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SPRING COLLEGE IN MATERIALS SCIENCE
ON
"METALLIC MATERIALS"
(11 May - 19 June 1987)

THEORETICAL MODELING OF DEFECTS AND EMBRITTLEMENT

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THEORETICAL MODELING OF DEFECTS AND EMBRITTLEMENT

1. Aims and methods of theory. The macroscopic theory of embrittlement; thermodynamics and fracture mechanics. What determines the strength of a grain boundary? Fundamental questions: the role of interfacial energy, the importance of precipitates and dislocations, leading to a discussion of elementary processes on the atomic scale.

2. The solid state physicist's contribution. The electron theory of cohesion and bonding in solids. The tight-binding description. Bond energies and interatomic forces.

3. Simpler models for atomistic simulation of defects and their interactions. The second moment approximation. The embedded atom method. The scope and limitations of these models will be described with some examples, including hydrogen embrittlement.

Suggested references and further reading :

D.G.Pettifor, in Theoretical Metallurgy , eds. R.W.Cahn and P.Haasen, North Holland, 1983.

Jong K.Lee, ed., Interatomic potentials and crystalline defects, The Metallurgical Society of AIME, 1981.

R.M.Latanision and J.R.Pickens, eds. Atomistics of fracture, Plenum 1983.

M.W.Finnis, Interatomic forces and the simulation of cracks, Invited lecture at the NATO Advanced Research Workshop on the Chemistry and Physics of Fracture, Bad Reichenhall, 1986, available as report no. TP.1196 from the Main Library, B465, Harwell Laboratory, Oxon OX11 0RA, UK. This contains several other references to papers dealing with the topics of these lectures.

3 LECTURES

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Theoretical modelling of defects and embrittlement

MIKE FINNIS (HARWELL)

LECTURE I

1. Introduction to embrittlement
2. The variety of parameters involved ($\gamma, d, \sigma_v, \sigma_0$)
3. The importance of a proper understanding of BOND ENERGY

Classes of Embrittlement

Solute segregation

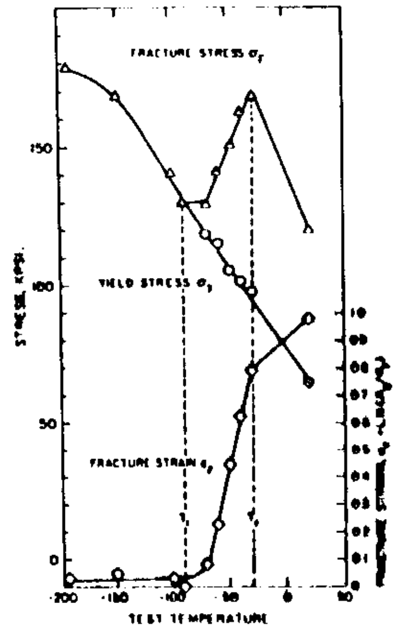
- Reduced high T creep properties of ferritic and Ni based alloys
- Cracking of welds
- RTE : (slow cooling through 300-600C)
  Fe embrittled by S
  Ni-Cr steels embrittled by P, Sn, Sb, As
  (inhibited by Mo)

LME

H embrittlement

He embrittlement

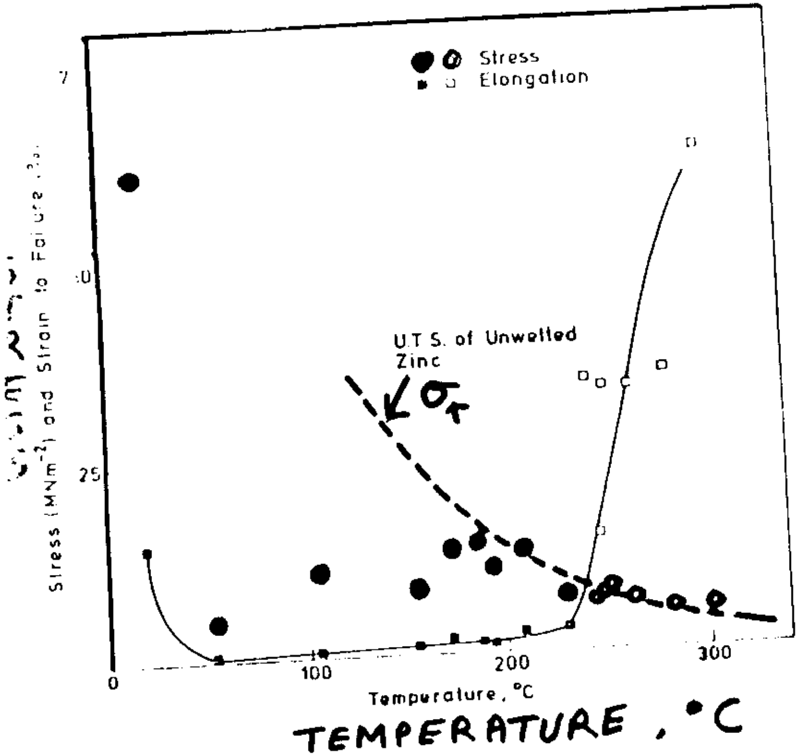
Molybdenum (Passmore, 1964)



Effect of test temperature on the tensile properties of annealed, fine-grained molybdenum.

Example [illegible] a bcc metal

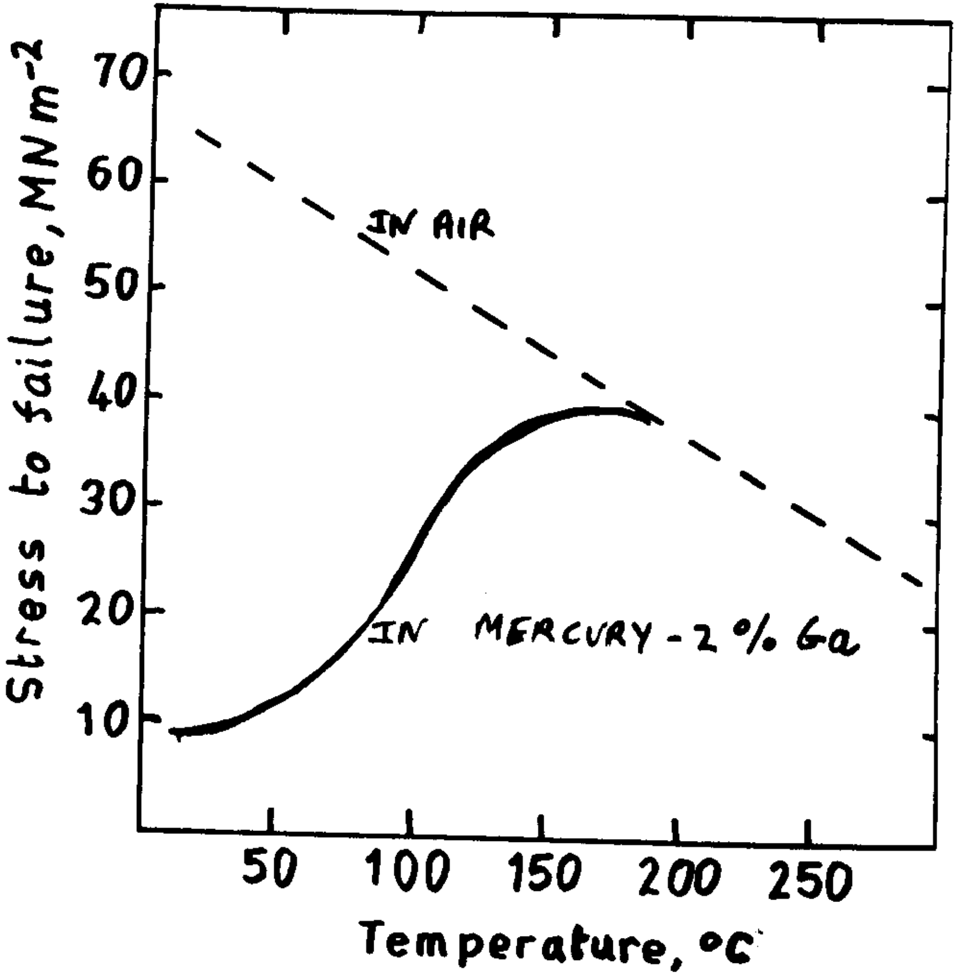
EMBRITTLEMENT OF Zn BY Ga



AFTER OLD & TREVENA

Example of an hcp metal

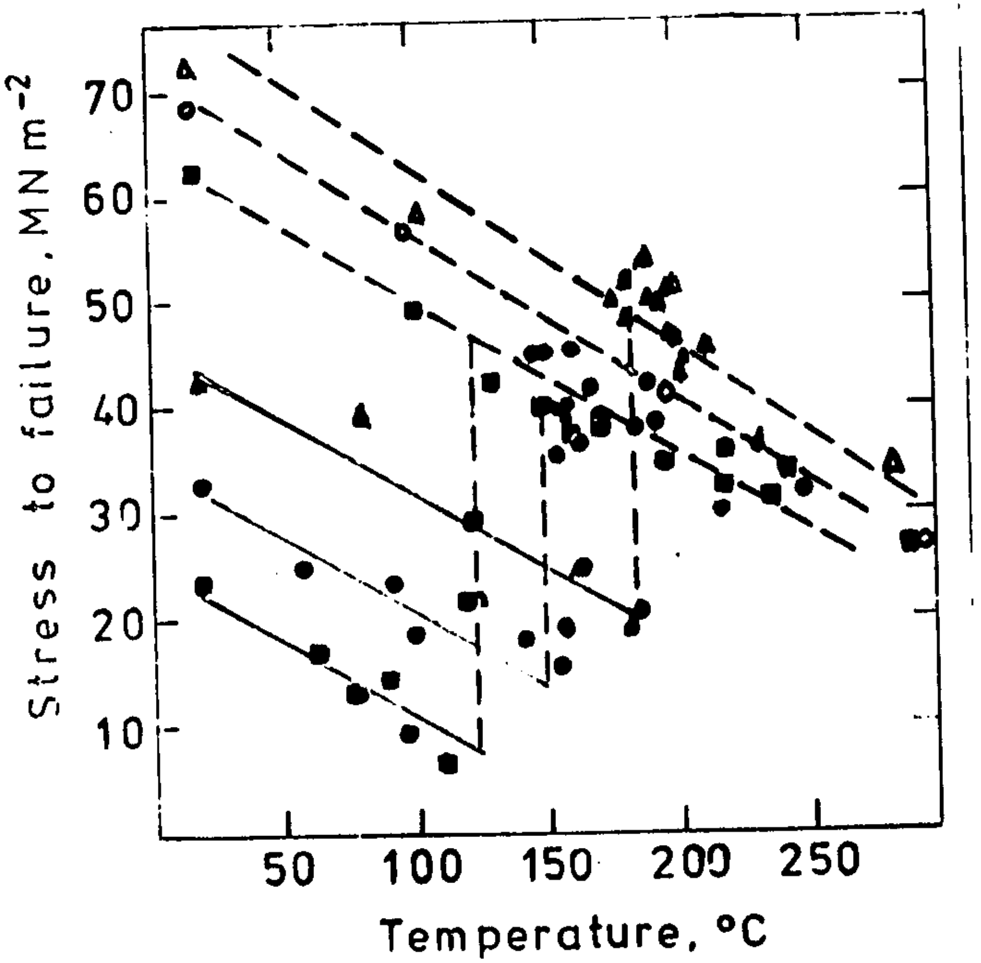
EMBRITTLEMENT OF AL by Hg-2%Ga



SCHEMATIC (AFTER PREECE & WESTWOOD)

A less abrupt transition

EMBRITTLEMENT OF AL by Hg-3%Zn

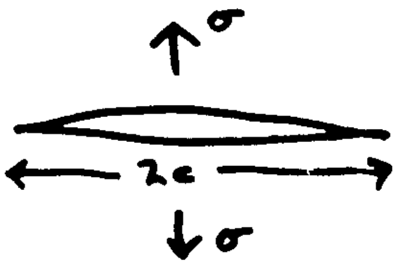


AFTER ICHINOSE

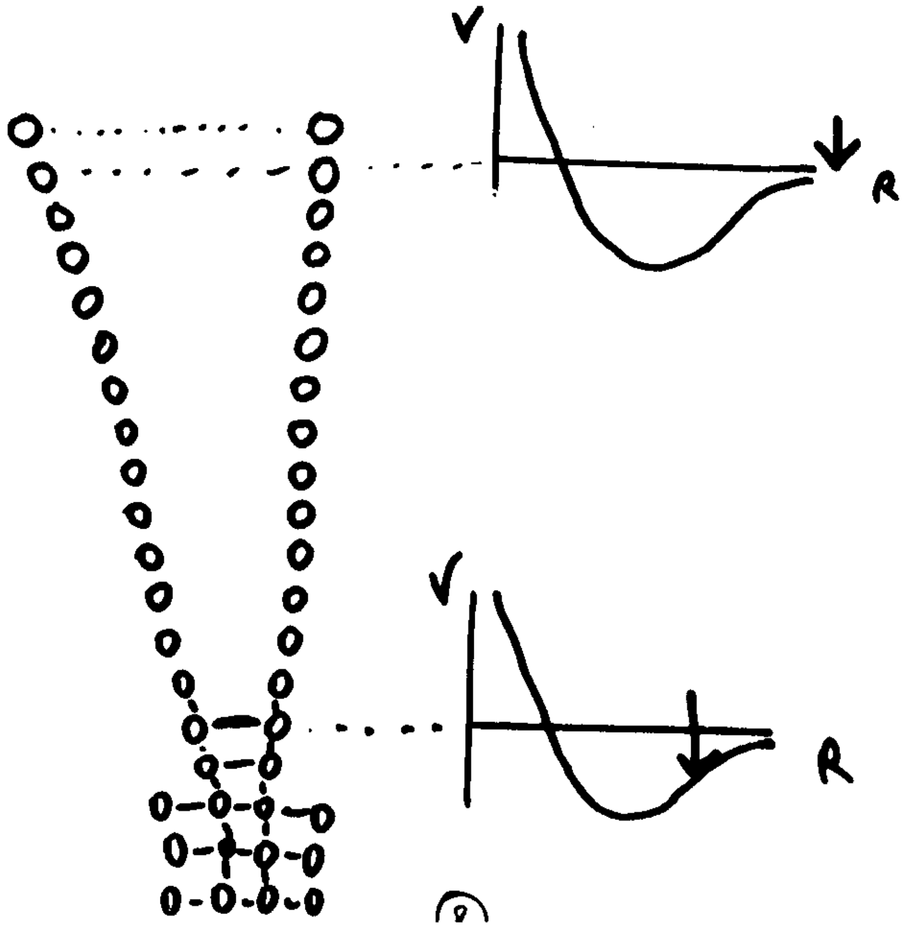
At 150°C get BRITTLE → DUCTILE as d is increased (unusual)

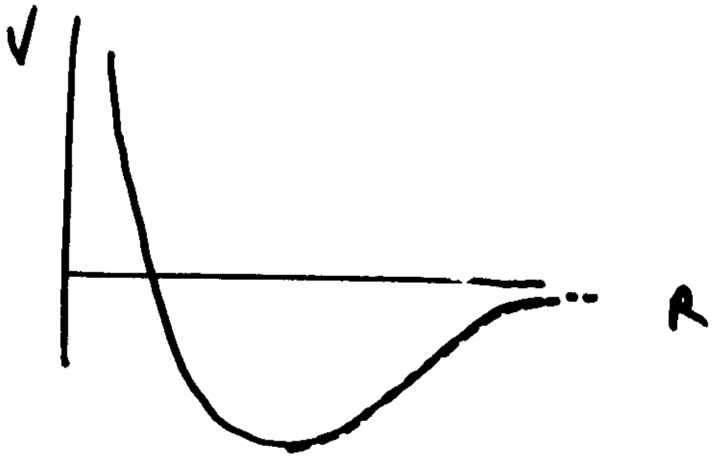
[illegible] metal

CRACK PROPAGATION



$$\sigma = \sqrt{\frac{\gamma E}{c}}$$





Integrated force

→ well depth = cohesion

= γ

Grain boundaries: $\gamma \equiv 2\gamma_s - \gamma_{gb}$

Environment:

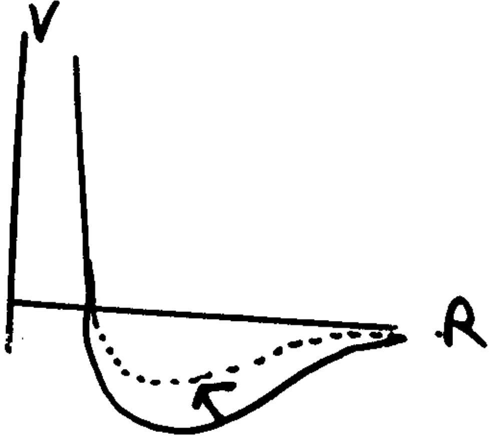
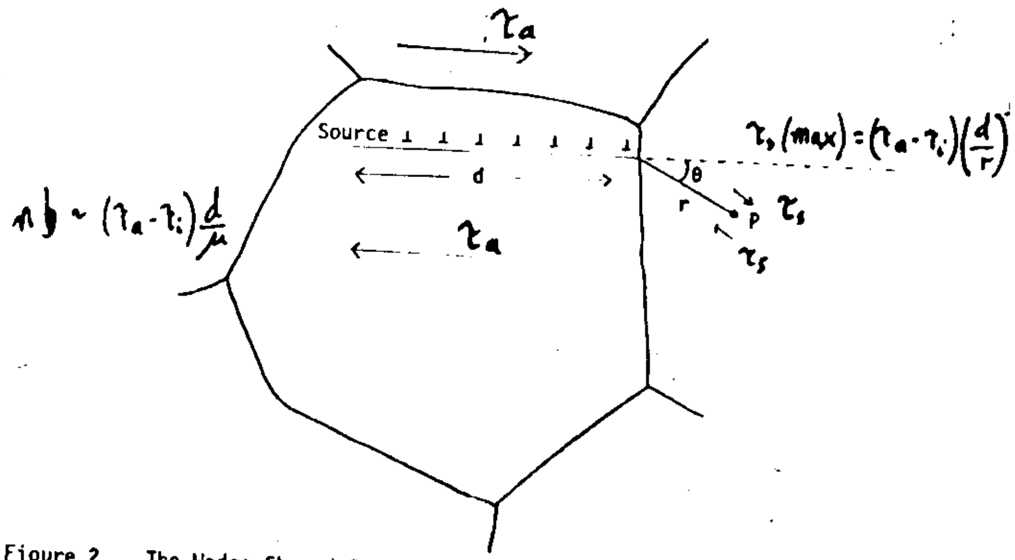


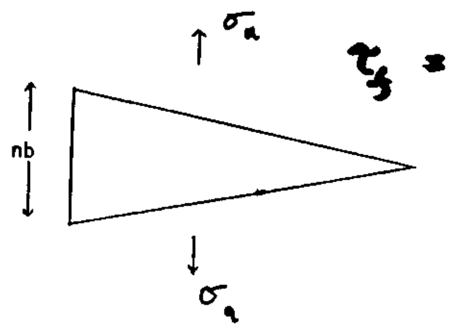
Figure 1. The Pile-up of Dislocations



$$nb \sim (\tau_a - \tau_i)\frac{d}{\mu}$$

$$\tau_s(\max) = (\tau_a - \tau_i)\left(\frac{d}{r}\right)$$

Figure 2. The Wedge Shaped Crack

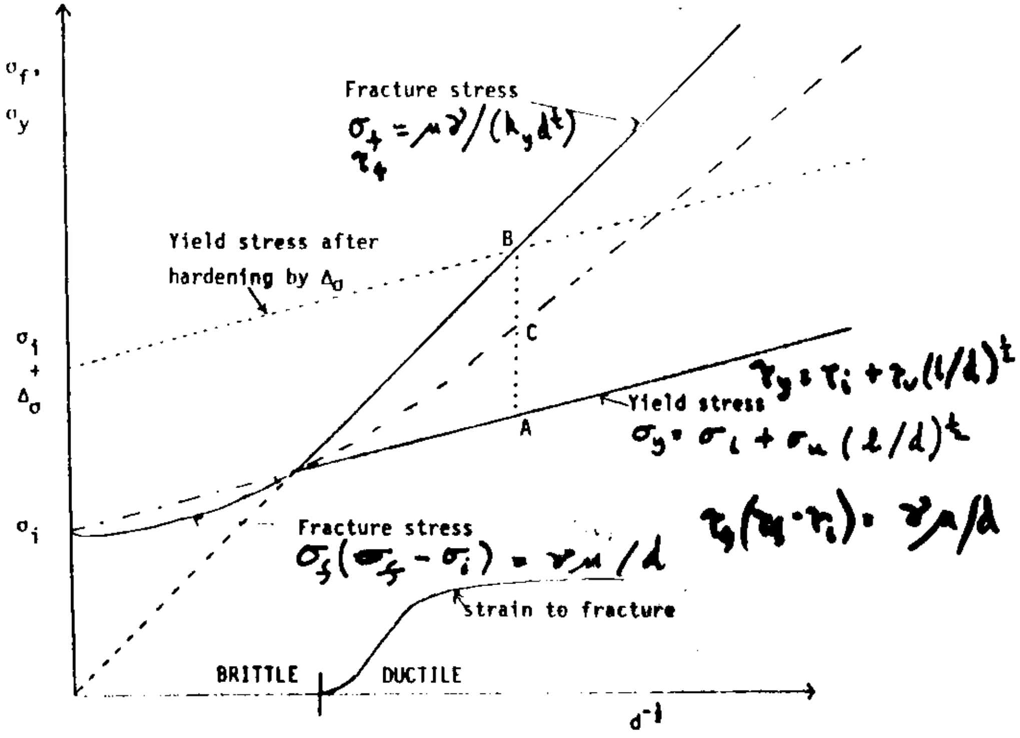


$$\tau_s = \frac{\gamma}{nb}$$

The Cottrell theory

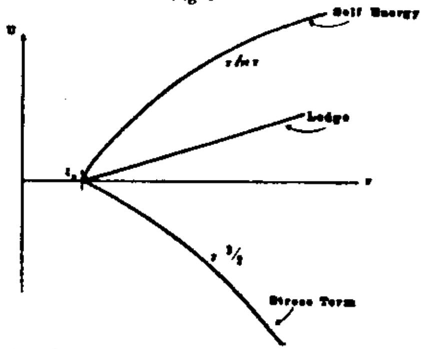
(Crack or Yield?)

Figure 3. Fracture and Yield Stresses



The Cottrell Theory
(Crack or yield?)

Fig. 6



Schematic variation of the three terms in eqn. (17) as a function of the radius.

Table 2. Three-dimensional results

Crystal	Activation energy (electron volts)	Radius of activated loop (in units of b)
Pb Au Cu Ag Al Ni	Spontaneous emission—No activated state for $r > \xi_0$.	
Na	0·03	1·5
Fe	2·2	5·1
W	329	30·7
Fe*	19	17
LiF	58	32
NaCl	{62 (240)}	{33 (96)}
MgO	306	37
A_2O_3	852	30
Si	111	30
Ge	280	42
C	361	27
Be	180	23
Zn	107	21·2

Cleave or blunt?
Not thermally activated
except Na and Fe

2. REASONS FOR ABANDONING PAIR POTENTIALS

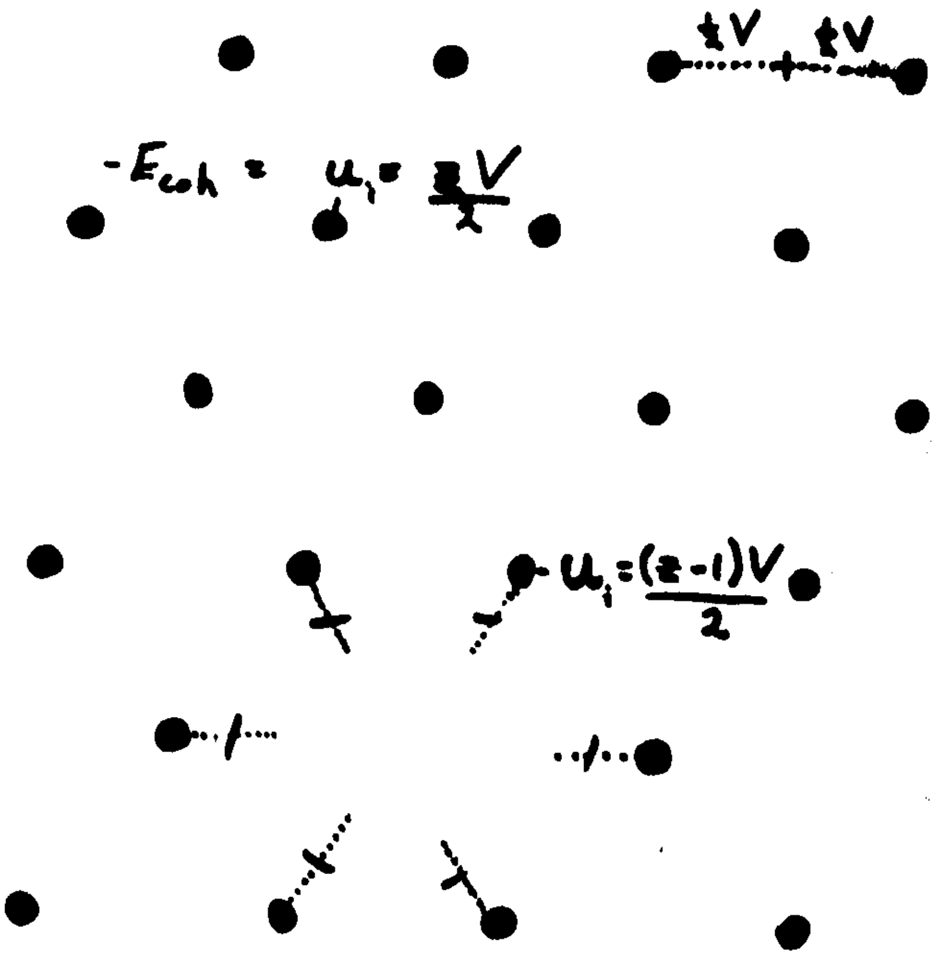
(1) Experimental E_v^f / E_{coh}

Nb	2.04 / 7.57
Ta	2.9 / 8.10
Cr	1.2 / 4.10
Mo	2.24 / 6.82
W	3.15 / 8.90
Fe	1.79 / 4.28

(2) Cauchy relation

$C_{12} \neq C_{44}$ in real cubic metals
(equilibrium pair potentials
predict $C_{12} = C_{44}$)

In the old pairwise models, e.g. Lennard Jones
Vacancy formation energy ≃ cohesive energy
Energy per atom u_i



$$E_v^f = z \times \left\{ \frac{(z-1)V}{2} - \frac{zV}{2} \right\}$$
$$= \frac{-zV}{2} = E_{coh}$$

Theoretical Modelling of defects and embrittlement

MIKE FINNIS (HARWELL)

LECTURE II

AIM : TO DERIVE A BOND ENERGY CONCEPT FOR METALS BASED ON ELECTRON THEORY (QUANTUM MECHANICAL)

→ THE TIGHT-BINDING BOND MODEL

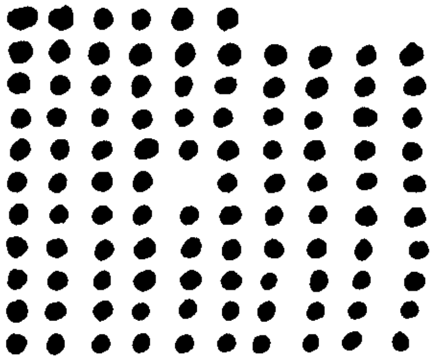
= A SOLID STATE PHYSICIST'S VERSION OF COULSON'S 'BOND ORDER' CONCEPT APPROPRIATE FOR 10^{23} ATOMS.

Some additional material is included here in the copied transparencies.

OUTLINE

1. RECAP - E_v^f and E_{coh}
2. SUMMARY OF ATOMISTIC SIMULATION WITH TB MODEL
3. SOLID STATE PHYSICS APPROACH TO TOTAL ENERGY - LDF THEORY
4. HARRIS - FOULKES APPROXIMATION $\rho = \rho^f$
5. THE DENSITY OF STATES and LOCAL DENSITY OF STATES
6. TB MODEL ⟶ TBB MODEL
7. MOMENTS OF LOCAL D.O.S.
8. EXAMPLES FOR D-BAND METALS
   - BOND ENERGY IN FCC AND HCP
   - VACANCY
9. ADVANTAGES AND DISADVANTAGES OF TBB - DISCUSSION.

VACANCY FORMATION



$$-E_v^f = \frac{1}{2} z V = E_{coh}$$

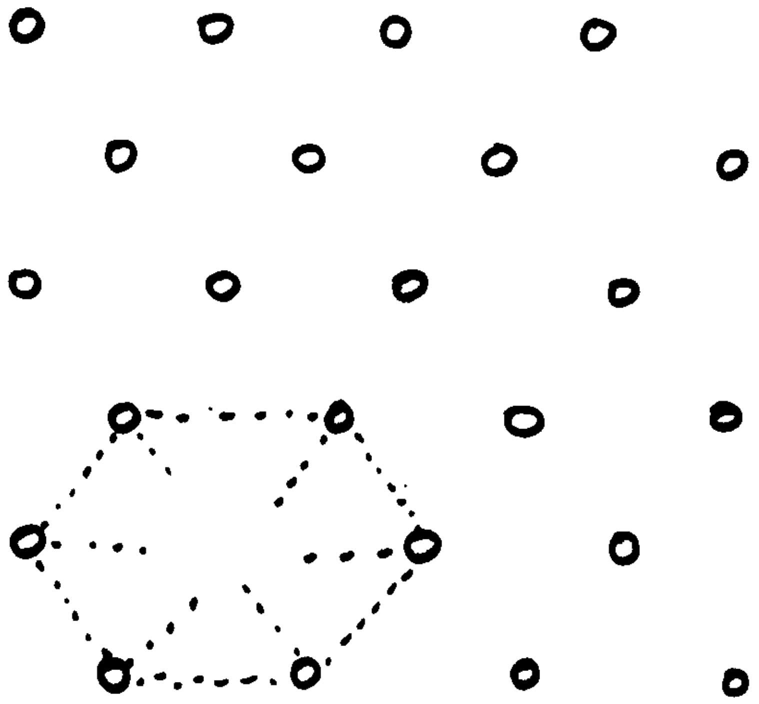
N atoms

ENERGY $N E_{coh} + E_v^f + N^{2/3}\gamma$

N+1 atoms (perfect)

ENERGY $(N+1) E_{coh} + N^{2/3}\gamma$

Volume change?. $\Delta E \approx B V \left(\frac{\delta V}{V}\right)^2 \sim B \frac{V}{N^2} \sim O\left(\frac{1}{N}\right)$



$$+E_{coh} = (z\phi)^{\frac{1}{2}} = u$$

$$\begin{aligned} E_v^f &= -(z u' - z u) \\ &= -z\left[\left((z-1)\phi\right)^{\frac{1}{2}} - (z\phi)^{\frac{1}{2}}\right] \\ &= -z\left[z^{\frac{1}{2}}\left(1 - \frac{1}{2z}\right)\phi^{\frac{1}{2}} - z^{\frac{1}{2}}\phi^{\frac{1}{2}}\right] \\ &= \frac{1}{2}(z\phi)^{\frac{1}{2}} \end{aligned}$$

$$\underline{E_v^f = \frac{1}{2} E_{coh}}$$

VIBES!

TB model for atomistic simulation

- Vacancy (metal) : Allan, Lannoo 1970
- Surfaces and interfaces

semiconductor, sp^3 : Chadi 1979

metal ; W, Mo : Spanjaard
Terakura, Terakura and Hamada 1981
Masuda-Jindo, Hamada and Terakura 1984

- Dislocations

bcc metals, μ_4 : Masuda, Yamamoto and Doyama 1983

hcp Ti, 'μ_6' : Legrand 1985

$$E = \sum_i \int^{E_F} n_i(E)\,dE + E_{PAIR}$$

Numerical procedure of previous TB approaches for μ_n, $n > 4$

$$\Delta E = \int \varepsilon\, n_i^{(1)}\, d\varepsilon - \int \varepsilon\, n_i^{(2)}\, d\varepsilon$$

For force on atom i, $n_j(\varepsilon)$ must be evaluated for <u>all</u> j to obtain $\sum \Delta n_j$.

e.g. Legrand evaluated Δn_i to μ_6, other Δn_j to μ_2.

<u>Direct</u> calculation of force ? → TBB
Tight Binding Bond model.

TBB model applications:

Pettifor and Podloucky (1985)

Separation of structures of metal-metalloid AB compounds of types:

NaCl
CsCl
NiAs
MnP
FeB
CrB

Ohta, Finnis, Sutton, Pettifor (tbp)
Grain boundary structures, vacancy.
Paxton et al, grain boundary in Si (to be published)

TOTAL ENERGY

1) Superimpose atomic charges ρ_i $\rightarrow \rho^f$

Kohn-Sham effective potential

$$V_{eff} = v(r) + v_H^f(r) + \mu_{xc}^f(r)$$

2) Solve single-particle Hamiltonian

$$\tilde{H} = -\tfrac{1}{2}\nabla^2 + V_{eff} \quad ; \quad \tilde{H}|n\rangle = \tilde{\epsilon}_n|n\rangle$$

3) Construct output charge density ρ^{out}

4) Iterate until $\rho \rightarrow \rho^{sc}$

$$E_{TOTAL}^{sc} = \sum_n a_n \epsilon_n^{sc} - \int \rho^{sc}\left(\tfrac{1}{2} v_H^{sc} + \mu_{xc}^{sc}\right) + E_{xc}[\rho^{sc}] + E_{ii}$$

FOULKES AND HARRIS APPROXIMATION

(J. Harris, PRB 31 1770 (1985))

$$E^{\mathrm{Harris}}_{\mathrm{TOTAL}} = \sum_n a_n \tilde{\varepsilon}_n - \int \rho^f \left(\tfrac{1}{2} v_H^f + \mu_{xc}^f \right)$$
$$+ E_{xc}[\rho^f] + E_{ii}$$
$$+ O[\rho^{sc} - \rho^f]^2$$

N.B.: $E^{\mathrm{Harris}}_{\mathrm{TOTAL}} \neq E[\rho^f]$

so we cannot say $E^{\mathrm{Harris}}_{\mathrm{TOTAL}} > E^{sc}_{\mathrm{TOTAL}}$

Spectroscopic constants of homonuclear dimers

J. Harris PRB 31 1770 (1985)

		Harris	Painter & Averill	Expt.
Be_2	E_{coh}	0.49	0.50	~0.1
	R	4.50	4.63	4.66
	ω	45	45	28
C_2	E_{coh}	8.7	7.19	6.2
	R	2.20	2.36	2.35
	ω	246	232	230
N_2	E_{coh}	10.7	11.34	9.91
	R	2.03	2.08	2.07
	ω	346	296	292
F_2	E_{coh}	3.7	3.32	1.65
	R	2.71	2.62	2.68
	ω	120	133	111
Cu_2	E_{coh}	2.9	2.65	2.03
	R	4.10	4.10	4.20
	ω	35	41	33

THE DENSITY OF STATES

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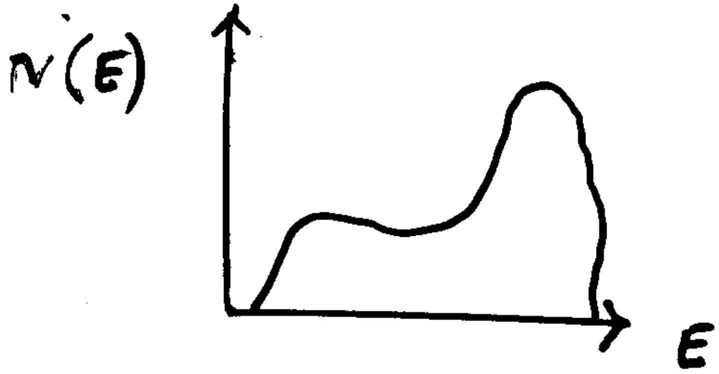


$$n(E) = \sum_n \delta(E-\varepsilon_n)$$

where

$$H\psi_n(r) = \varepsilon_n \psi_n(r)$$

LOCAL D.O.S. :

$$n_i(E) = \sum_n \delta(E-\varepsilon_n)|a^i_n|^2$$

$$a^i_n = \int d^3r\, \phi^*_i(r)\psi_n(r)$$

$\phi_i(r)$ is an atomic orbital on site i (index i includes site & L)

Notation

$$H|n\rangle = \varepsilon_n|n\rangle$$

$$\psi_n(r) = \langle r|n\rangle$$

$$a^i_n = \int d^3r\, \phi_i(r)\psi_n(r)$$

$$= \int d^3r \;\langle i|r\rangle\langle r|n\rangle$$

$$\left.\begin{aligned} \int d^3r\; |r\rangle\langle r| &= 1 \\ \sum_n |n\rangle\langle n| &= 1 \end{aligned}\right\}$$ COMPLETENESS

$$a^i_n = \langle i|n\rangle$$

$$n_i(E) = \sum_n \delta(E-\varepsilon_n)\langle i|n\rangle\langle n|i\rangle$$

$$= -\frac{1}{\pi}\mathrm{Im}\,(E^+-\varepsilon_n)^{-1}\langle i|n\rangle\langle n|i\rangle$$

$$= -\frac{1}{\pi}\mathrm{Im}\,\langle i|n\rangle\langle n|(E^+-H)^{-1}|n\rangle\langle n|i\rangle$$

$$= -\frac{1}{\pi}\mathrm{Im}\,\langle i|(E^+-H)^{-1}|i\rangle$$

$$(E - H)^{-1} \equiv G$$

i.e. $$EG = HG + 1$$

$$\mathrm{Im}\langle i|EG|j\rangle = \mathrm{Im}\langle i|HG|j\rangle$$

Cohesive energy

Convenient notation results if we introduce the output density operator

$$\rho^{out} = \sum_n a_n |n\rangle\langle n|$$

where

$$\tilde{H}|n\rangle = \tilde{\varepsilon}_n |n\rangle .$$

so that

$$\sum_n a_n \tilde{\varepsilon}_n \rightarrow \mathrm{Tr}\,\rho^{out}\tilde{H}$$

We then have the basis independent form:

$$E^{Harris}_{total} = \mathrm{Tr}\,\rho^{out}\tilde{H} - \mathrm{Tr}\,\rho^{f}(\delta v^{f}_{H} + \mu^{f}_{xc}) + E_{xc}[\rho^{f}] + E_{II}$$

Cohesive energy

Subtract from E_{TOTAL} the energy of separated atoms E^{sc}_{ATOMS} =

$$\sum_i \left\{ \mathrm{Tr}\, \rho_i \left(T + \tfrac{1}{2} v_{Hi} + v_i\right) + E_{xc}[\rho_i] \right\}$$

to get

$$E^{Harris}_{COH} = E^{Harris}_{TOTAL} - E^{sc}_{ATOMS}$$

$$\boxed{\begin{aligned} E^{Harris}_{COH} &= \mathrm{Tr}\left(\rho^{out} - \rho^{f}\right)\tilde{H} \\ &\quad + \Delta E_{es}[\rho^{f}] + \Delta E_{xc}[\rho^{f}] \end{aligned}}$$

The 'Δ' represent changes on formation of the solid.

E_{es} represents all electrostatic terms.

So far have not even made LDA - above is <u>exact</u>

BOND ENERGY

Recall

$$E^{Harris}_{COH} = \mathrm{Tr}\left(\rho^{out} - \rho^{f}\right)\tilde{H} + \Delta E_{es}[\rho^{f}] + \Delta E_{xc}[\rho^{f}]$$

The first term will be the chemical bonding, the last terms are a pair potential.

Work with a basis of atomic orbitals. Orbitals on atom i are $|\phi_{i\alpha}\rangle$.

Atomic charge density

$$\rho_i(\mathbf{r}) = \sum_\alpha \langle \mathbf{r}|\phi_{i\alpha}\rangle \rho^{i\alpha i\alpha} \langle \phi_{i\alpha}|\mathbf{r}\rangle$$

and

$$\begin{aligned} \rho^{f} &= \sum \rho_i \\ &= \sum_{i\alpha} \langle \mathbf{r}|\phi_{i\alpha}\rangle (\rho^{f})^{i\alpha i\alpha} \langle \phi_{i\alpha}|\mathbf{r}\rangle \end{aligned}$$

Bond energy

$$\mathrm{Tr}\,(\rho^{out} - \rho^{f})\,\tilde{H}$$

$$= \sum_i \sum_{\alpha\beta} \left((\rho^{out})^{i\alpha i\beta} - (\rho^{f})^{i\alpha i\beta}\, \delta^{i\alpha}_{i\beta} \right) \tilde{H}_{i\beta i\alpha}$$

$$+ \sum_{i\alpha} \sum_{j\neq i,\beta} (\rho^{out})^{i\alpha j\beta}\, \tilde{H}_{j\beta i\alpha}$$

First term is site-diagonal part

= energy associated with change in occupancy of atomic orbitals

e.g $2\tilde{\varepsilon}_s + 2\tilde{\varepsilon}_p \rightarrow \tilde{\varepsilon}_s + 3\tilde{\varepsilon}_p$

Second term = BOND ENERGY

$$E_{BOND} = \sum_{i\neq j,\alpha\beta} (\rho^{out})^{i\alpha j\beta}\, \tilde{H}_{j\beta i\alpha}$$

$$\equiv \sum_{i\alpha} \int^{E_f} n_{i\alpha}(E)\,(E - \tilde{H}_{i\alpha i\alpha})\, dE$$

The pair potential

$$\Delta E_{es} = \sum_{i\neq j} \mathrm{Tr}\, \rho_i \left(\tfrac{1}{2} v_{Hj} + v_j \right) + E_{ii}$$

= pairwise

$$\Delta E_c = \frac{1}{2} \sum_{i\neq j} \iint \rho_i(\underline{r}) \frac{h_c(\{\rho(r)\}, r, r')}{|\underline{r} - \underline{r}'|} \rho_j(\underline{r}')$$

(Lindholm and Lundqvist suggest that $h_c \sim$ constant)

So $\Delta E_c \simeq$ pairwise.

From exchange energy:

$$E_x = -\frac{1}{4} \sum_{i\alpha} \sum_{j\beta} \sum_{l\mu} \sum_{m\nu} \rho^{i\alpha j\beta} \rho^{l\mu m\nu} (i\alpha m\nu | l\mu j\beta)$$

where

$$(i\alpha m\nu | l\mu j\beta) = \iint d\underline{r}\, d\underline{r}'\, \phi^*_{i\alpha}(\underline{r})\, \phi_{m\nu}(\underline{r})\, \phi^*_{l\mu}(\underline{r}')\, \phi_{j\beta}(\underline{r}') \cdot 1/|\underline{r} - \underline{r}'|$$

$$\Delta E_x = -\frac{1}{4} \sum_{i\neq j,} \sum_{\alpha\beta} (\rho^{f})^{i\alpha i\alpha} (\rho^{f})^{j\beta j\beta} (i\alpha j\beta | j\beta i\alpha)$$

= pairwise

Interatomic Forces

$$E_{COH} = \mathrm{Tr}\,(\rho^{out} - \rho^{s})\tilde{H} + E_{PAIR}$$

$$\frac{\partial E_{COH}}{\partial x_k} = \mathrm{Tr}\,(\rho^{out} - \rho^{s})\frac{\partial \tilde{H}}{\partial x_k} + \frac{\partial E_{PAIR}}{\partial x_k}$$

$$+ \mathrm{Tr}\left(\frac{\partial \rho^{out}}{\partial x_k} - \frac{\partial \rho^{s}}{\partial x_k}\right)\tilde{H}$$

$$\swarrow \qquad\qquad \downarrow$$

$$\underset{\overset{\shortparallel}{0}}{\sum_n \frac{\partial a_n}{\partial x_k}\tilde{\varepsilon}_n} \qquad\qquad \underset{\overset{\shortparallel}{0}}{\sum_{i\alpha} \frac{\partial (\rho^{s})^{i\alpha i\alpha}}{\partial x_k}\tilde{H}_{i\alpha i\alpha}}$$

So
$$\frac{\partial E_{coh}}{\partial x_k} = \sum_{i\alpha}\sum_{j\beta}(\rho^{out})^{i\alpha}{}_{j\beta}\frac{\partial \tilde{H}^{j\beta}{}_{i\alpha}}{\partial x_k} - \sum_{i\alpha}(\rho^{s})^{i\alpha i\alpha}\frac{\partial \tilde{H}_{i\alpha i\alpha}}{\partial x_k} + \frac{\partial}{\partial x_k}E_{PAIR}$$

[illegible]

i) $S = 1$ (diagonal overlap matrix)

ii) 2 centre H

iii) Neutral atoms (perfect screening)

iv) $\hat{H}_{i\alpha i\beta} = 0$ if $\alpha \neq \beta$

$$\frac{\partial E_{coh}}{\partial x_k} = 2\sum_{j\neq k}\sum_{\alpha\beta}(\rho^{out})^{k\alpha j\beta}\frac{\partial \tilde{H}_{j\beta k\alpha}}{\partial x_k}$$

$$(\rho^{out})^{k\alpha j\beta} = -\frac{2}{\pi}\int^{E_F}\mathrm{Im}\,\tilde{G}^{k\alpha j\beta}(E+i0)\,dE$$

The following 2 pages are a briefer 'derivation' of the above TBB model from the TB model.

The TBB model

TIGHT BINDING BOND

Band picture:

Pairwise

$$U = \int^{\varepsilon_F} \varepsilon\, n(\varepsilon)\, d\varepsilon \;+\; U_{rep}$$

U_{rep}

$$= -\int d\underset{\sim}{r}\; n(\underset{\sim}{r})\left(\tfrac{1}{2}\phi(r) + \mu_{xc}(\underset{\sim}{r})\right) + E_{xc}[n(\underset{\sim}{r})] + E_{ii}$$

Kohn-Sham 1965
Harris 1985, PRB 31, 1770
(Justifies pairwise description of U_{rep})

$$U_{band} = \int^{\varepsilon_F} \varepsilon\, n(\varepsilon)\, d\varepsilon$$

$$\equiv -\frac{1}{\pi}\int^{\varepsilon_F} \varepsilon\, \mathrm{Im}\,\mathrm{Tr}\, G$$

Definition of G:

$$(\varepsilon - H)G = 1$$

U_{band}

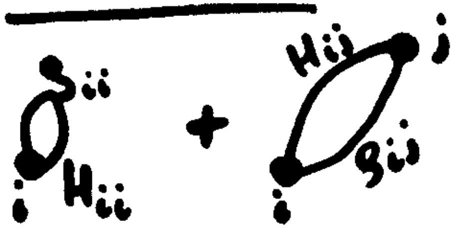
$$= -\frac{1}{\pi}\int^{\varepsilon_F} \varepsilon\, \mathrm{Im}\,\mathrm{Tr}\, G\, d\varepsilon$$

$$= -\frac{1}{\pi}\int^{\varepsilon_F} \mathrm{Im}\,\mathrm{Tr}\, HG\, d\varepsilon$$

$$= -\frac{1}{\pi}\int^{\varepsilon_F} \sum_{ij} \mathrm{Im}\, G_{ij} H_{ji}\, d\varepsilon$$

$$= \underline{\sum_{ij} \rho_{ji} H_{ij}}$$

=



'charge' or 'potential'

$$U_{coh} = \sum_i \sum_{j \neq i} \rho_{ji} H_{ij} \;+\; U_{rep}$$

Forces:

$$\delta U = \sum_i \sum_{j \neq i} \rho_{ji}\, \delta H_{ij} \;+\; \delta U_{rep}$$

Moments of local DOS

$$\mu_N = \int_{-\infty}^{\infty} E^N n_i(E)\, dE$$

$$= \int E^N \sum_k \delta(E-\varepsilon_k) \langle i|k\rangle\langle k|i\rangle$$

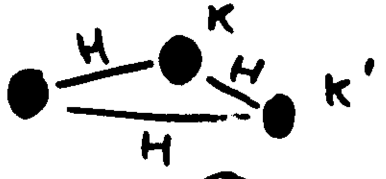
$$= \sum_k \langle i|k\rangle E^N \langle k|i\rangle$$

$$= \sum_k \langle i|k\rangle\langle k|H^N|k\rangle\langle k|i\rangle$$

$$= \sum_{k,k'} \langle i|k\rangle\langle k|H^N|k'\rangle\langle k'|i\rangle$$

$$= \langle i|H^N|i\rangle$$

$$= \sum_{k,k',k''\dots} \langle i|H|k\rangle\langle k|H|k'\rangle\langle k'|H|k''\rangle \cdots |H|i\rangle$$



CANONICAL d-BAND PARAMETERS

$$H_{11} = H_{44} = dd\delta(R) = -2\big($$

$$H_{22} = H_{33} = dd\pi(R) = $$

$$H_{55} = dd\sigma(R) = -$$

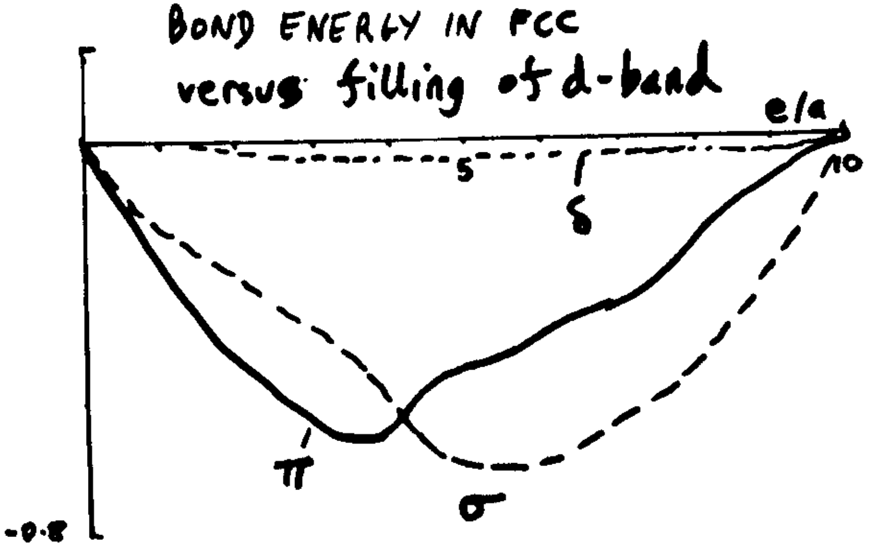
Energy of bond

$$U^{ij}_{bond} = dd\sigma \times \rho_{55} + dd\pi \times (\rho_{22} + \text{[illegible]}) + dd\delta \times (\rho_{11} + \text{[illegible]})$$

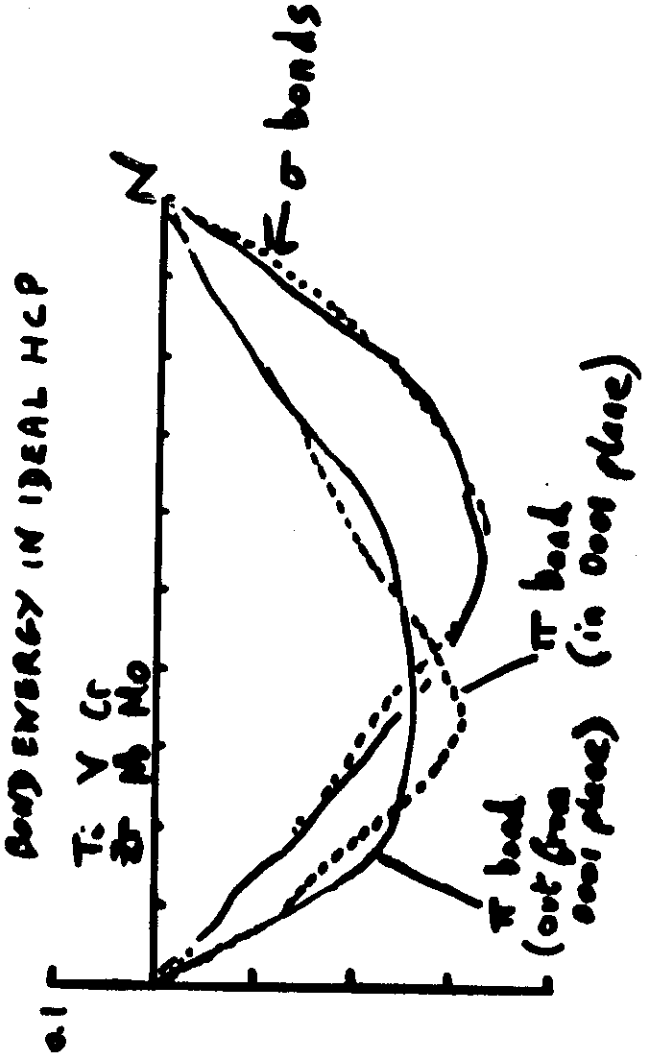
Radial force

$$F^{ij}_{bond} = \frac{-5}{R} \times U^{ij}_{bond}$$

But generally also transverse $\underline{F}$.



(39)



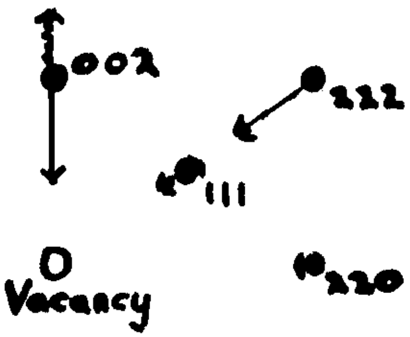
(40)

$\frac{c}{a} \rightarrow < 1.6$ in Zr, Ti

Vacancy in bcc transition metals

Ohta, Finnis, Pettifor & Sutton
to be published

Results (μ_s)
e.g. Mo



····› = Force in perfect lattice
⟶ = Force due to vacancy

Due to vacancy:
Bond strengthening enhances defect forces

Ohta, Finnis, Pettifor and Sutton, to be published

····› Forces on perfect lattice due to atom at origin; only 1st + 2nd neighbour occur

→ Defect forces. In a pair-potential model these are equal and opposite to ···›.

TBB MODEL: DISCUSSION

ADVANTAGES (with recursion method)

1. Physical description of charge redistribution between bonds
2. Controlled introduction of local environment (μ_n)
3. Simplest physical model of structural energy differences
4. CPU time $\propto N$ (c.f. N^3 for matrix inversion) so large problems should be suitable

DISADVANTAGES

1. Limited basis. Need to investigate transferability of H_{ij}. How good are the simplest assumptions, e.g. d orbitals, orthogonality?
2. Still costly ($10^2 - 10^3 \times$ EAM and V_{ij})
3. $F \simeq \nabla E$

Theoretical Modelling of defects and embrittlement

MIKE FINNIS (HARWELL)

LECTURE III

AIM : TO EXPLAIN A SIMPLE MODEL OF BOND ENERGY

→ THE EMBEDDED ATOM MODEL (N-BODY POTENTIAL)

INTERATOMIC FORCES

1. PAIR POTENTIALS :

$$U_i = \frac{1}{2} \sum_j V_{ij} \quad \left(+ F(\text{volume}) \right)$$

2. BOND ANGLE FORCES

$$U_i = \sum_{jk} f(\underline{R}_{ij} \cdot \underline{R}_{ik})$$

3. EMBEDDED ATOM MODELS

$$U_i = f(\rho_i) + \frac{1}{2} \sum_j V_{ij}$$

4. TIGHT-BINDING MODELS

$$U_i = \sum_n \varepsilon_n w_{ni} + \frac{1}{2} \sum_j V_{ij} \equiv$$

TBB

$$U_i = \sum_{j \neq i} \rho_{ij} H_{ij} + \frac{1}{2} \sum_j V_{ij}$$

5. DENSITY FUNCTIONAL

$$\sum_i U_i = \int^{E_F} E\, n(E)\, dE - \int n(r) \left(\frac{1}{2} \phi(r) + \mu_{xc}(r) \right) + E_{xc}[n(r)] + E_{ii}$$

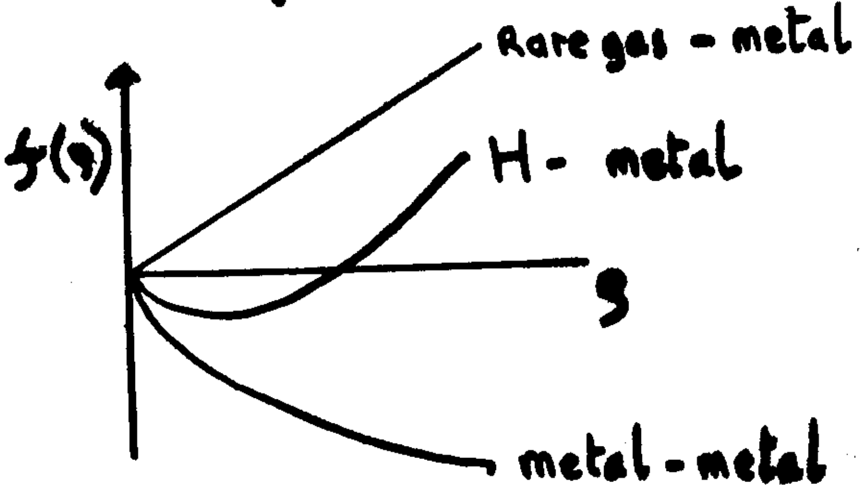
Empirical N-body potentials - EAM

Stott & Zaremba
Norskov
Daw & Baskes

Finnis & Sinclair
Ackland et al
Bacon et al
Ercolessi et al

$$E_i = f(\rho_i) + \tfrac{1}{2}\sum_j V(R_{ij})$$

$$\rho_i = \sum_j \phi(R_{ij})$$



'EFFECTIVE' PAIR INTERACTION

$$f(\rho_i) = f(\rho_i^\circ) + f' \cdot \delta\rho_i + \tfrac{1}{2} f'' \cdot (\delta\rho_i)^2 +$$

$$\delta\rho_i = \sum_j \frac{\partial\phi}{\partial R_{ij}}(R_{ij}^\circ)\cdot(\delta R_i - \delta R_j)$$
$$+ \tfrac{1}{2}\sum_j \frac{\partial^2\phi}{\partial R_{ij}^2}(\delta R_i - \delta R_j$$

So: $f(\rho_i) = f(\rho_i^\circ) + f' \cdot \sum_j \delta\phi(R_{ij})$
$$+ \tfrac{1}{2} f'' \Big(\sum_j \delta\phi(R_{ij})\Big)^2 + \cdot$$

$$\underline{V_{eff}(R) = V(R) + 2 f'(\rho_0)\phi(R)}$$

bcc: $\Omega C_{44} = \frac{8}{9} V'_{eff}(R_1) + \frac{4}{9} V''_{eff}(R_1) R_1^2$
$$+ V'_{eff}(R_2) R$$

$$\Omega(C_{11} - C_{12}) = \frac{4}{3} V'_{eff}(R_1) R_1 + V''_{eff}(R_2)$$

$$\Omega(C_{12} - C_{44}) = \underline{\underline{f''(\rho_0)}}\Big(\frac{8}{3}\phi'(R_1)R_1 + 2\phi'(R_2)R_2\Big)$$

$H\psi = E\psi$

$U_{bond} = \sum_i \int^{E_F} \varepsilon\, n_i(\varepsilon)\, d\varepsilon$ ← energy

↖ density of states on atom i

Moments

$$\mu_n = \int_{-\infty}^{\infty} \varepsilon^n n_i(\varepsilon)\, d\varepsilon$$

The densities of states n_i are characterised by calculating their lowest n moments.

Simplest is μ_2 approximation.

$\mu_2 = \sum_j H_{ij}^2 \propto$ no. of neighbours

$$\Rightarrow n(E) = \frac{10}{\sqrt{2\pi\mu_2}} \exp\left(\frac{-E^2}{2\mu_2}\right)$$

$$\Rightarrow \int^{E_F} E\, n(E) = -10\sqrt{\frac{\mu_2}{2\pi}} \exp\left(-\frac{E_F^2}{2\mu_2}\right)$$

$$\propto \sqrt{z}$$

Finnis and Sinclair : bcc transition metals

$$E_i = -\sqrt{\rho_i} + \tfrac{1}{2}\sum_j V(R_{ij})$$

$$\rho_i = \sum_j \phi(R_{ij})$$

$\phi(R_{ij}) = A^2 (R_{ij} - d)^2 \qquad R_{ij} < d$

$V(R_{ij}) = (R_{ij} - c)^2 (c_0 + c_1 r + c_2 r^2) \qquad R_{ij} < c$

cutoffs c and d between 2nd and 3rd neighbours.

PARAMETERS

c_0, c_1, c_2, A are determined by fitting to E_{coh}, p, B, $c_{12}-c_{44}$.

Various cutoffs then to fit C_{44} (non-linear) and $\sim E_v^f$.

c and d.

Vacancy formation energies and volumes

Matthai and Bacon 1985
Harder and Bacon 1986

$$V_{1v}^{f} = -\frac{\Omega}{B}\frac{dE_{1v}^{f}}{d\Omega}$$ (Finnis & Sachdev 1976)

	E_{1v}^{f} (eV)		V_{1v}^{f} (Ω)
	Calc.	Expt.	Calc.
V	1.83	2.1±0.2	0.74
Nb	2.48	2.6±0.3	0.96
Ta	2.89	2.9±0.6	0.83
Cr	1.91	-	0.84
Mo	2.54	3.0±0.2	0.93
W	3.62	4.0±0.3	0.68
Fe	1.81	1.6±0.2	0.85

Vacancy migration energies

Harder and Bacon 1986 Phil Mag A 54 65

	E_{1v}^{m} (eV)	
	calc.	expt.
V	0.76	1.3±0.3
Nb	0.91	1.4±0.3
Ta	1.22	1.4±0.6
Cr	0.71	-
Mo	1.32	1.5±0.2
W	1.49	1.5±0.3
Fe	0.91	1.3±0.3

Divacancy binding energies

	1st neighbour	2nd neighbour
V	0.20	0.18
Nb	0.28	0.23
Ta	0.28	0.28
Cr	0.22	0.24
Mo	0.30	0.26
W	0.43	0.40
Fe	0.16	0.20

Harder and Bacon 1985

Interstitial Formation Energies

Ackland + Thetford 1986

	<100>	<110>	<111>	Crowdion
V	4.94	4.16	4.61	4.60
Nb	4.82	4.49	4.80	4.86
Ta	8.07	6.83	7.16	7.16
Mo	7.21	7.04 (6.98)	7.22	7.19
W	9.82	9.64	8.92	8.88

Without added core:

Ta	4.10	3.97	3.93	3.81
Mo	7.20	7.05	7.23	7.21

Miller (1981) pair potential

Mo	6.91	4.81	5.85	5.73

} Harder + Bacon 1986

All calculations used a 7a×7a×7a block. Estimated maximum error: +0.04eV.

NB.: Bent interstitial ≈<530> in Mo.

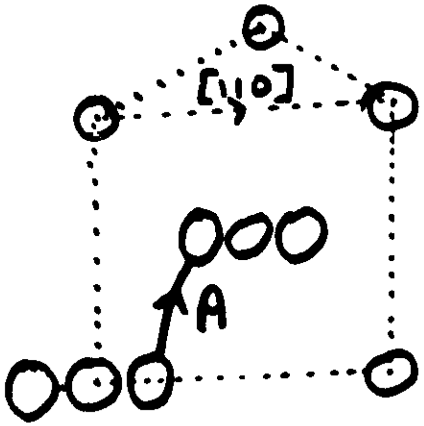
: Crowdion in W.

Interstitial Migration

Mo (Harder + Bacon 1986)

3 Paths for ⟨110⟩ dumbbell migration.

	E_i^m N-body	2-body	Expt.
A : 2-d	0.17	1.03	~0.05 eV (recovery)
B : 3-d	0.16	0.63	
C : double 2-d	0.24	0.92	



Interstitial migration

W (Ackland + Thetford)

Migration of **crowdion**

Barrier to rotation ⟨111⟩ to ⟨11$\bar{1}$⟩ via ⟨110⟩ = 0.72 eV

Barrier to 1-d migration via ⟨111⟩ dumbbell = 0.03 eV

CONCLUSIONS

1. Atomistic simulation with empirical N-body (embedded atom) potentials is more realistic than with pairwise potentials and not significantly more expensive BUT

2. For structures and strain fields more quantum mechanical models are required - 1000 x more computation. For 0.1 eV accuracy, we need fully self-consistent calculations (LDF).

3. Better ask for mechanisms and plausible structures rather than precise numbers.

Theoretical Modelling of Defects and Embrittlement

M. W. Finnis

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LECTURE II

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The TBB model and the vacancy problem. Preprints on request.
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LECTURE III

1. The article by Heine in Lecture II ref 3 gives an account of the $\sqrt{Z}$ dependence of site energy in the μ_2 approximation.

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   – Erratum, Phil. Mag. A 53 (1986) 161.

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Refs. 3 - 7 are versions of the embedded atom method with applications.

SUPERCOMPUTERS

Notes on an ad hoc lecture

by M. W. Finnis

SUPERCOMPUTERS

$10^2 - 10^3$ MFLOPS

CRAY-2 — 1,200 MFLOPS
256 Mwords (4 PROCESSORS)

Machines:

USA: CRAY, ETA
(IBM 3090 & CRAY-1)

JAPAN: NEC (Osaka)
FUJITSU (Nagoya)
HITACHI (Tokyo)

Fastest single processor = NEC

CRAY-2 useful for its very large memory, 256MW

Farid Abraham, IBM:
500 processors

To achieve, more than another ×10 in speed will probably require parallel processing, which is developing rapidly.

HEIRARCHY OF MODELS

1. ENGINEERING MODELS (e.g. hot pressing finite elements - 3D calculations need more computer power

$$\dot{\varepsilon} = f(\sigma, T)$$

↓↑

2. DERIVATION OF CONSTITUTIVE LAWS

- MICROSTRUCTURE MODELS

$$\dot{\rho} = f(\rho, T, d, \sigma, c)$$

↓↑

3. ATOMISTIC MODELS (e.g. molecular dynamics monte carlo

E^f, E^m, σ_u,

↓↑ Cascade effects, diffusion mechanisms

4. ELECTRONIC MODELS (e.g. LDF model)

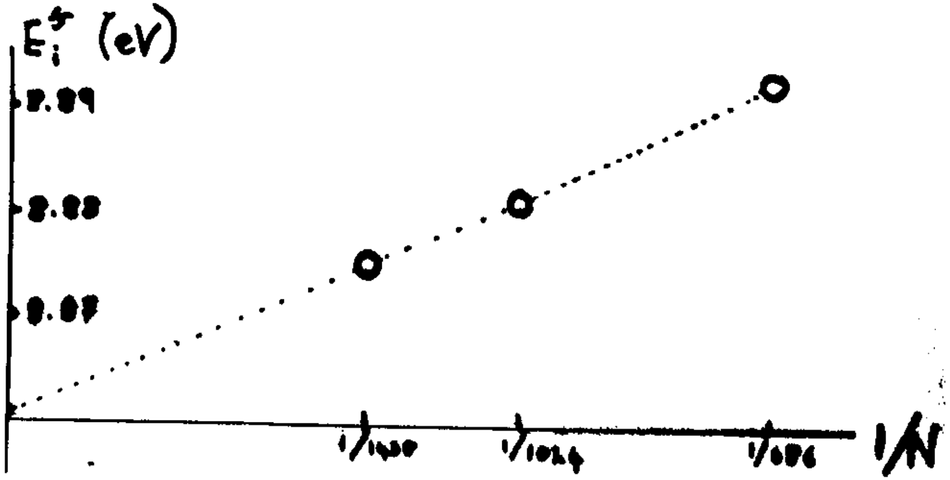
$$E = F[\rho]$$

Solve $H\psi = \varepsilon_n \psi$

PROGRESS LIMITED BY: 1) MODEL
(BOTTLENECKS) 2) ALGORITHMS
3) COMPUTERS

E_i^f versus Number of relaxed atoms

(W potential, F5 + core
Ackland + Thetford, TP1194, 1986)



1024 atoms = 8a × 8a × 8a

This slide, which I had no time to show, indicates the size of block needed in a molecular dynamics calculation to get a converged interstitial formation energy. The block has flexible periodic boundary conditions.

Bob Averbach & Roy Benedek (Argonne)

CASCADE SIMULATION

200,000 atoms (36a × 36a × 36a)

Cu, Gibson-II

2000 timesteps ≡ 10^{-11} sec

5 hours on 1 processor of CRAY-2
(cost at Harwell prices £1.5k)
40 Mwords.

Results

A few interstitials, [redacted]
f.c.s.

Vacancies lost as spike solidifies epitaxially.

These are my notes from a talk given by Averbach in Feb 1987.