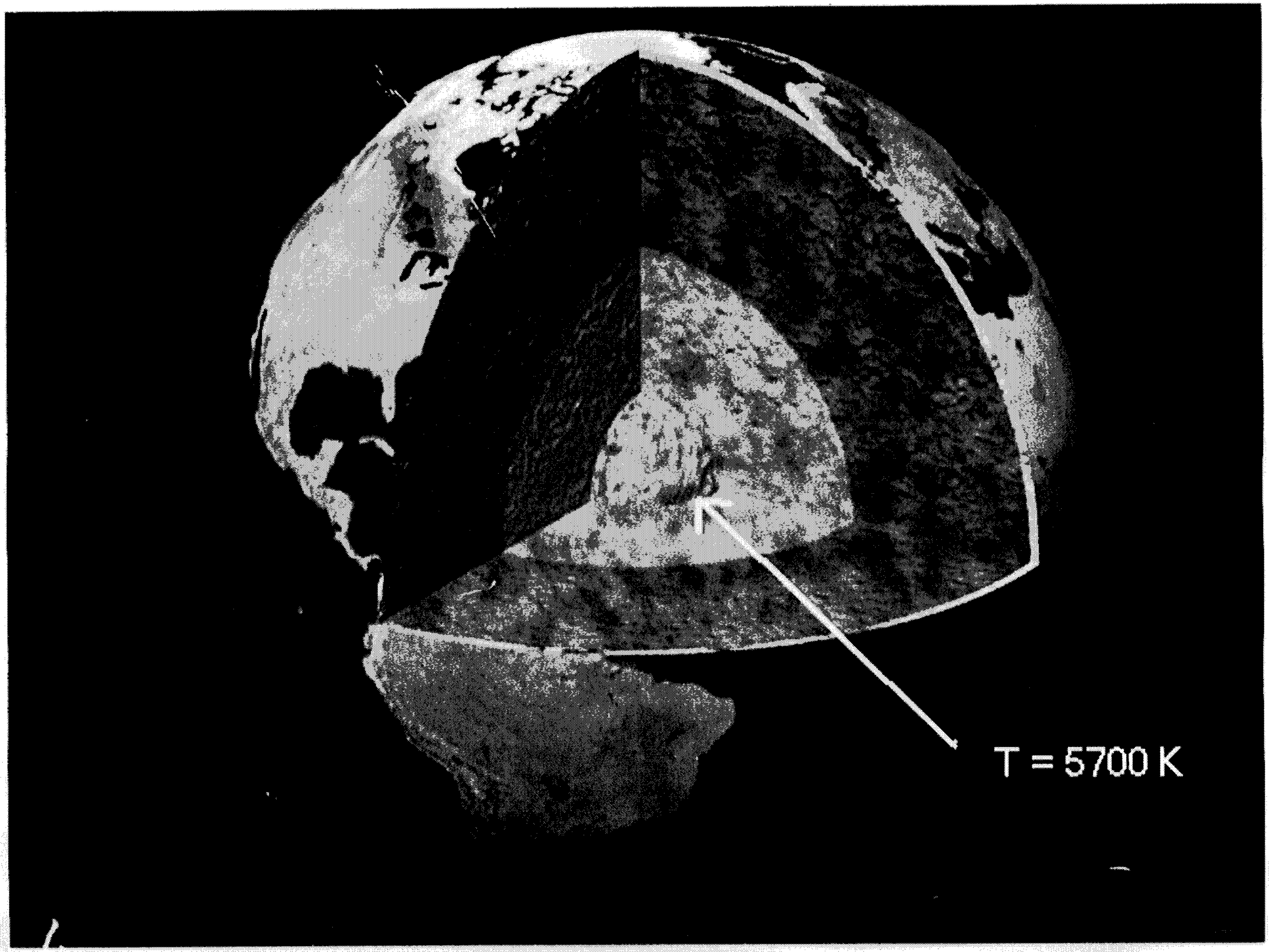
Shift of melting temperature

$$\mu_X(p,T,c_X) \simeq k_B T \ln c_X + \mu_X^0(p,T) + \lambda c_X$$

$$\mu_{Fe}(p,T,c_X) \simeq (k_B T + \lambda)\ln(1 - c_X) + \mu_{Fe}^0(p,T) + \lambda c_X$$

$$\mu_{Fe}^l(p,T,c_X^l) = \mu_{Fe}^s(p,T,c_X^s)$$

$$\Delta T \simeq \frac{k_B T}{\Delta S_0}(c_X^s - c_X^l)$$


T = 5700 K