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Computational Physics and Materials Science:
Total Energy and Force Methods**

11 - 13 January 2007

Ab-initio theory of alloys: New possibilities for materials design

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SWEDEN

AB INITIO THEORY OF ALLOYS: NEW POSSIBILITIES FOR MATERIALS DESIGN

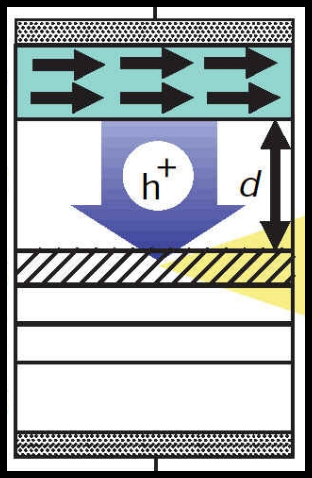
Igor A. Abrikosov

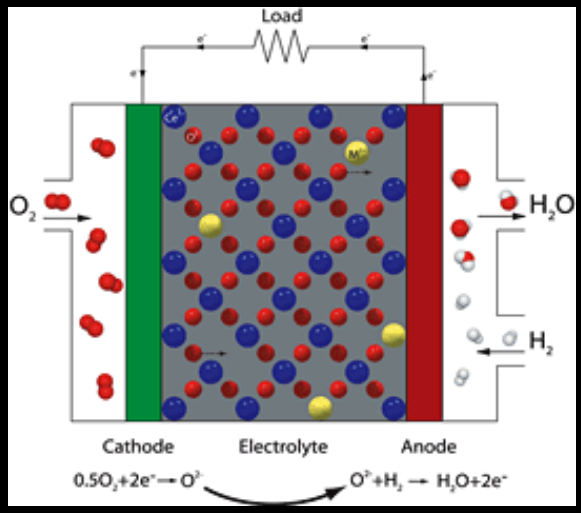
Theoretical Physics,

Department of Physics, Chemistry and Biology, Linköping University, Sweden

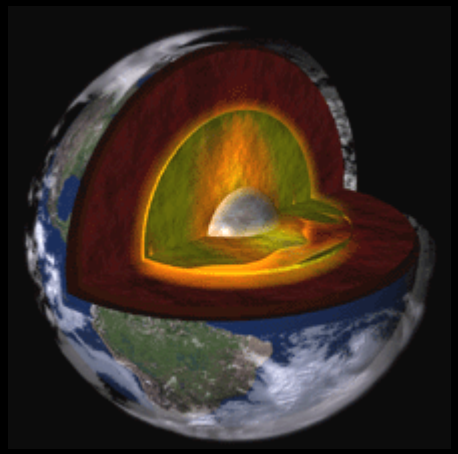
COLLABORATION :

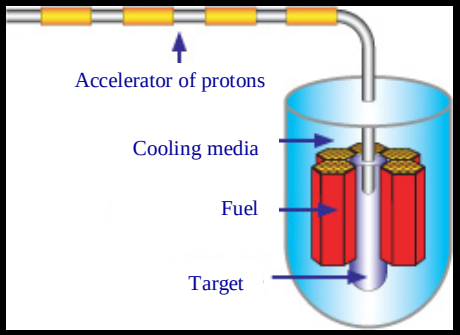
- B. Alling and S. I. Simak, LiU, Sweden
- L. Vitos, D. Andersson, and B. Johansson, KTH, Sweden
- P. Olsson, CAE, France, and J. Wallenius, KTH, Sweden
- N. Skorodumova and O. Peil, UU, Sweden
- A. Karimi, EPFL, Switzerland


h+
d


Load
O2
H2O
H2
Cathode
Electrolyte
Anode
0.5O2+2e- → O2-
O2-+H2 → H2O+2e-

Alloys



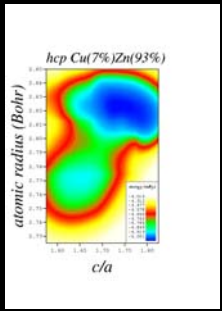

Accelerator of protons
Cooling media
Fuel
Target

CONTENTS :

- Recent developments in the alloy theory
- Phase stability: a role of the electronic structure

  Mixing and decomposition thermodynamics of nanocomposite hard coating (TiAl)N alloys.

  Anomalous stability of low Cr steels.
- Optimization of the ionic conductivity in doped ceria
- Conclusions



INALLOY toolkit

- Coherent potential approximation:
  KKR-ASA basis set
  Exact Muffin-Tin Orbitals (EMTO) basis set
  Screened Impurity Model for charge fluctuations
  Model treatment of the local lattice relaxations
- Locally self-consistent Green's function method
- Supercell technique combined with conventional band structure methods using Special Quasirandom Structures
- Multiscale modeling based on Hamiltonians with parameters determined *ab initio*

The EMTO method

Potential:

overlapping MT potential

Kink cancellation equation:

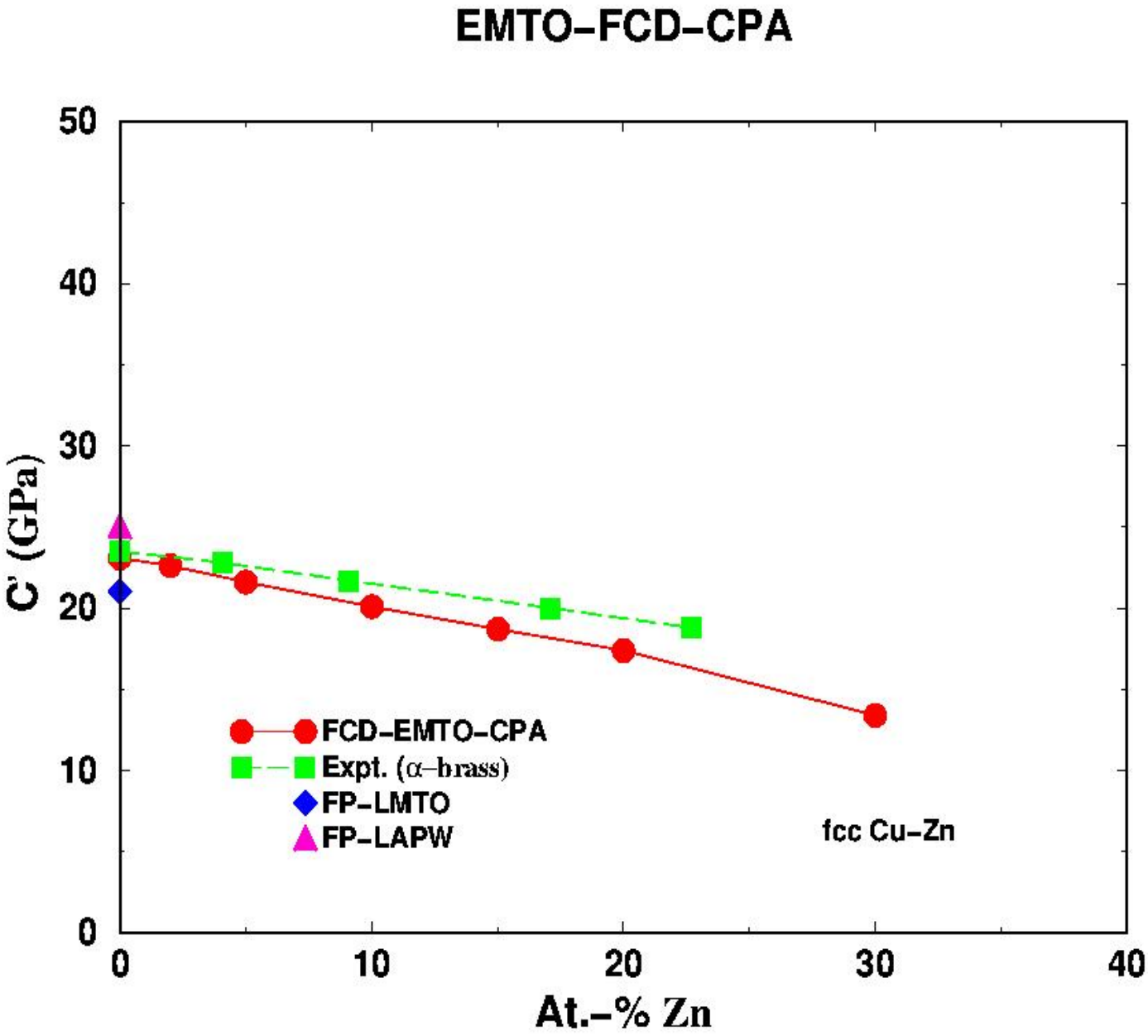
$[D(\varepsilon)-S(\varepsilon,\mathbf{k})]g(\varepsilon,\mathbf{k})=1$

$D(\varepsilon)$ potential
$S(\varepsilon,\mathbf{k})$ slope matrix

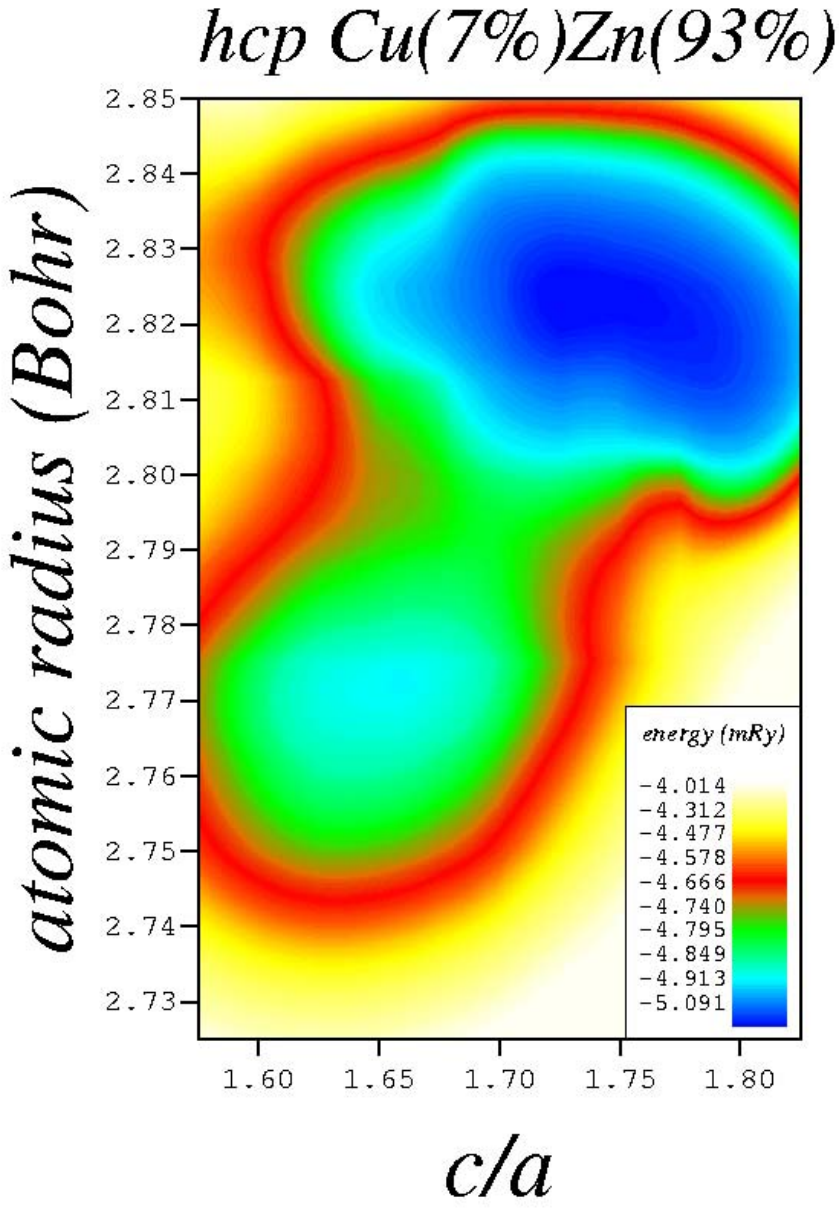
Density:

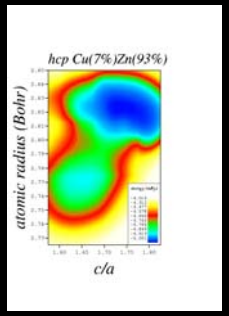
$n(\mathbf{r})\sim\langle Z(\varepsilon,\mathbf{r})g(\varepsilon,\mathbf{k})Z(\varepsilon,\mathbf{r})\rangle_{\varepsilon,\mathbf{k}}$

- **Localized MT orbitals (screened KKR)**
- **Smooth energy dependence of $S(\varepsilon,\mathbf{k})$**
- **Optimized overlapping MT potential**
- **Proper normalization (CC term)**
- **Accurate Full Charge Density**
- **Accurate kinetic energy**



L. Vitos, I. A. Abrikosov, and B. Johansson, Phys. Rev. Lett. **87**, 156401 (2001)


hcp Cu(7%)Zn(93%)
atomic radius (Bohr)
2.85
2.84
2.83
2.82
2.81
2.80
2.79
2.78
2.77
2.76
2.75
2.74
2.73
1.60
1.65
1.70
1.75
1.80
c/a
energy (mRy)
-4.014
-4.312
-4.477
-4.578
-4.666
-4.740
-4.795
-4.849
-4.913
-5.091



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  Screened Impurity Model for charge fluctuations
  Model treatment of the local lattice relaxations
- Locally self-consistent Green's function method, (O(N) method for metallic alloys, Phys. Rev. Lett. **76**, 4203 (1996)).
- Supercell technique combined with conventional band structure methods using Special Quasirandom Structures (A. Zunger *et al.*, Phys. Rev. Lett. **65**, 353 (1990)).
- Multiscale modeling based on Hamiltonians with parameters determined *ab initio*

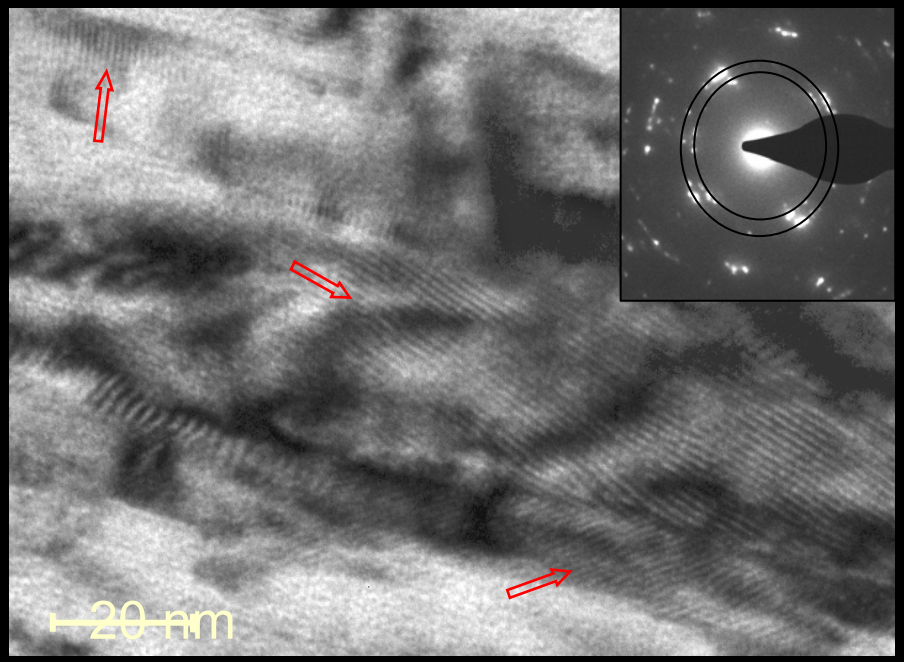
Nanocomposite hard coating (Ti-Al)N alloys

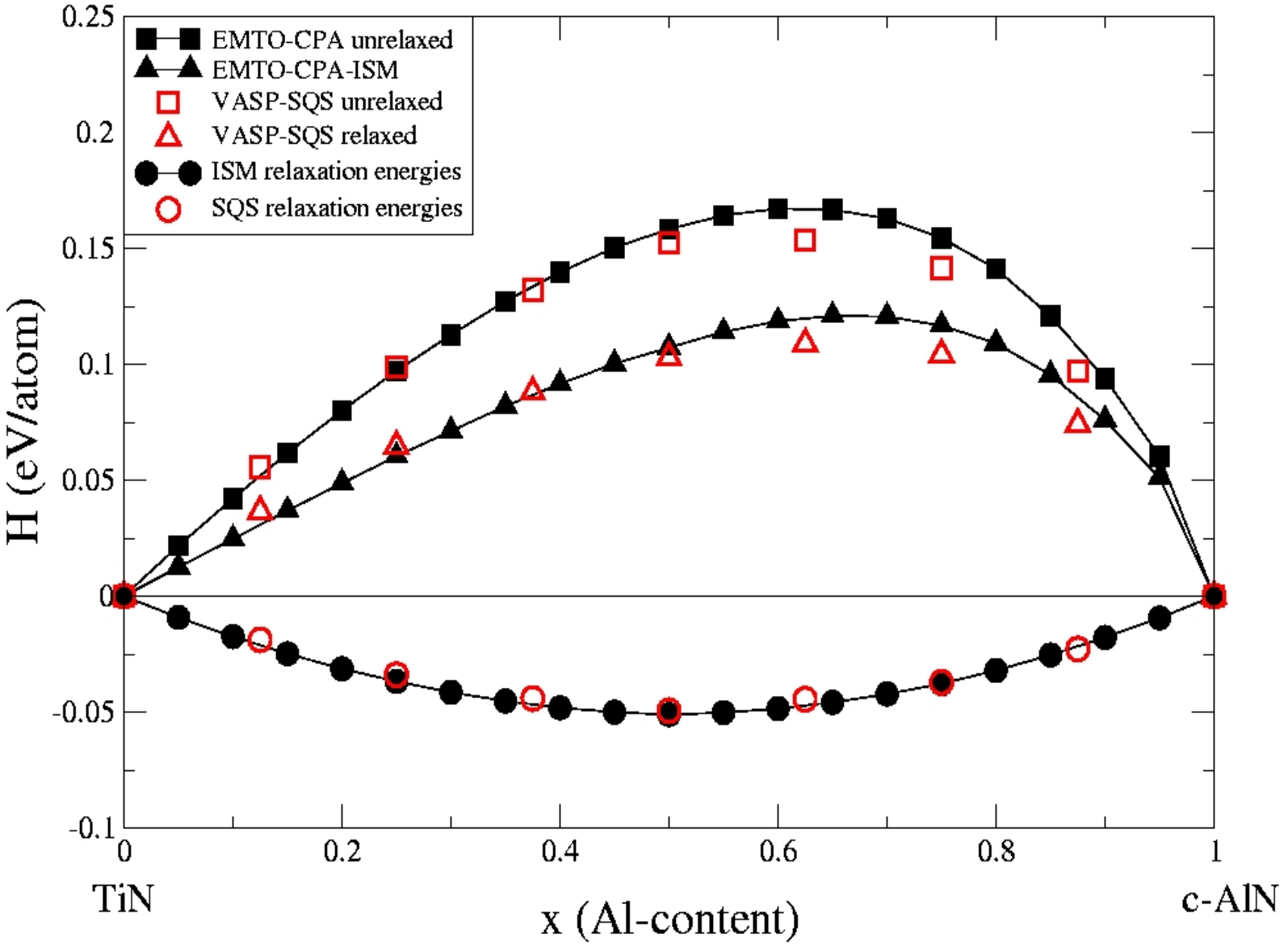
- The new universal high-performance coating (drilling, milling, etc.)
- Increasing Al content leads to very high heat resistance, dry

  high-speed machining,

  and increased oxidation

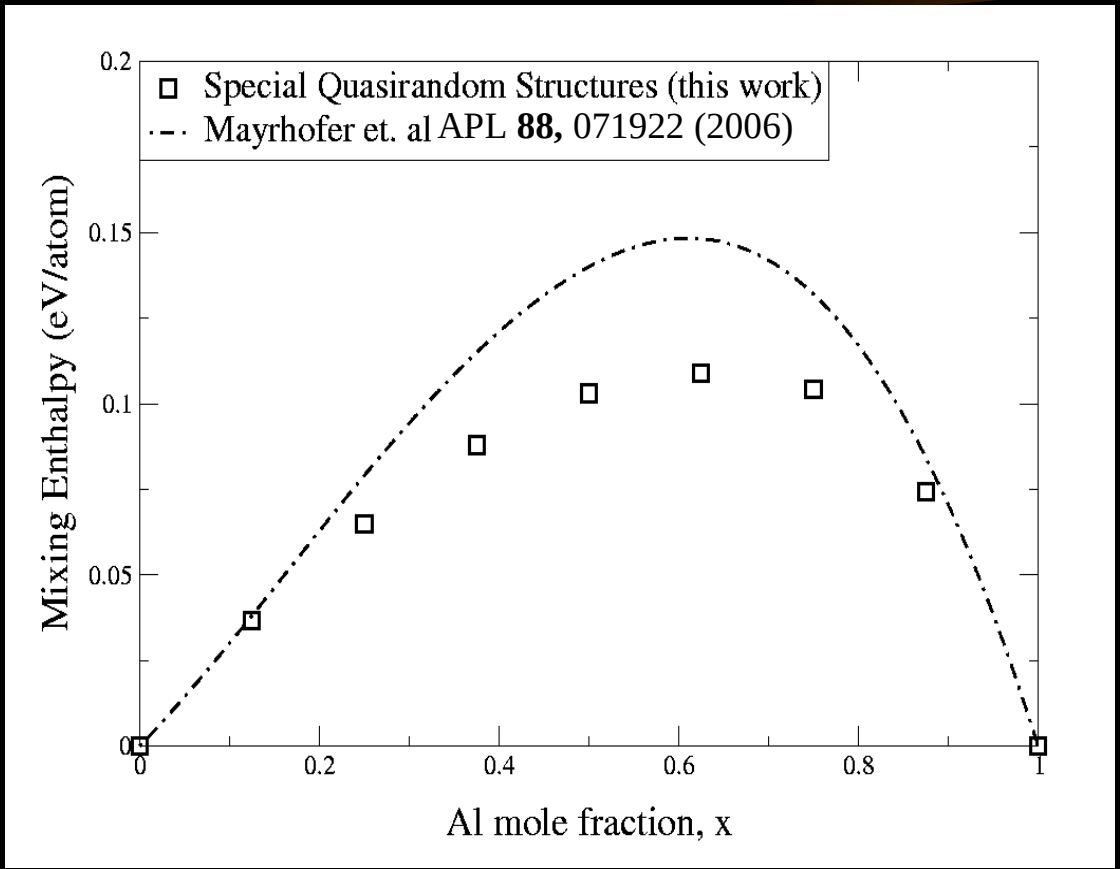
  resistance
- Spinodal decomposition

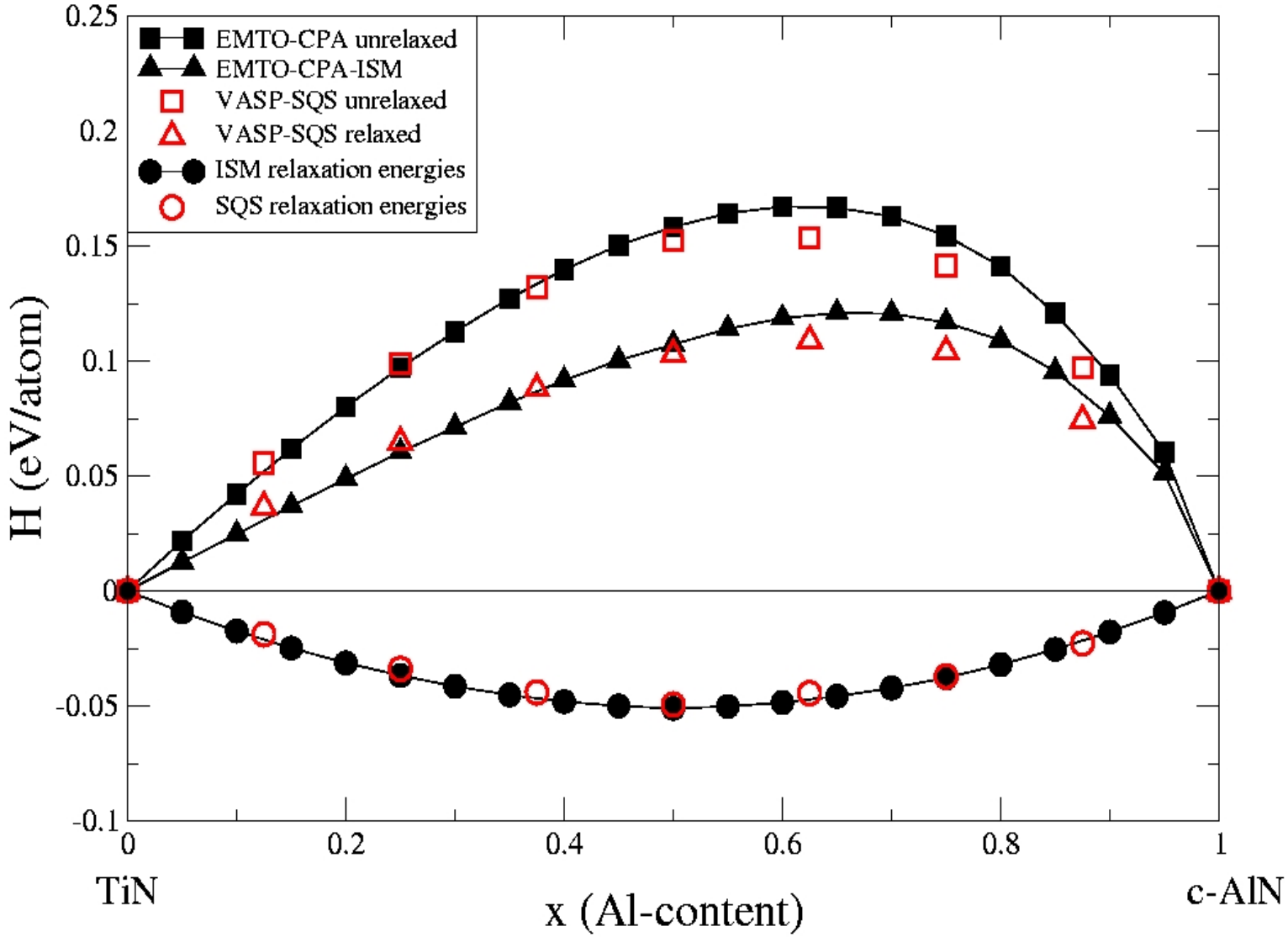


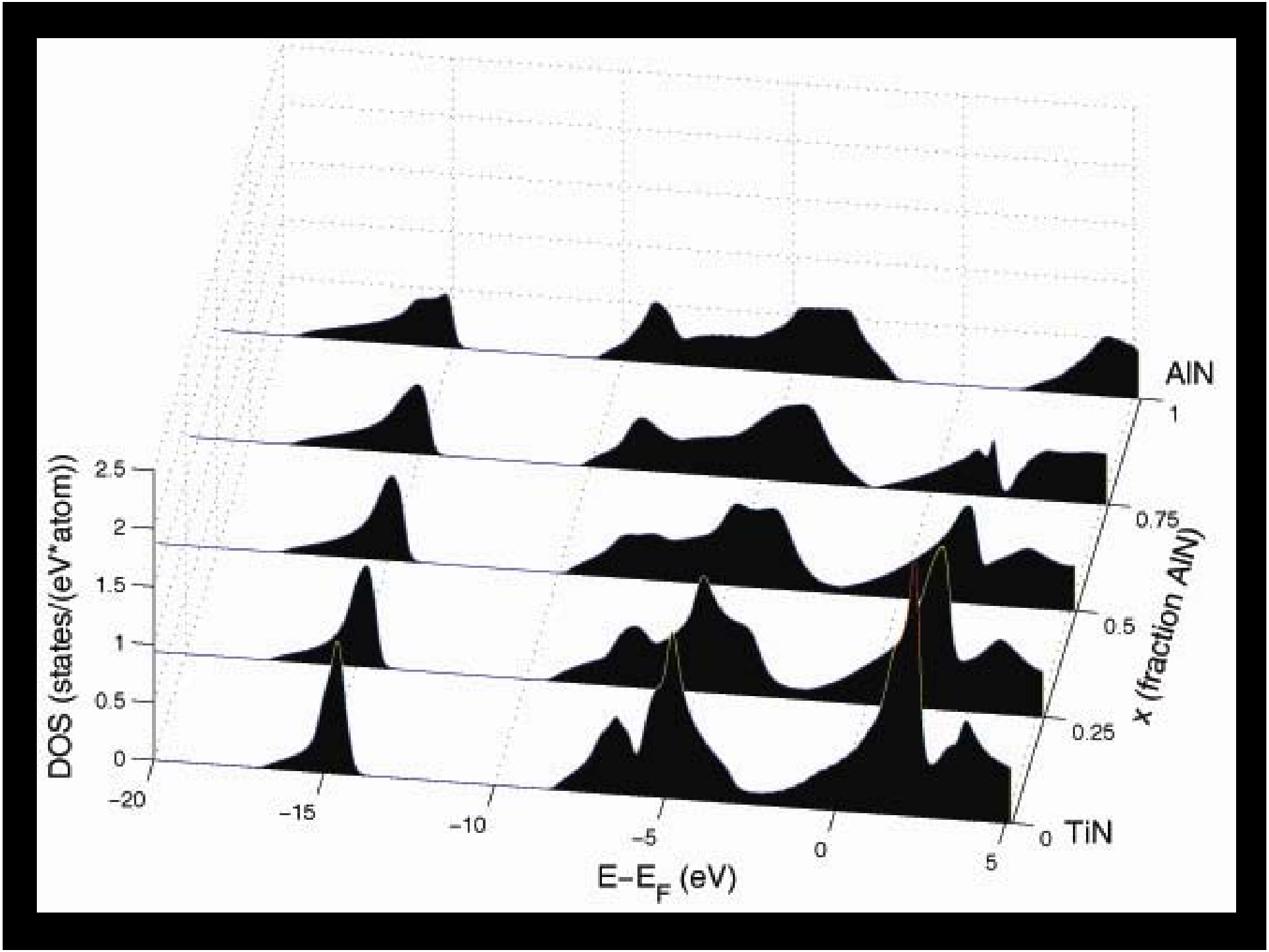


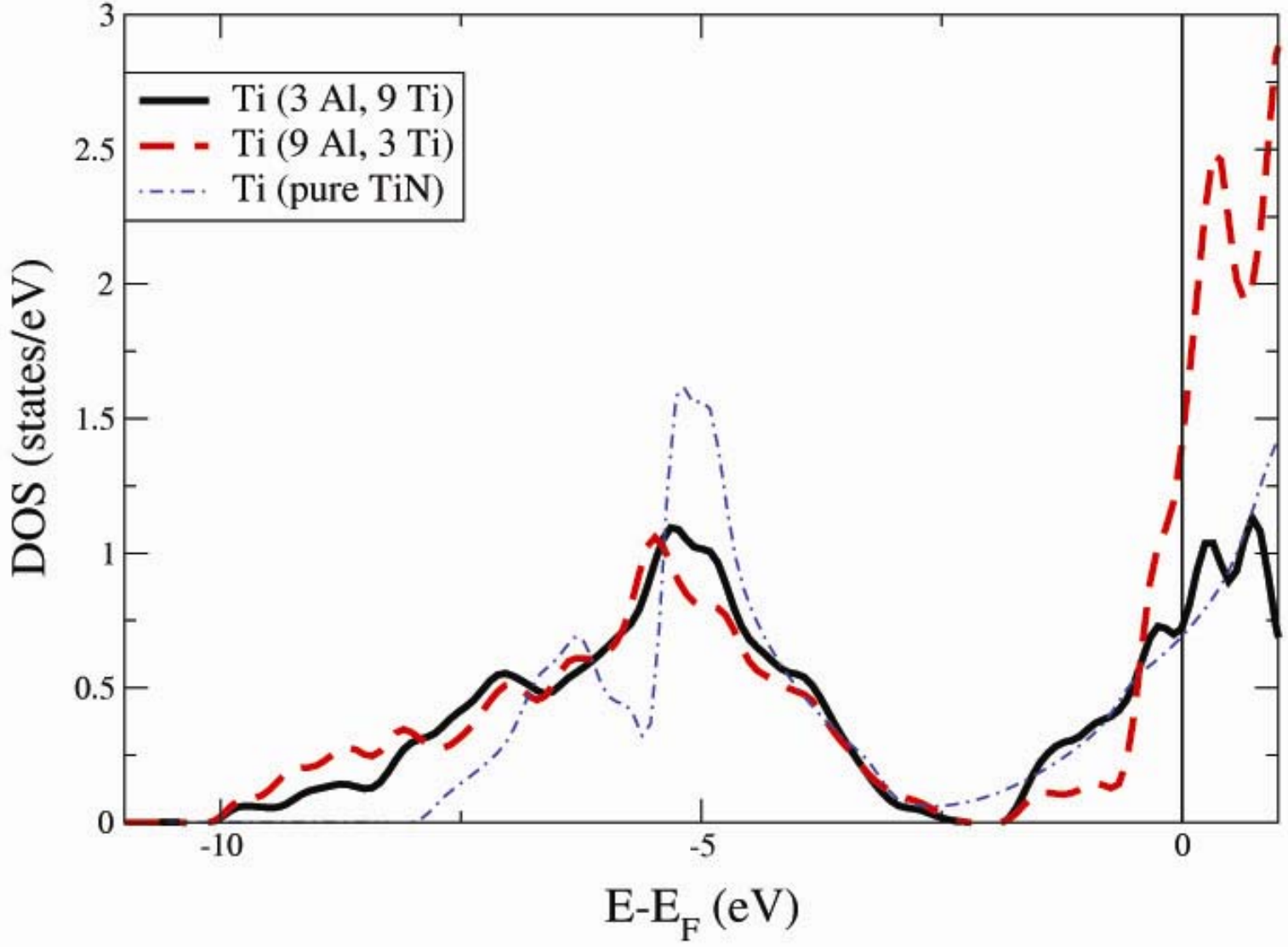
B. Alling, A. V. Ruban, A. Karimi, O. E. Peil, L. Hultman, and I. A. Abrikosov, Phys. Rev. B (in press).

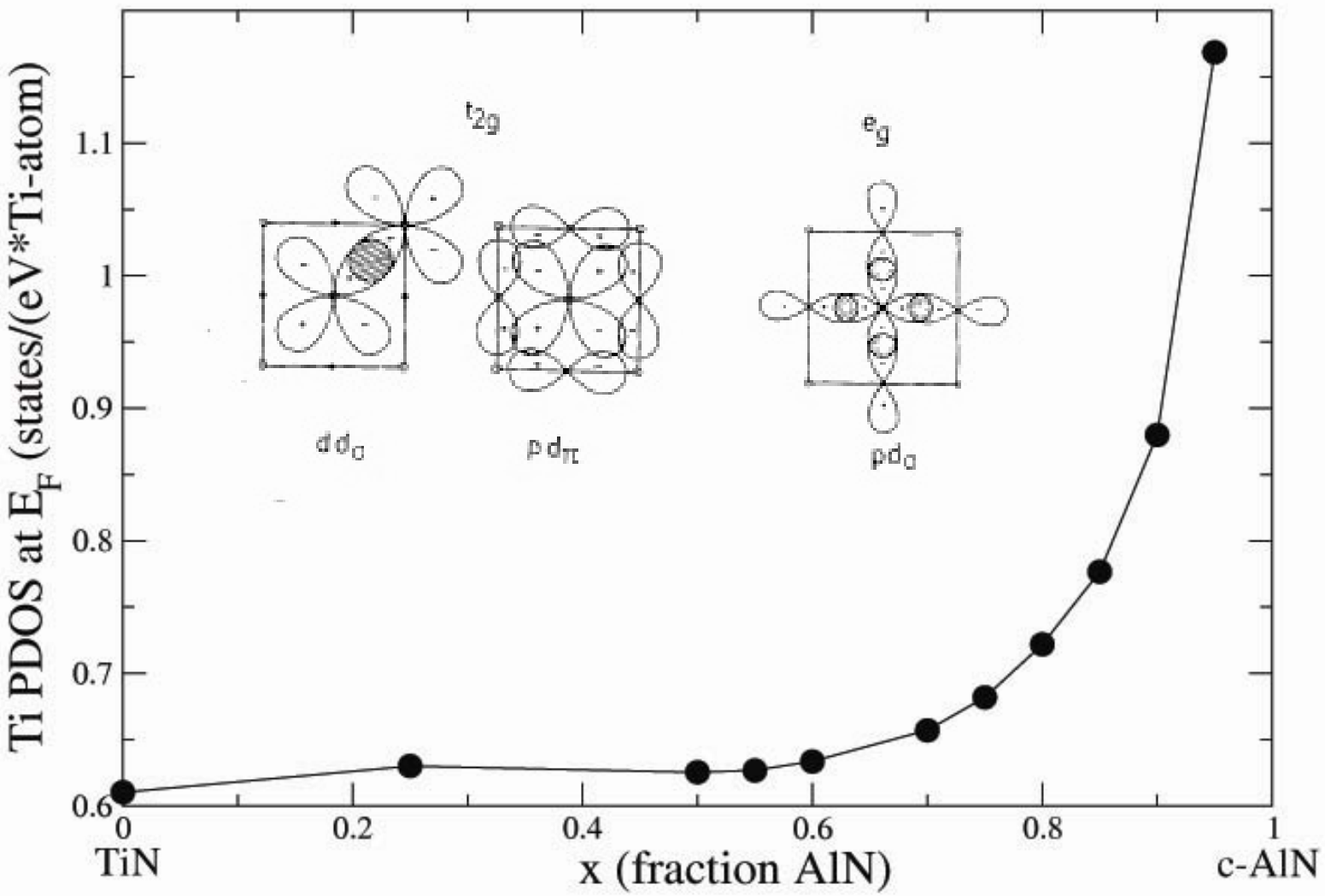
Caution: the use of the supercell technique

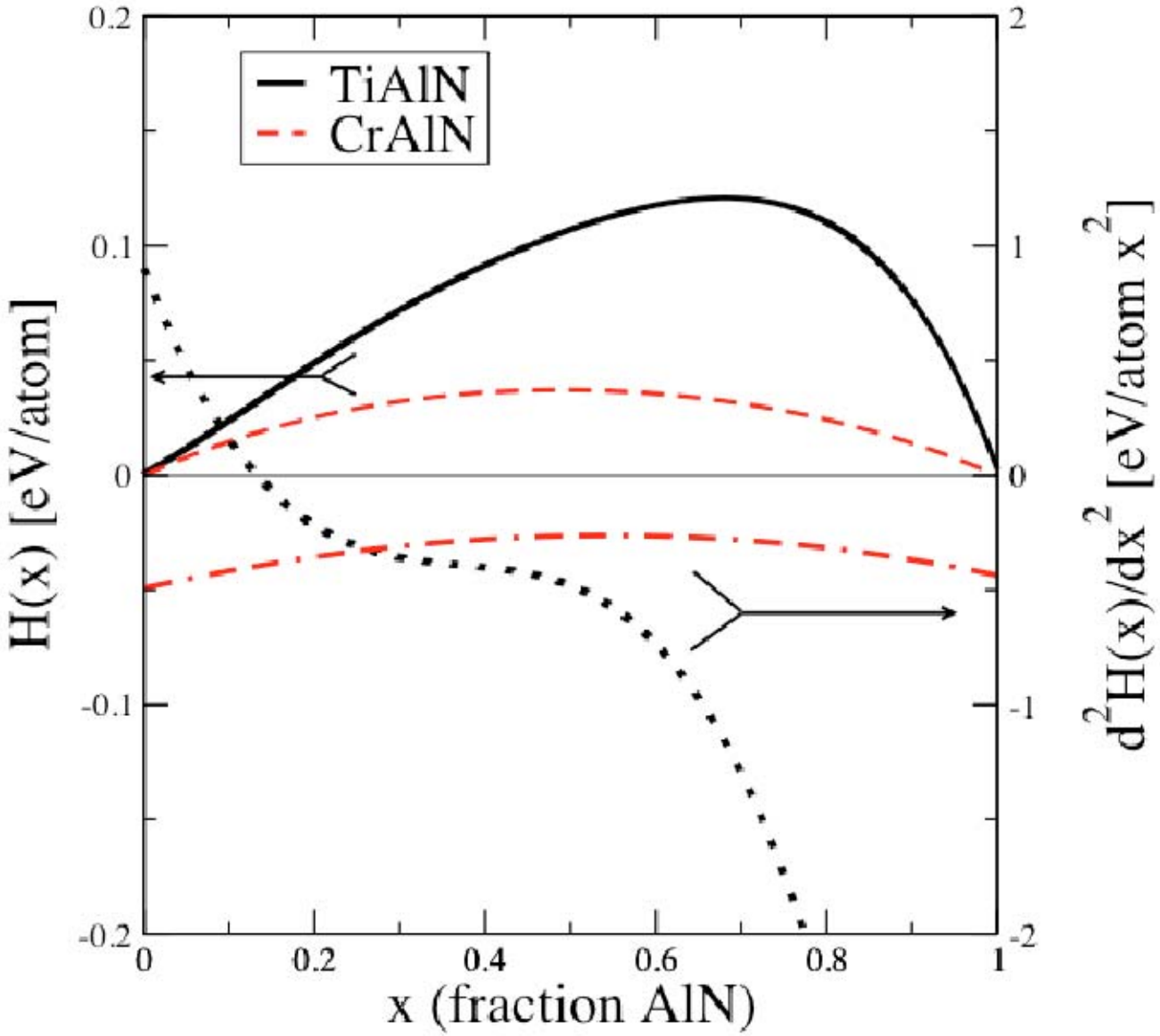



EMTO-CPA unrelaxed
EMTO-CPA-ISM
VASP-SQS unrelaxed
VASP-SQS relaxed
ISM relaxation energies
SQS relaxation energies
H (eV/atom)
0.25
0.2
0.15
0.1
0.05
0
-0.05
-0.1
0
0.2
0.4
0.6
0.8
1
TiN
x (Al-content)
c-AlN


DOS (states/(eV*atom))
2.5
2
1.5
1
0.5
0
−20
−15
−10
−5
0
5
E−E_F (eV)
AlN
1
0.75
0.5
0.25
0
TiN
x (fraction AlN)

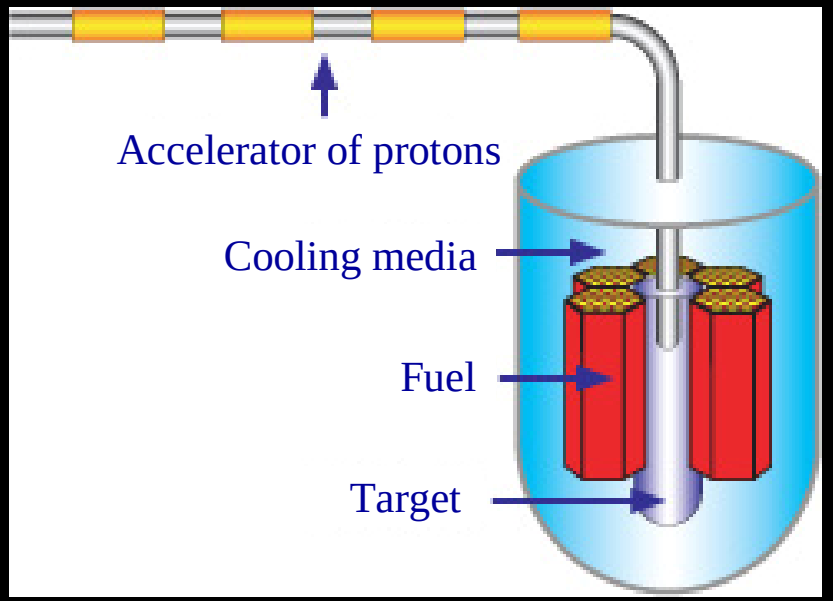

Ti (3 Al, 9 Ti)
Ti (9 Al, 3 Ti)
Ti (pure TiN)
DOS (states/eV)
E-E_F (eV)
3
2.5
2
1.5
1
0.5
0
-10
-5
0

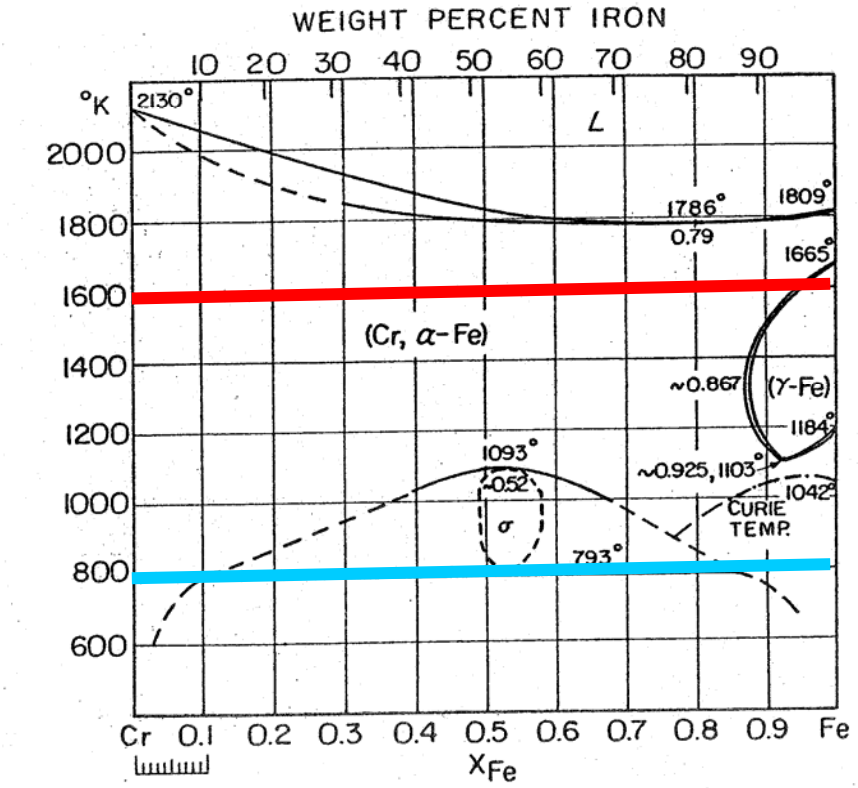

Ti PDOS at E_F (states/(eV*Ti-atom)
1.1
1
0.9
0.8
0.7
0.6
0
0.2
0.4
0.6
0.8
1
TiN
x (fraction AlN)
c-AlN
t_{2g}
e_g
$d d_\sigma$
$p d_\pi$
$p d_\sigma$


TiAlN
CrAlN
H(x) [eV/atom]
$d^2H(x)/dx^2$ [eV/atom x^2]
x (fraction AlN)
0.2
0.1
0
-0.1
-0.2
2
1
0
-1
-2
0
0.2
0.4
0.6
0.8
1

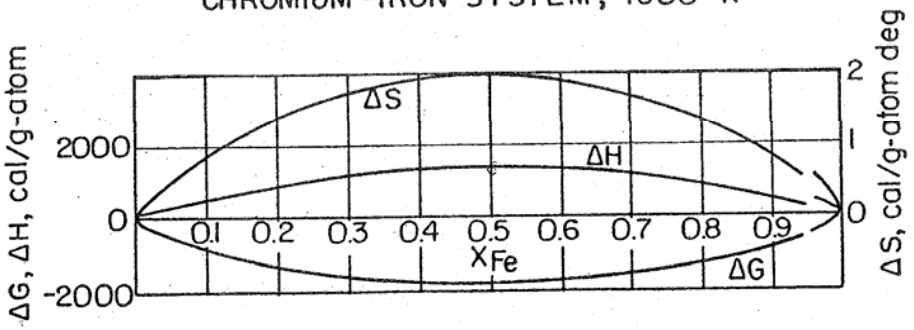
Fe-Cr alloys

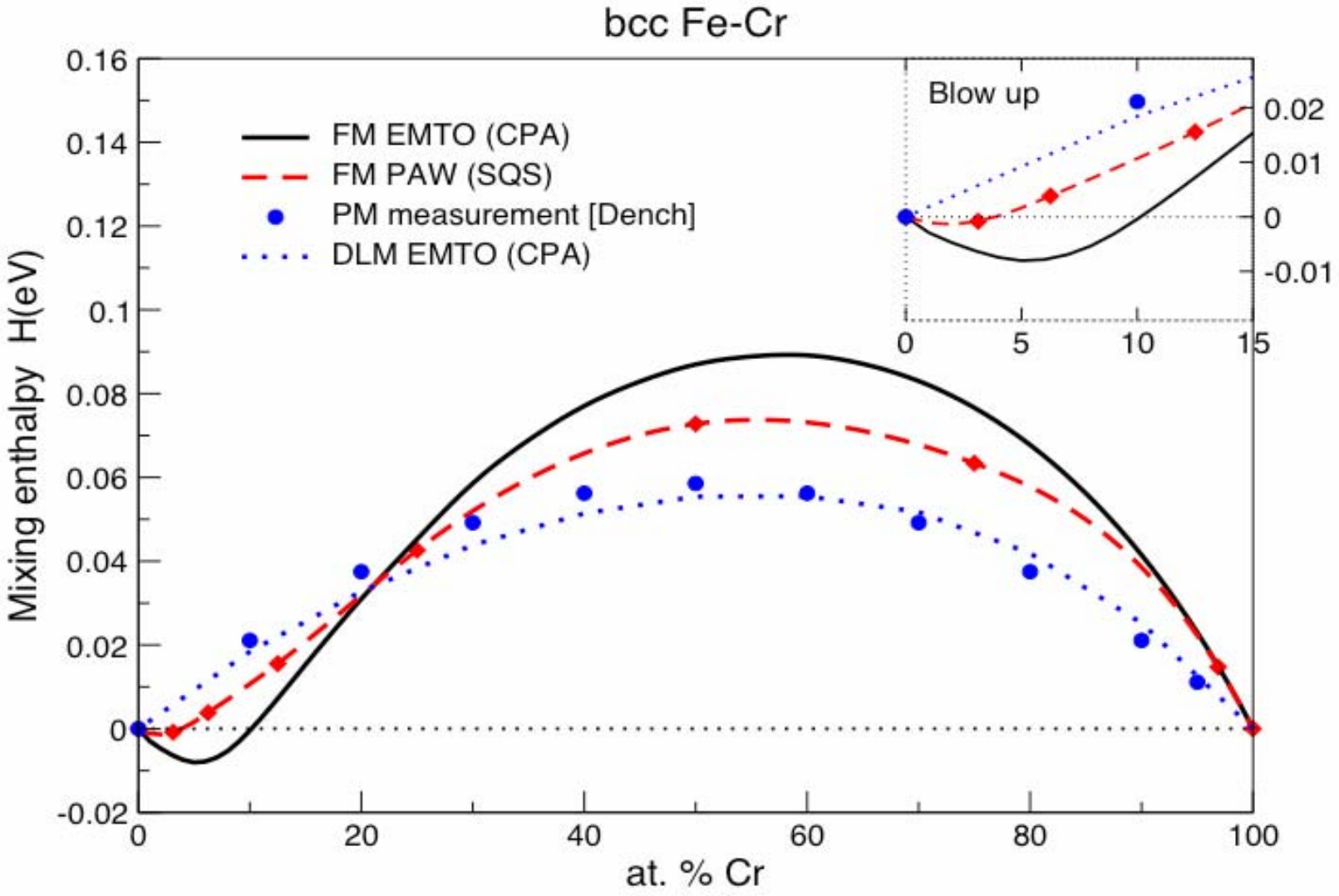
- Are the base for many important industrial steels
- Used as cladding material in fast neutron reactors
- Low Cr steels, up to 10 % Cr, show:
  anomalous stability
  resistance to neutron
  radiation induced swelling
  corrosion resistance
  increased ductile to brittle
  transition temperature



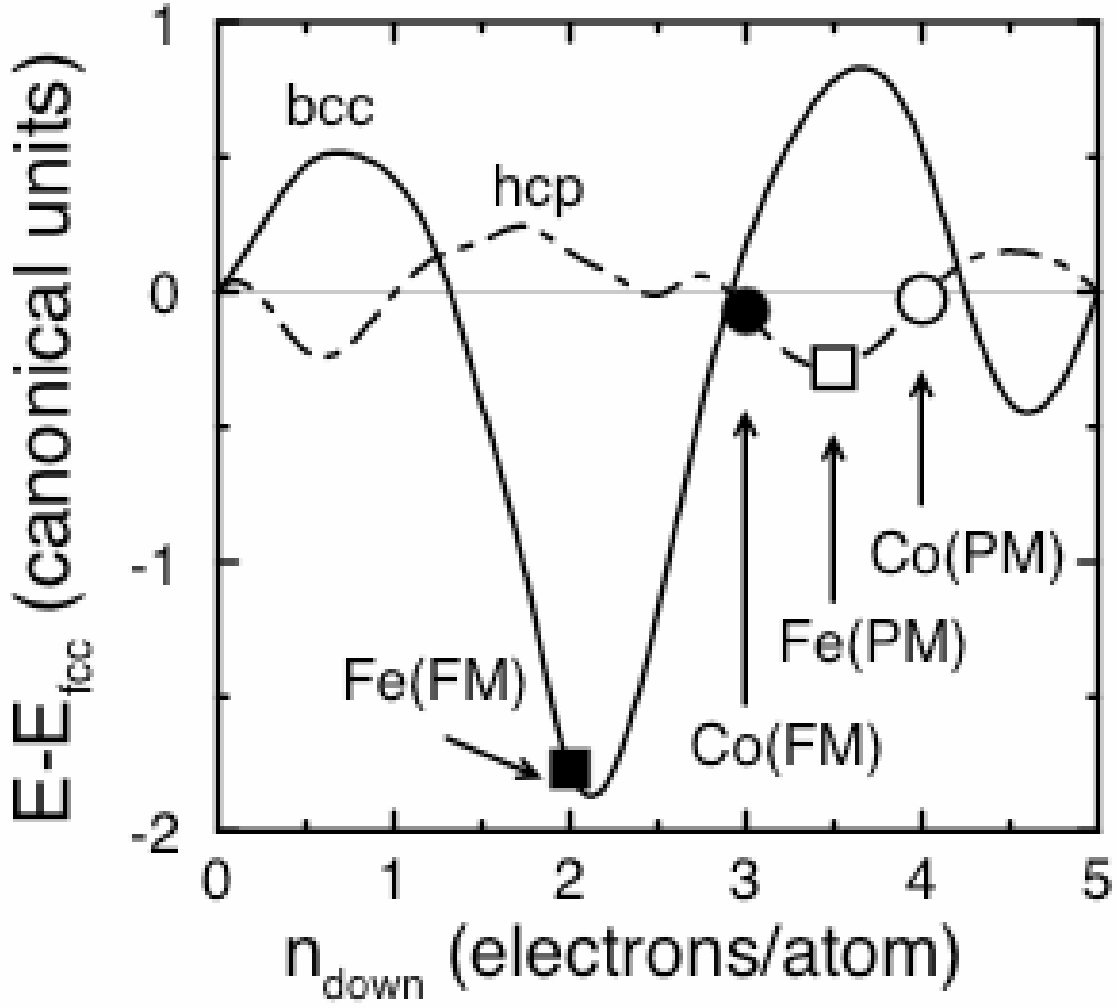


CHROMIUM-IRON SYSTEM, 1600 °K





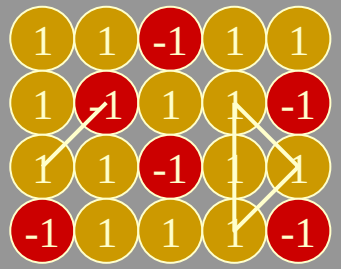
P. Olsson, I. A. Abrikosov, and J. Wallenius, Phys. Rev. B **73**, 104416 (2006)


E-E$_{fcc}$ (canonical units)
n$_{down}$ (electrons/atom)
bcc
hcp
Fe(FM)
Co(FM)
Fe(PM)
Co(PM)
1
0
-1
-2
0
1
2
3
4
5

Ising Hamiltonian and effective cluster interactions

$$\vec{\sigma}_s = \{\sigma_i\} \qquad \sigma_i = \begin{cases} 1 & \text{if site } i \text{ is occupied by atom } A \\ -1 & \text{otherwise} \end{cases}$$

$$\left\langle \sigma_i \sigma_j \right\rangle^s, \quad \left\langle \sigma_i \sigma_j \sigma_k \right\rangle^s, \ldots$$



$$E_{tot} = V^{(0)} + V^{(1)} \langle \sigma \rangle +$$

$$\sum_s V^{(2,s)} \langle \sigma_i \sigma_j \rangle + \sum_s V^{(3,s)} \langle \sigma_i \sigma_j \sigma_k \rangle + \ldots$$

Calculations of effective interatomic potentials

The generalized perturbation method

1. **Calculate electronic structure of a random alloy (for example, use the CPA):** $\tilde{g}\,,\ t^{A(B)}$

2. $$E_{one} = E_{one}(c) + \frac{1}{2}\sum_{RR'} V_{RR'} \left\langle \sigma_i \sigma_j \right\rangle^{(RR')} \ldots$$

-determine a perturbation of the band energy due to small varioations of the correlation functions

where the effective interatomic interactions are given by an analytical formula:

$$V_{RR'} = -\frac{1}{\pi}\int dE \left\{ t^{A}_{R}\gamma_{RR'} t^{B}_{R'}\gamma_{R'R} t^{A}_{R} \right\}$$

J. Phys. F: Met. Phys. 13 (1983) 2351–2358. Printed in Great Britain

Chemical SRO effects in ferromagnetic Fe alloys in relation to electronic band structure

M Hennion

Laboratoire Léon Brillouin, CEN Saclay, 91191 Gif-sur Yvette Cédex, France

Received 3 May 1983

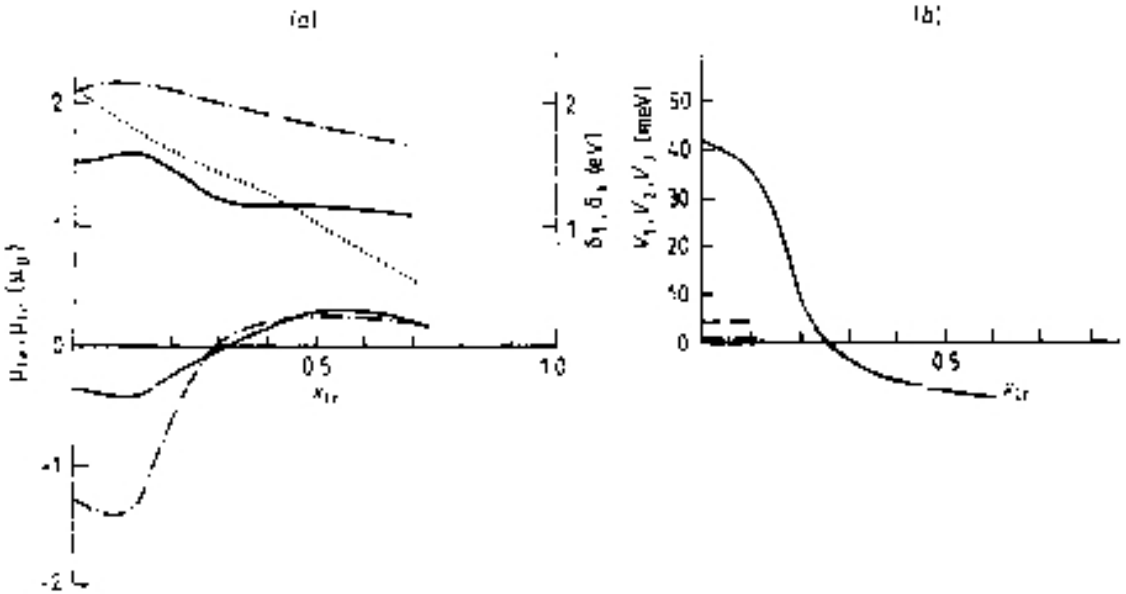
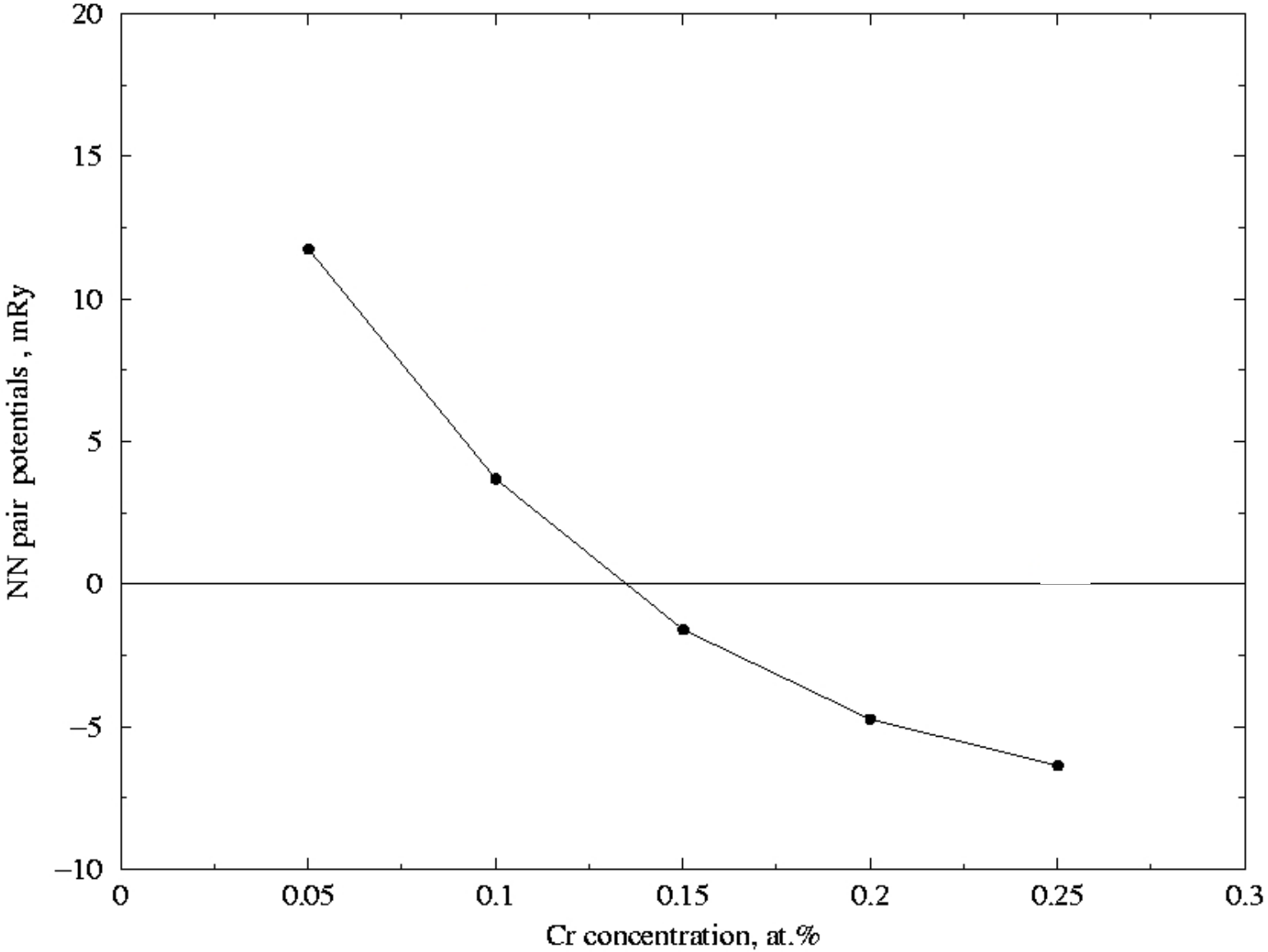
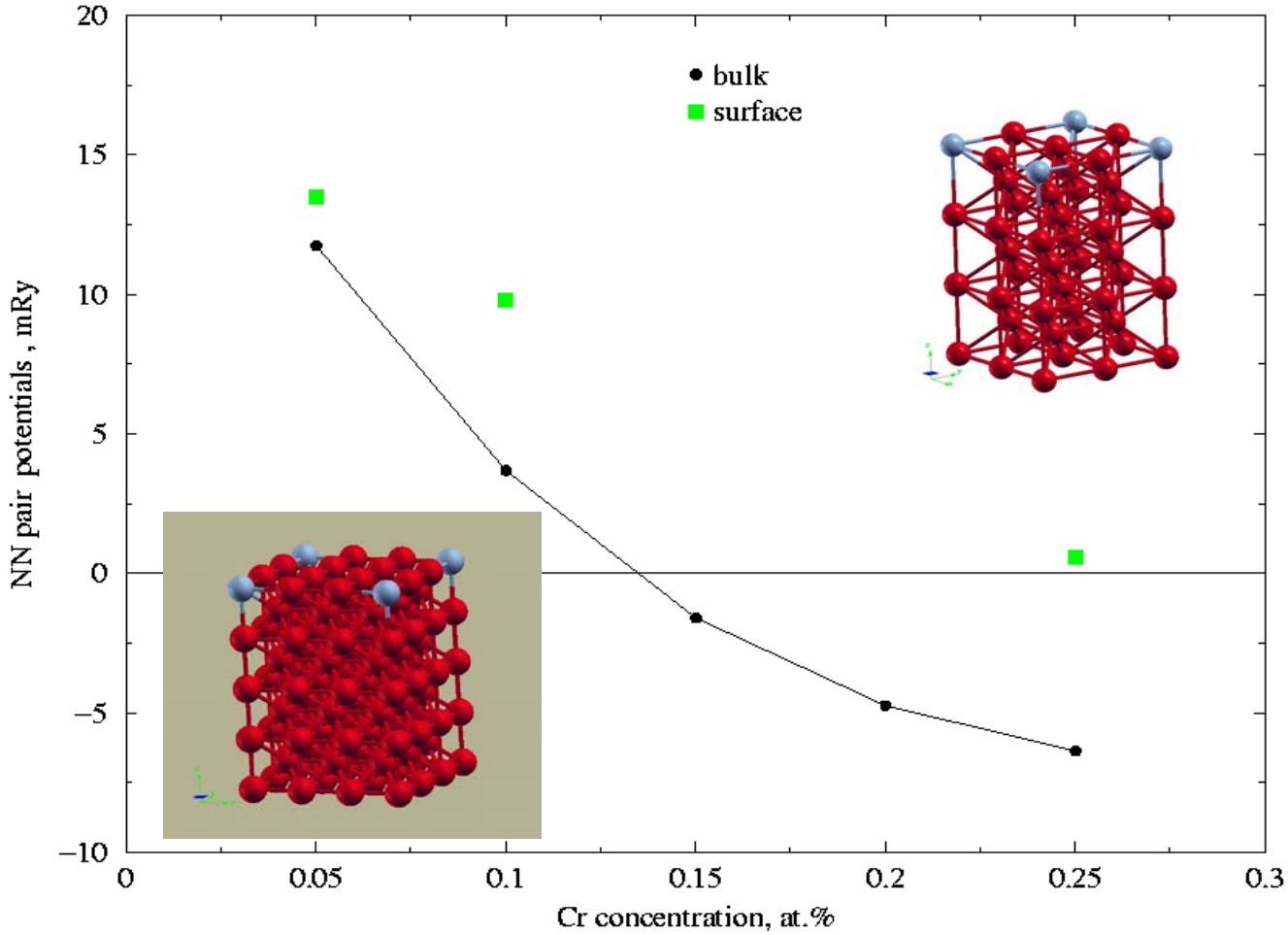


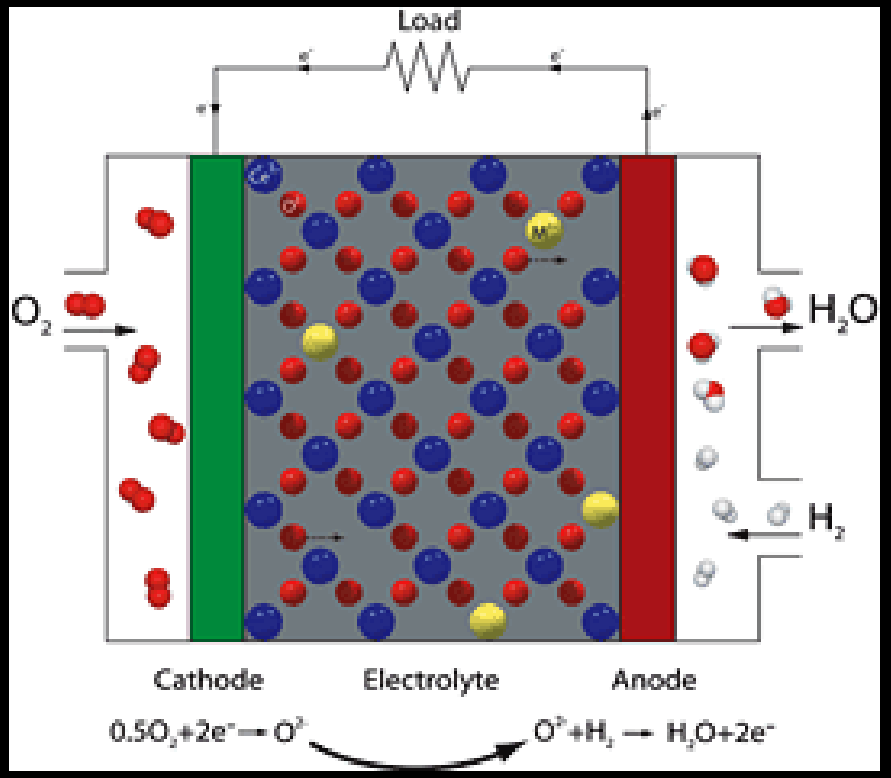
Figure 2. FeCr alloys. (*a*) Calculated curves of the partial $\mu_{Fe}(c)$ and $\mu_{Cr}(c)$ (— · · —) and total (. . .) magnetisations, and calculated curves of the energy disorder parameters δ_σ ($\sigma = \uparrow, \downarrow$) with chromium concentration (——). (*b*) Calculated variations of the pair potentials with Cr concentration: V_1(——), V_2(· · ·) and V_3(— · · —).


20
15
10
5
0
−5
−10
0
0.05
0.1
0.15
0.2
0.25
0.3
NN pair potentials , mRy
Cr concentration, at.%


bulk
surface
NN pair potentials , mRy
Cr concentration, at.%
20
15
10
5
0
−5
−10
0
0.05
0.1
0.15
0.2
0.25
0.3

Optimization of ionic conductivity in doped ceria

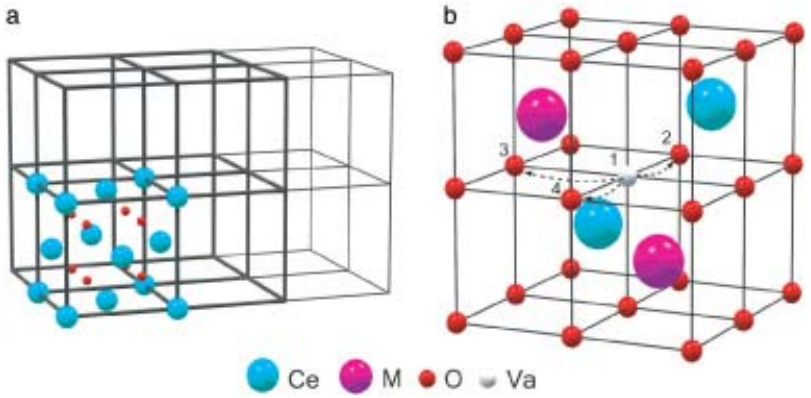
- CeO_2 is known to be good solid elictrolyte when it is doped with cations of lower valence than the host cation.
- Attractive electrolyte for solid-oxide fuel cells
- It is important to optimize the ionic conductivity in order to decrease the operation temperature



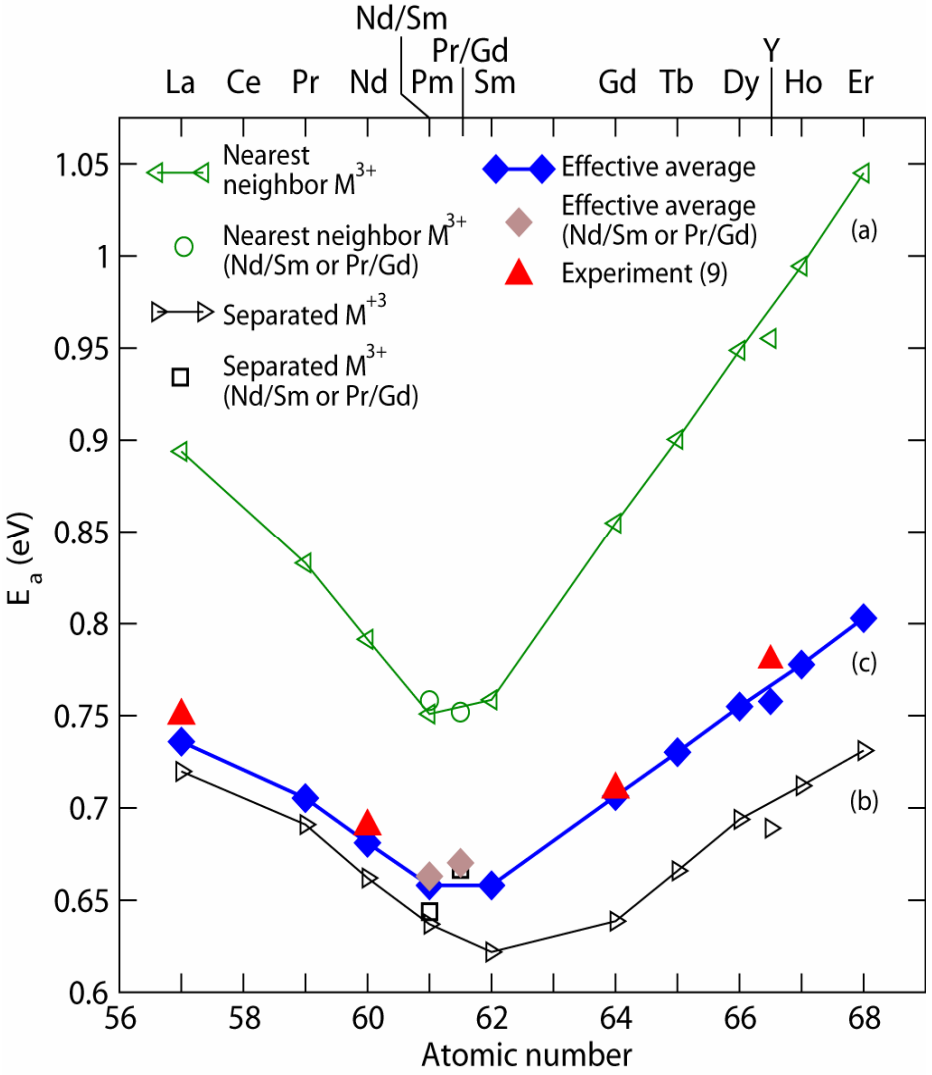
Activation energy for diffusion

E_a determines the ionic conductivity (σ):

$$\sigma = \sigma_0 / T \cdot \exp\left(-\frac{E_a}{k_B T}\right)$$

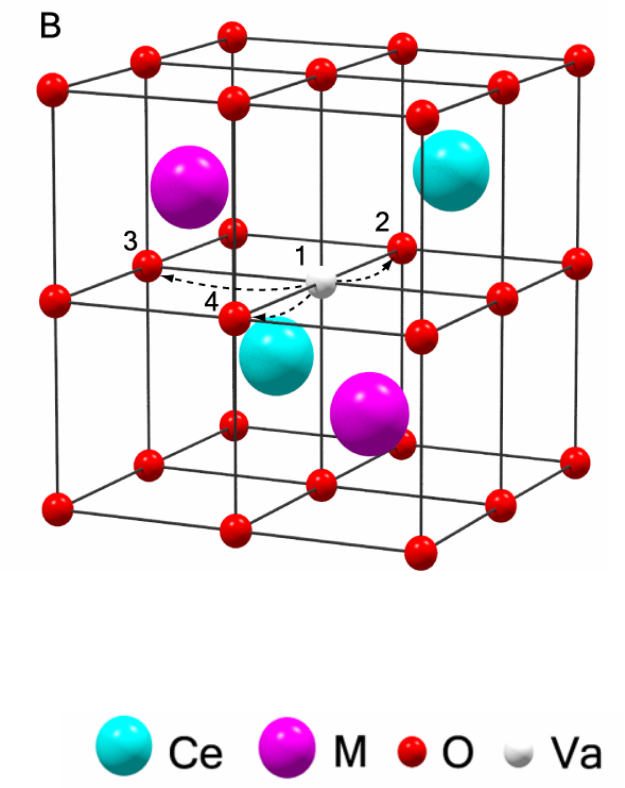


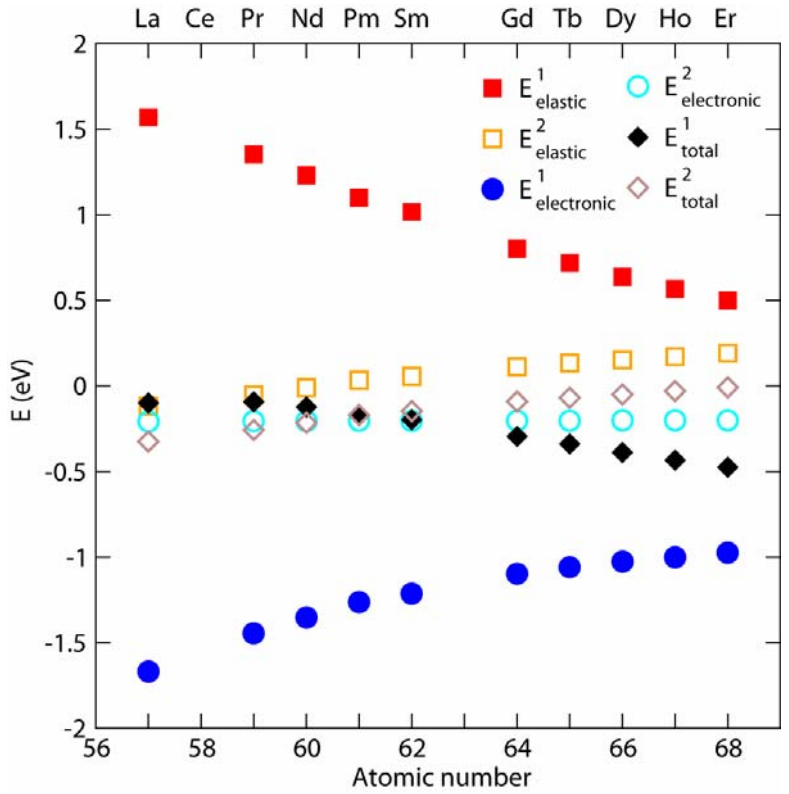
$$E_a = E_{ass} + E_m$$

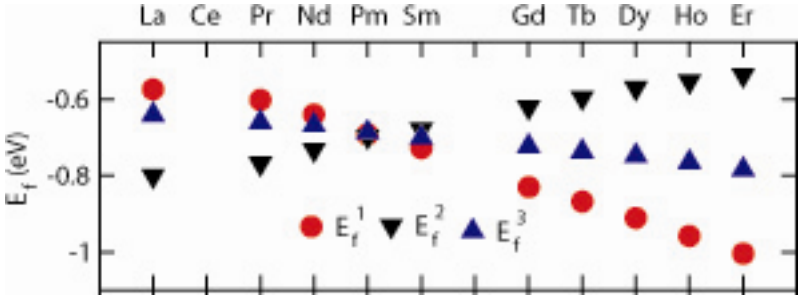


D. A. Andersson, S. I. Simak, N. V. Skorodumova, I. A. Abrikosov, and B. Johansson, PNAS **103**, 3518 (2006)

Defect formation energies







Activation energy for diffusion

PATENT COOPERATION TREATY

From the INTERNATIONAL SEARCHING AUTHORITY

PCT

To:

STENBORG Anders
Aros Patent AB P.O. Box 1544
SE-751 45 Uppsala

NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL SEARCH REPORT AND THE WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY, OR THE DECLARATION

(PCT Rule 44.1)

	Date of mailing *(day/month/year)* 27-12-2006
Applicant's or agent's file reference P494PC00	**FOR FURTHER ACTION** See paragraphs 1 and 4 below
International application No. PCT/SE2006/050299	International filing date *(day/month/year)* 29-08-2006
Applicant ANDERSSON David et al	

1. [X] The applicant is hereby notified that the international search report and the written opinion of the International Searching Authority have been established and are transmitted herewith.

Filing of amendments and statement under Article 19:
The applicant is entitled, if he so wishes, to amend the claims of the international application (see Rule 46):

When? The time limit for filing such amendments is normally 2 months from the date of transmittal of the international search report.

Where? Directly to the International Bureau of WIPO, 34 chemin des Colombettes 1211 Geneva 20, Switzerland, Facsimile No.: +41 22 338 82 70

For more detailed instructions, see notes on the accompanying sheet.

2. [ ] The applicant is hereby notified that no international search report will be established and that the declaration under Article 17(2)(a) to that effect and the written opinion of the International Searching Authority are transmitted herewith.

3. [ ] **With regard to the protest** against payment of (an) additional fee(s) under Rule 40.2, the applicant is notified that:
   - [ ] the protest together with the decision thereon has been transmitted to the International Bureau together with the applicant's request to forward the texts of both the protest and the decision thereon to the designated Offices.
   - [ ] no decision has been made yet on the protest; the applicant will be notified as soon as a decision is made.

4. **Reminders**

Shortly after the expiration of **18 months** from the priority date, the international application will be published by the International Bureau. If the applicant wishes to avoid or postpone publication, a notice of withdrawal of the international application, or of the priority claim, must reach the International Bureau as provided in Rules 90*bis*.1 and 90*bis*.3, respectively, before the completion of the technical preparations for international publication.

The applicant may submit comments on an informal basis on the written opinion of the International Searching Authority to the International Bureau. The International Bureau will send a copy of such comments to all designated Offices unless an international preliminary examination report has been or is to be established. These comments would also be made available to the public but not before the expiration of 30 months from the priority date.

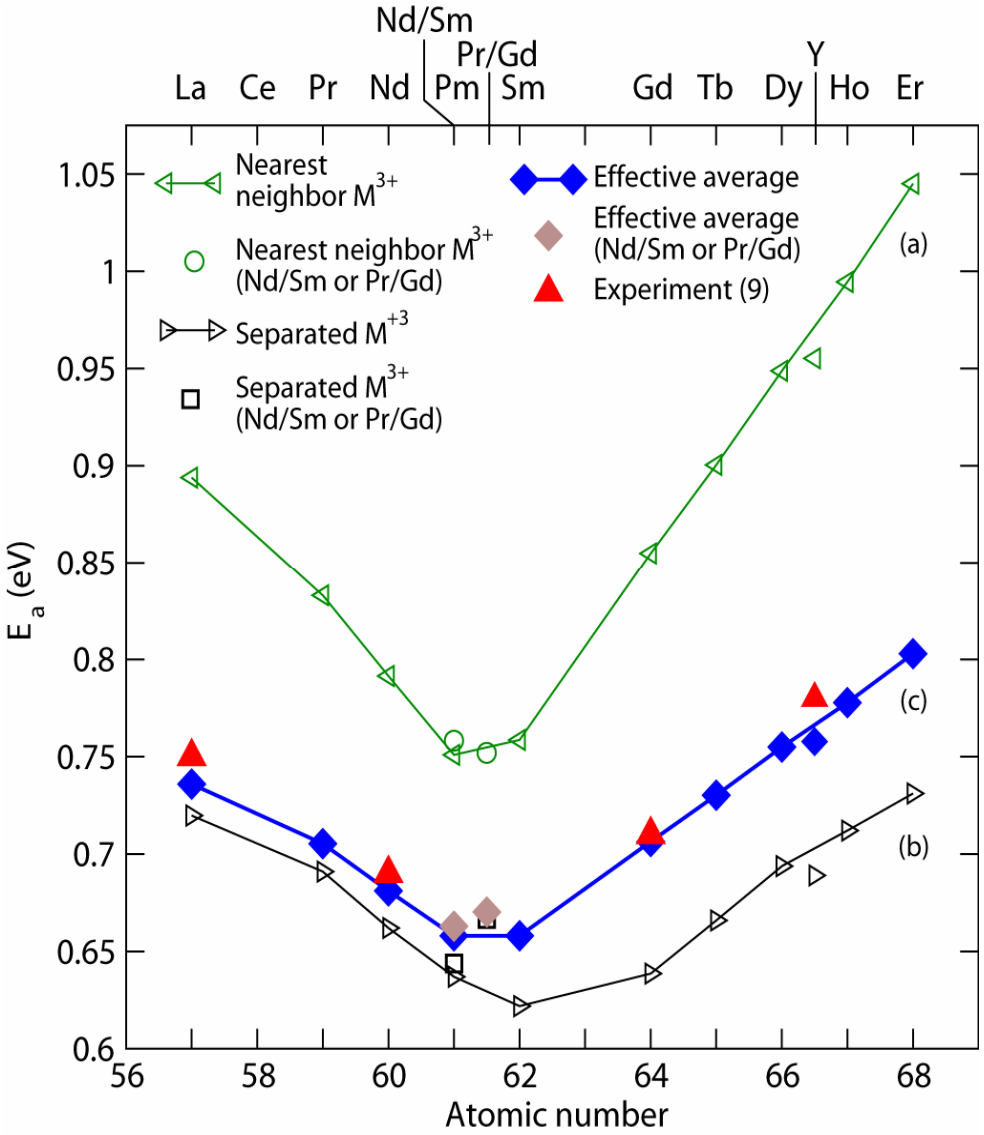
Within **19 months** from the priority date, but only in respect of some designated Offices, a demand for international preliminary examination must be filed if the applicant wishes to postpone the entry into the national phase **until 30 months** from the priority date (in some Offices even later); otherwise, the applicant must, **within 20 months** from the priority date, perform the prescribed acts for entry into the national phase before those designated Offices.

In respect of other designated Offices, the time limit of **30 months** (or later) will apply even if no demand is filed within 19 months.

See the Annex to Form PCT/IB/301 and, for details about the applicable time limits, Office by Office, see the *PCT Applicant's Guide*, Volume II, National Chapters and the WIPO Internet site.

Name and mailing address of the ISA/ Patent- och registreringsverket Box 5055 S-102 42 STOCKHOLM Facsimile No. 08-667 72 88 Telex 17978 PATOREG-S	Authorized officer [redacted] Telephone No. 08-782 25 00

Form PCT/ISA/220 (October 2005) *(See notes on accompanying sheet)*



CONCLUSIONS :

- Treatment of the alloying effects within the electronic structure theory can be carried out at different levels and by differenet methods, depending on the problem at hand, but with certain degree of caution.
- Analysis of the electronic structure allows for the fundamental understanding of the physics behind the technologically relevant phenomena.
- The decomposition in (TiAl)N hard coating alloys with high Al content is enhanced by the increased localization of non-bonding states at transition metal sites.
- Anomalous stability of low Cr steels is determined by the band-filling effects.
- We predicted theoretically new alloy compositions which should optimization the ionic conductivity in doped ceria