Ab initio modeling of mechanical and elastic properties of solids

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Motivation

- Mechanical properties crucial in range of engineering applications
- Processes underlying mechanical behaviour of materials poorly understood
- A need of simple estimates of critical fracture properties
- Intrinsic behaviour of material $\longrightarrow$ theoretical atomic-level treatment

Outline of talk

- PART 1: Mechanical and elastic properties
  - Correlation between elasticity and fracture[1]
- PART 2: Ductility improvement
  - Microalloying of NiAl[2]

[1] P. Lazar, R. Podloucky, W. Wolf, *Applied Physics Letters*, in print
[2] P. Lazar, R. Podloucky, *Phys. Rev B*, submitted

Elasticity and fracture

- ELASTICITY:
  - response of material to small strains
  - related physical quantities are elastic constants
    $\longrightarrow$ easy to measure or calculate

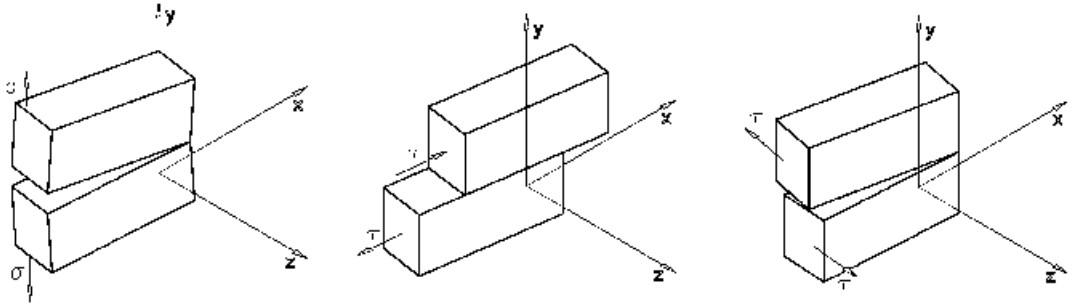
- FRACTURE: describes nucleation and propagation of cracks.
  - the processes which contribute to crack energy span over several length scales
  - a description within one general theory impossible

Correlating fracture and elasticity

ELASTICITY . . . non-local response to small strain
$\longrightarrow$ energy distributed over the **macroscopic solid**

CRACK / CLEAVAGE . . . energy localised near to crack
$\longrightarrow$ **atomistic level**

HOW TO CORRELATE ???

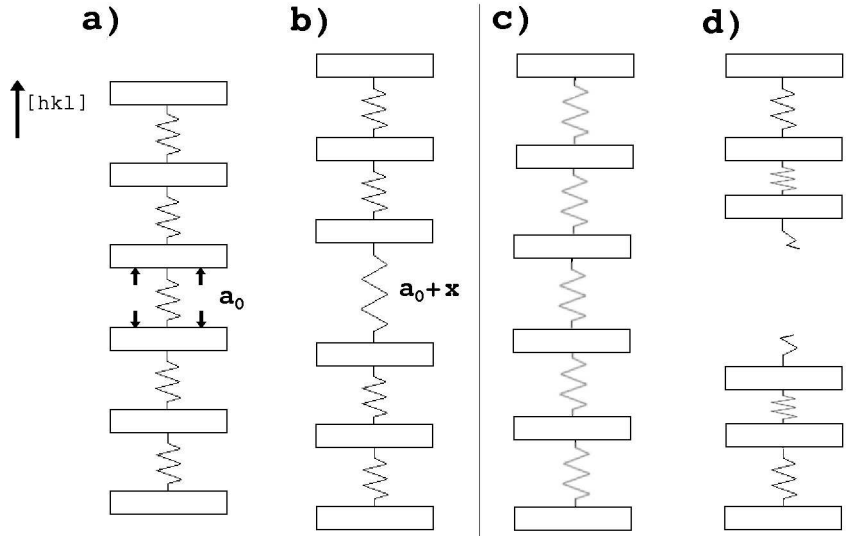


Crack at the atomic level

- direct *ab initio* modelling of real cracks impossible

- at atomic level crack propagates by consequent breaking of atomic bonds; cleavage decohesion of atoms in crystal

- cleavage decohesion can be modeled via DFT method:



Ideal BRITTLE cleavage: *a-b*

RELAXED cleavage *a-c*,*a-d*

Ideal Brittle Cleavage

NO atomic RELAXATION when material is cleaved:
very FAST crack formation
UPPER limit of strength for ideal brittle materials

\+ analytic model for crack formation

\+ analytic model for
CONNECTION ELASTICITY - CRACK FORMATION

\+ model parameters determined by fit to DFT calculations

Calculation of elastic constants

- ENERGY-STRAIN approach: DFT energy for selected lattice distortions
- STRESS-STRAIN approach: from stress tensor

Rigid modulus C depends on direction $[hkl]$:

Cubic lattice

$$C = c_{11} - 2\,(c_{11} - c_{12} - 2c_{44})(h^2k^2 + h^2l^2 + k^2l^2)$$

Tetragonal lattice

$$C = c_{11}(h^4 + k^4) + c_{33}l^4 + h^2k^2(2c_{12} + c_{66}) + l^2(1 - l^2)(2c_{13} + c_{44})$$

Analytic model for brittle cleavage

For rigid block separation the energy is a function of x (UBER): [3]

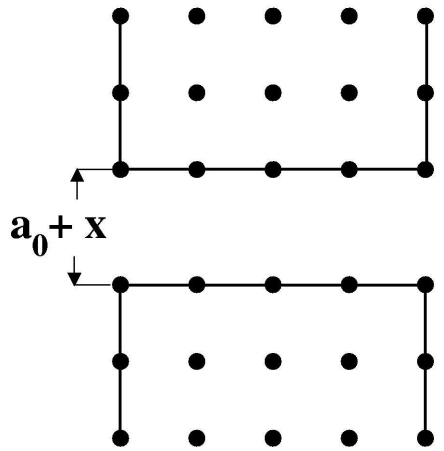
$$E_{DFT}(x) = G_b \left[\left(1 + \frac{x}{l_b} \right) \exp\left(-\frac{x}{l_b} \right) - 1 \right]$$

G_b ..... cleavage energy
l_b ..... critical length

Stress $\sigma(x) = \frac{dE}{dx}$

Critical stress $\sigma_b = \max \sigma(x)$

$$\sigma_b = \frac{1}{e} \frac{G_b}{l_b}$$



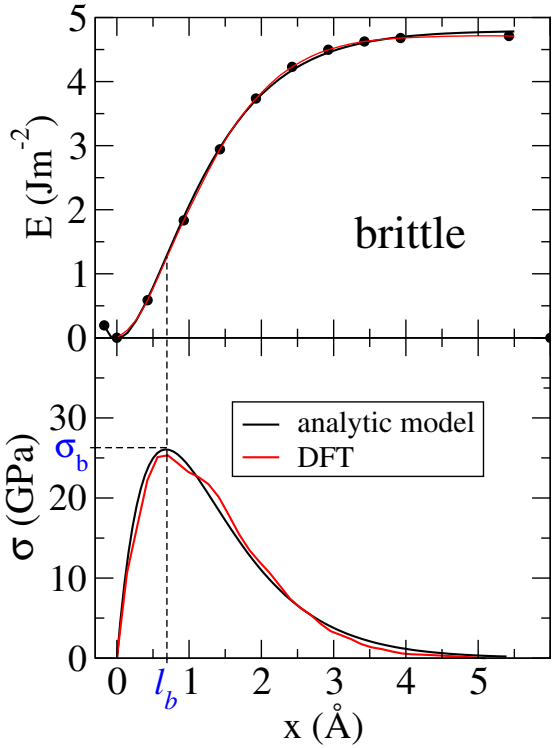
[3] Rose et al. *Phys. Rev.* B **28**, 1835 (1983)

The UBER

- universal curve, broad classes of materials
- presumably valid for metals, proved for covalent and ionic materials

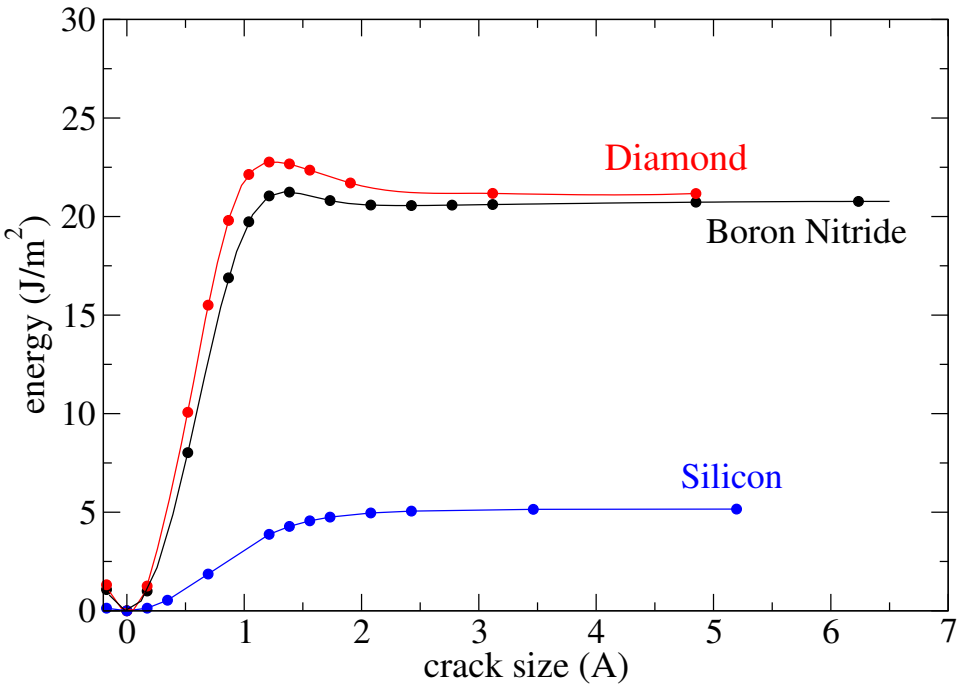
NiAl (001):

UBER: —; DFT: •



(111) diamond structure - narrow planes

(DFT results)



Historical: estimates of theoretical cleavage stress

- Orowan-Gilman criterion:[4][5][6] model with sinusoidal restraining force

$$\sigma_{max} = \sqrt{\frac{E\gamma_s}{a_0}}$$

E...rigid or Young's modulus
γ_s...surface energy
a_0...distance between layers

- Orowan-Gilman criterion often overestimates theoretical cleavage stress

- fit to ab-initio calculations[7]: model not reliable

[4] M. Polanyi, Z. Phys **7** p. 323 (1921)
[5] E. Orowan, Rep. Prog. Phys. **12** p. 185 (1949)
[6] J. J. Gilman: Proc. symp. on the physics and chemistry of ceramics, p. 240 (1963)
[7] M. H. Yoo and C. L. Fu, Mat. Sci. Eng, **A153**:470 (1992)

Connecting elasticity and brittle cleavage - key relations

Taylor expansion for UBER $E_b(x)$ for VERY SMALL crack size x:

$$E_b(x \to 0) \approx \frac{1}{2} G_b \frac{x^2}{l_b^2}$$

$\rightarrow$ equal to elastic energy with (unknown) fitting parameter[8] $\mathbf{L_b}$:

$$\frac{1}{2} G_b \frac{x^2}{l_b^2} = \frac{1}{2} C x^2 \frac{A}{\mathbf{L_b}}$$

A . . . area of cleavage plane (known), C . . . elastic modulus (known)[9]

$\mathbf{L_b}$ . . . **new materials parameter of dimension** $[l]$

"LOCALISATION LENGTH" for brittle cleavage

[8] for correct physical dimension $[E]$

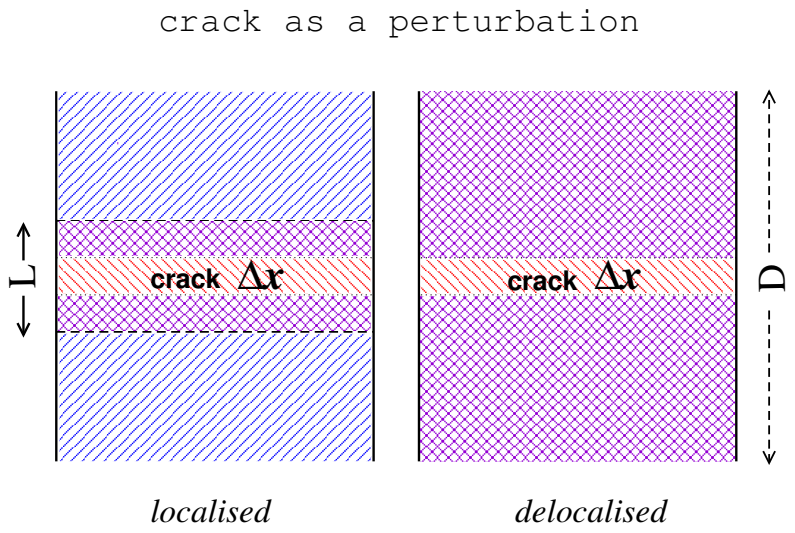
[9] $G_b, l_b, C, \sigma_b, L_b$ depend on material and cleavage plane (hkl)

Calculated values - simple metals

- Fe, Al, W: important structural materials
- brittle at low temperatures

	$[hkl]$	C	G_b/A	l_b	σ_b/A	a_0	L_b
Al (fcc)	100	110	1.8	0.57	12	2.03	2.01
	110	113	2.1	0.64	12	1.43	2.24
	111	114	1.6	0.54	11	2.34	2.08
Fe (bcc)	100	302	5.3	0.58	34	1.41	1.93
	110	338	5.0	0.54	35	1.99	1.97
	111	350	5.8	0.61	35	0.82	2.25
W (bcc)	100	540	8.4	0.66	47	1.59	2.80
	110	516	6.5	0.55	44	2.24	2.40
	111	508	7.3	0.64	42	0.92	2.83

Localisation length



D . . . macroscopic dimension of material in direction $[hkl]$

L . . . intrinsic LOCALISATION LENGTH

A . . . surface area of crack kept fixed $\longrightarrow$ rigid modulus C

V = AD . . . macroscopic volume

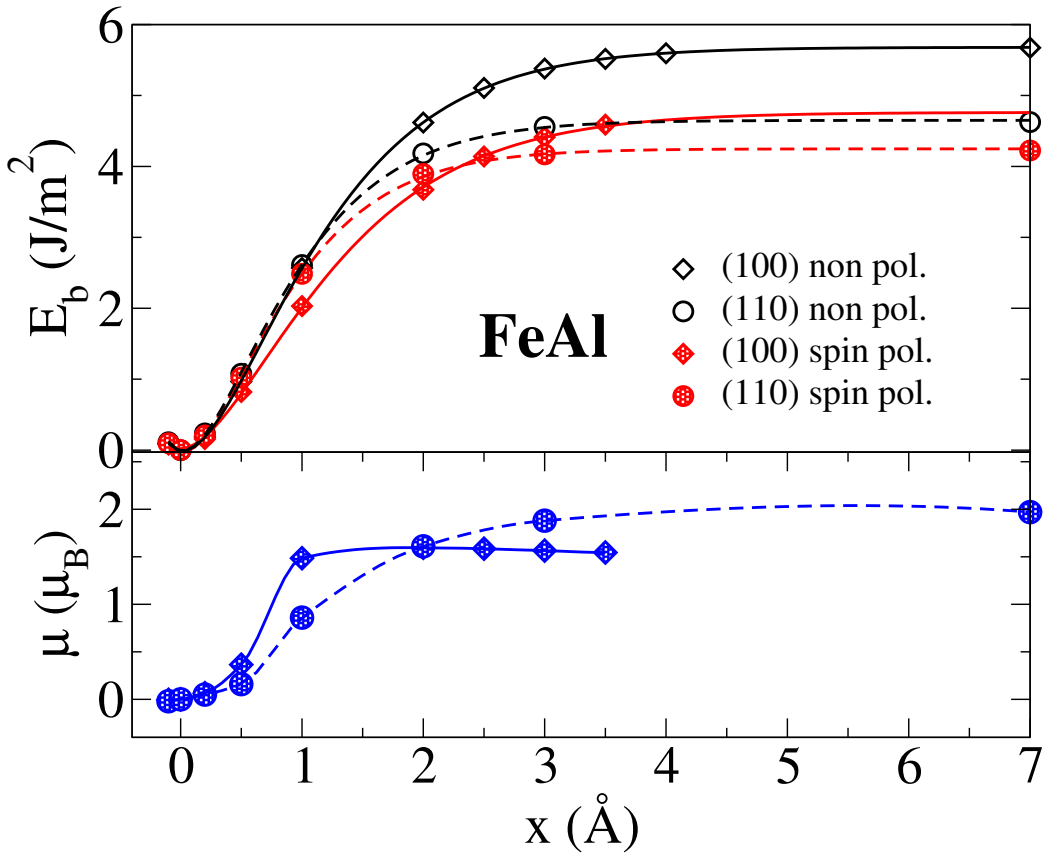
V = AL . . . localisation volume

Calculated values - intermetallic compounds

- perspective high-strength high-temperature materials
- turn brittle at ambient temperatures

		$[hkl]$	C	G_b/A	l_b	σ_b/A	a_0	L_b
NiAl	B2	100	203	4.8	0.69	**26**	1.45	2.01
		110	284	3.2	0.54	**22**	2.05	2.59
		111	311	4.1	0.58	26	0.84	2.68
		211	284	4.0	0.60	24	1.18	2.56
Ni_3Al	$L1_2$	100	225	4.3	0.66	24	1.78	2.28
		111	331	3.7	0.52	26	2.06	2.42
FeAl	B2	100	278	4.8	0.71	**25**	1.43	2.92
		110	354	4.3	0.50	**32**	2.03	2.06
		111	380	5.1	0.61	31	0.83	2.77
TiAl	$L1_0$	001	185	4.4	0.70	23	2.03	2.06
		100	190	3.3	0.58	21	2.00	1.98
		110	240	4.1	0.69	22	1.41	2.82
		111	268	3.5	0.58	22	2.32	2.57

FeAl and magnetism



- magnetic moment induced during cleavage
- change of cleavage habit plane

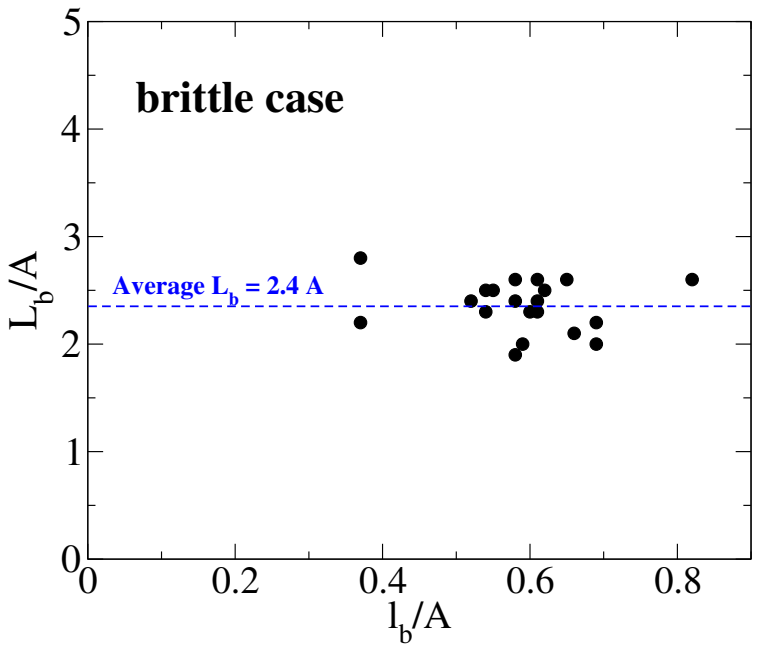
Calculated values - covalent and ionic compounds

- transition metal carbides: hard but brittle materials, strong covalent bonding
- MgO: important ceramic material

		$[hkl]$	C	G_b/A	l	σ_b/A	a_0	L_b
VC	B1	100	**647**	3.2	0.37	32	2.08	2.77
		110	**585**	7.0	0.55	46	1.47	2.53
		111	**564**	9.9	0.58	63	1.20	2.06
TiC	B1	100	515	3.5	0.42	31	2.17	2.57
		110	489	7.7	0.56	51	1.53	1.97
		111	481	11.6	0.70	61	1.25	2.03
MgO	B1	100	299	1.8	0.37	18	2.11	2.27
		110	345	4.4	0.54	30	1.53	2.29
NaCl	B1	100	52	0.3	0.49	**2**	2.83	**4.16**
		110	45	0.7	0.66	**4**	2.00	2.84

New "Orowan" equation

LOCALISATION LENGTH L_b
vs. UBER length l_b



STRESS - ELASTIC MODULUS RELATION

$$\frac{\sigma_b}{A} = \frac{\mathbf{1}}{\mathbf{e}\sqrt{\mathbf{L_b}}}\sqrt{\frac{G_b}{A}C}$$

$$\frac{\sigma_b}{A} \approx \frac{\mathbf{1}}{\mathbf{4.18}}\sqrt{\frac{G_b}{A}C}$$

"Orowan - type"

$$\frac{\sigma_{max}}{A} = \frac{1}{\sqrt{2\,a_0}}\sqrt{\frac{G_s}{A}C}$$

Conclusions - brittle cleavage

+ Utilising the idea of localisation of elastic energy, the connection between elasticity and cleavage is established via introduction of a new materials quantity called localisation length L_b.

+ By combining *ab initio* results and analytic models the parameter L_b is determined. For brittle cleavage it is rather constant, $L_b \approx 2.4$ Å, for all (studied) materials and directions.

+ Model tested for different types of bonding (metallic, ionic, covalent).

Relaxed cleavage

FULL atomic RELAXATION when material is cleaved:
SLOW crack formation
HIGHEST limit of strength for ideal materials (rigid A)

+ analytic model for crack formation

+ analytic model for
  CONNECTION ELASTICITY - CRACK FORMATION

+ model parameters determined by fit to DFT calculations

Model of relaxed cleavage[10]

Relaxed cleavage energy $E_r(x)$ quadratic in crack size x: $\boxed{E_r(x) = G_r \frac{x^2}{l_r^2}}$

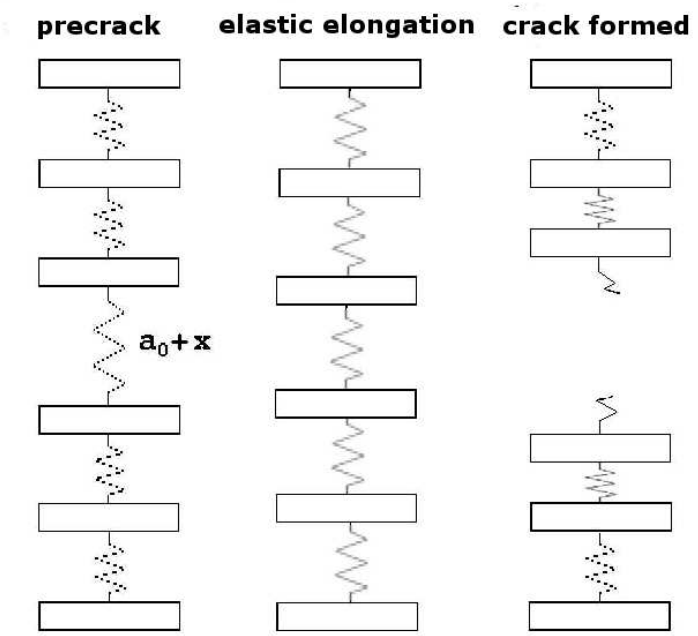
G_r . . . relaxed cleavage energy, l_r . . . critical length
FIT PARAMETERS G_r, l_r: [11] fit $E_r(x) \rightarrow E_{\mathbf{DFT}}(x)$

STRESS

$$\sigma(x) = \frac{dE_r}{dx} = 2x\,\frac{G_r}{l_r^2}$$

CRITICAL STRESS

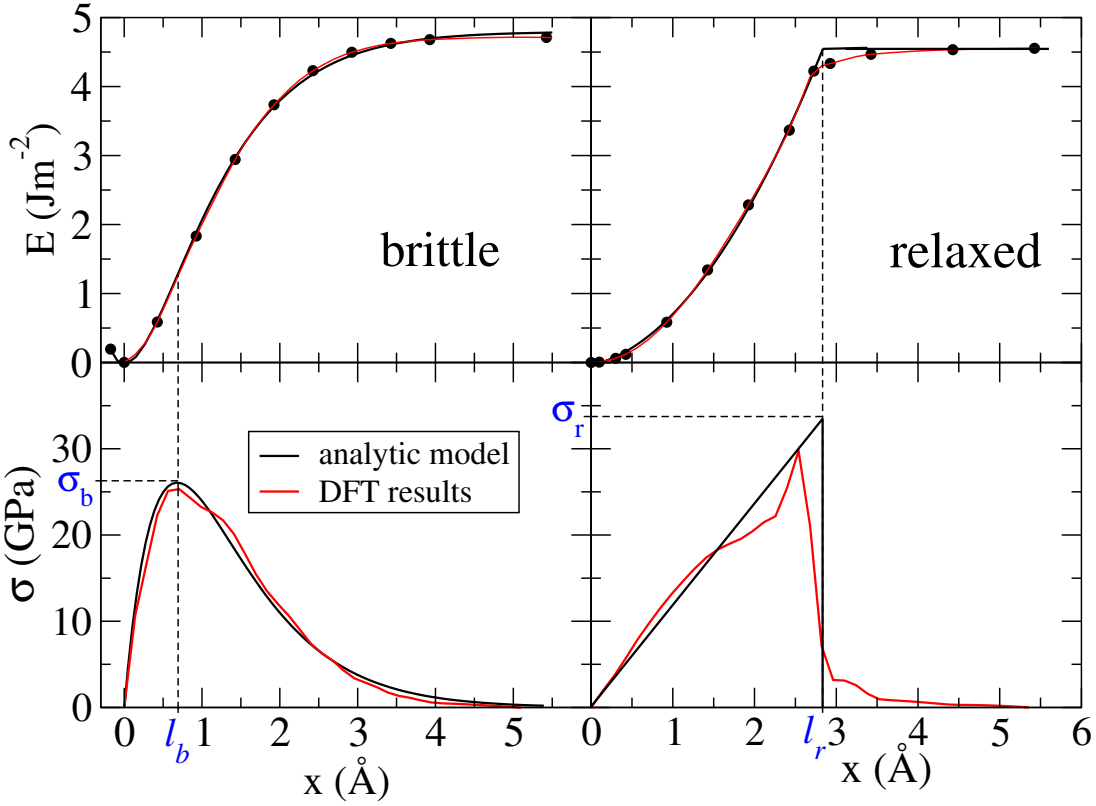
$$\boxed{\sigma_r = 2\frac{G_r}{l_r}}$$



[10] P. Lazar, R. Podloucky, W. Wolf, *Phys. Rev. B*, submitted
[11] $G_r, l_r, C, \sigma_r, L_r$ depend on material and cleavage plane (hkl)

DFT vs. analytical models

NiAl (001)
analytic models −; DFT •



The connection for relaxed cleavage

relaxed cleavage energy $E_r(x)$ quadratic in x
$\longrightarrow$ equal to elastic energy with (unknown) fitting parameter $\mathbf{L_r}$: [12]

$$E_r(x) = G_r \frac{x^2}{l_r^2} = \frac{1}{2} C x^2 \frac{A}{\mathbf{L_r}}$$

A . . . area of cleavage plane (known), C . . . elastic modulus (known),

$\mathbf{L_e}$ . . . **new materials parameter of dimension** $[l]$

"LOCALISATION LENGTH" for relaxed cleavage

critical stress relation ("Orowan type"): $$\frac{\sigma_r}{A} = 2\frac{G_r}{A\, l_r} = \sqrt{\frac{\mathbf{2}}{\mathbf{L_r}}}\sqrt{\frac{G_r}{A} C}$$

[12] for correct physical dimension $[E]$

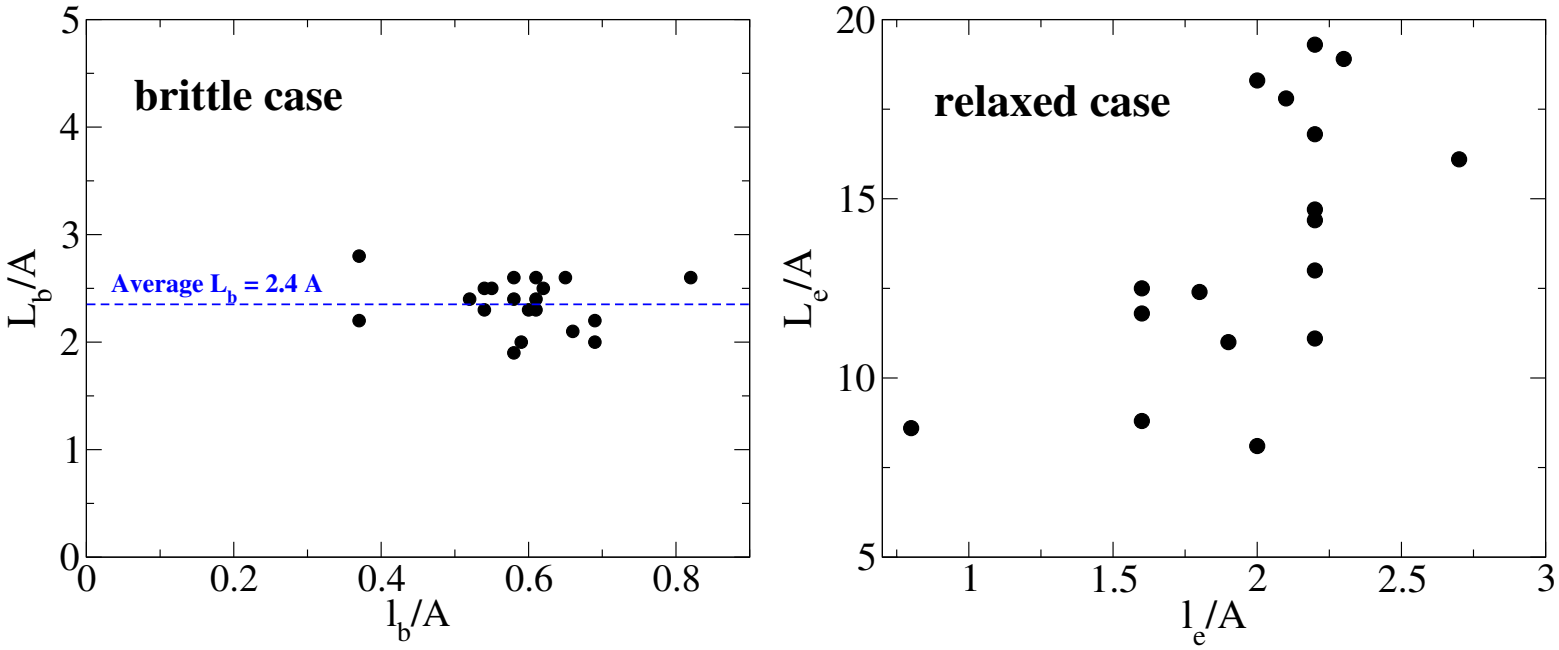
Comparation of brittle and relaxed results

BRITTLE | RELAXED

	(hkl)	C GPa	G_b/A J/m^2	σ_b/A GPa	G_r/A J/m^2	σ_r/A GPa
Al	(001)	110	1.8	12	1.8	19
	(011)	113	2.1	12	1.9	20
	(111)	114	1.7	11	1.7	15
W	(001)	540	8.4	47	7.8	78
	(011)	516	6.5	44	6.4	85
	(111)	508	7.9	46	6.6	82
NiAl	(001)	203	4.8	26	4.6	34
	(011)	284	3.2	22	3.1	32
	(111)	327	4.1	26	3.1	36
VC	(001)	647	3.2	32	2.4	60
	(011)	585	7.0	46	6.0	75
	(111)	564	9.9	63	8.4	105

Localisation lengths L vs. critical lengths l

BRITTLE | RELAXED



Conclusions - part I.

+ BRITTLE and RELAXED cleavage (crack mode I) described by analytic models: fit to *ab initio* results reasonable

+ formal connection between elasticity and cleavage established by a localisation length L: new materials parameter

+ L determined from *ab initio* calculations. Brittle cleavage $L_b \approx 2.4$ Å: for all (studied) materials and directions

+ models valid for all types of bonding (metallic, ionic, covalent)

+ Similar (but more complicated) connections between elasticity and cleavage for more complex crack modes can be established ???

+ **derivation of model potentials for crack tip simulations**

PART II.

Microalloying of NiAl

Microalloying of NiAl modelling

Intrinsic brittleness or ductility improved?
Atomic level effect of alloying additions
Change of cleavage and stacking fault energetics

+ model for brittle cleavage

+ model for dislocation emission - stacking fault energy

  COMPETITION BRITTLE - DUCTILE CRACK BEHAVIOR

+ model parameters determined by fit to DFT VASP calculations

NiAl properties

+ low density, high melting point, high strength at elevated temperatures
  $\longrightarrow$ INTERESTING MATERIAL FOR AEROSPACE INDUSTRY

+ wide range of stability in atomic composition

+ site occupancy probability of additions can be varied by chemical composition[13]

- BUT - poor ductility at room temperature

[13] Hao et al., *Mat. Sci. Eng.* **A365** (2004)

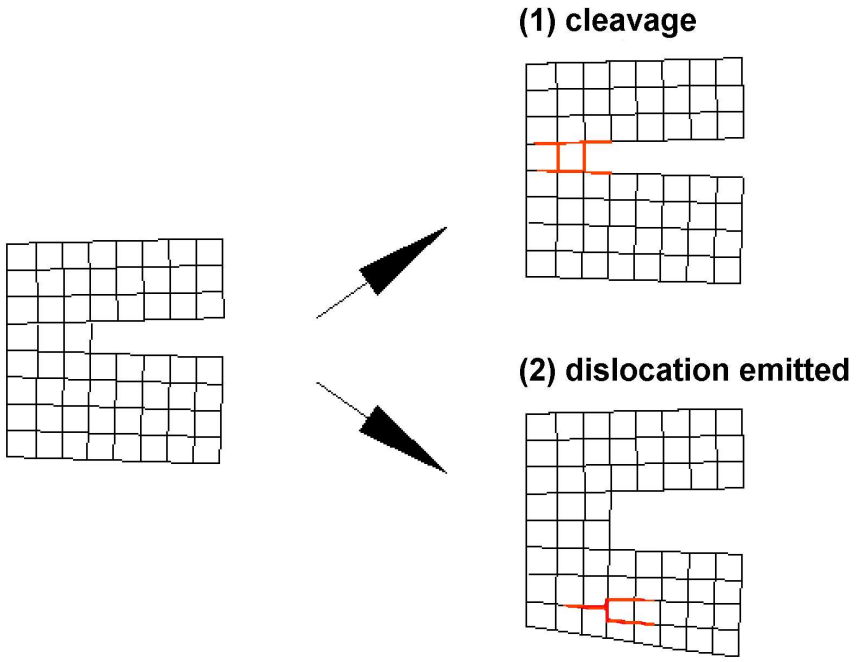
Competition between cleavage crack growth and dislocation emission

Stress intensity at the tip of the sharp crack $\rightarrow$
cleavage decohesion (brittle fracture) or **dislocation emission** (ductile fracture).

Prefered fracture mode -
$\rightarrow$*critical energy release rate* G

(1). CLEAVAGE DECOHESION
- brittle propagation of crack
- critical energy release rate for cleavage

$$G = G_b \qquad \gamma_s = G_b/2$$



(2). DISLOCATION EMISSION
- crack is blunted by one atomic plane
- material has DUCTILE behavior
- critical energy release rate G_d??

Estimation of G_d for dislocation emission

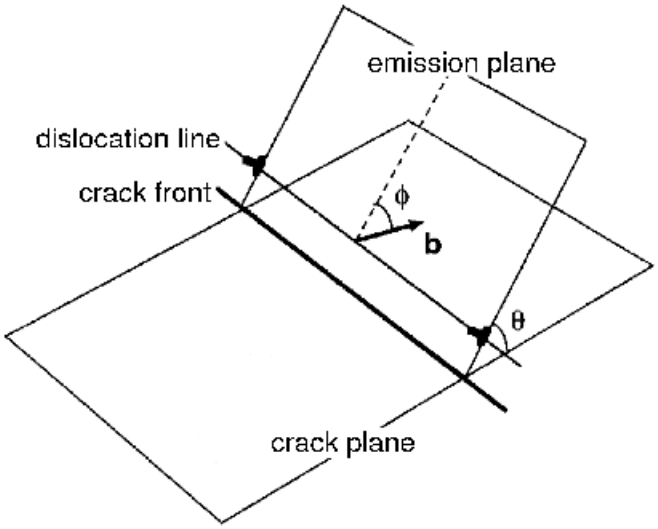
Rice's concept: a new material parameter - unstable stacking fault energy γ_{us}

For mode II configuration

$$G_d = \gamma_{us}$$

In mode I configuration

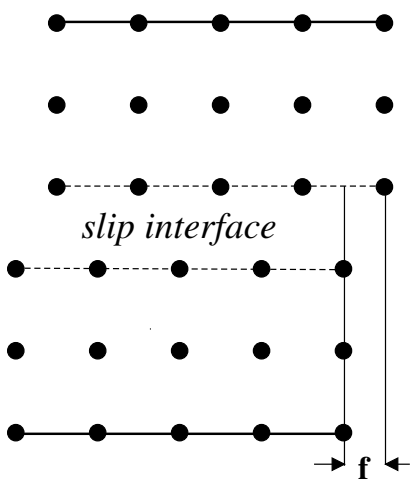
$$G_d = 8\frac{1 + (1-\nu)\tan^2(\phi)}{1 + \cos(\theta)\sin^2(\theta)}\gamma_{us}$$



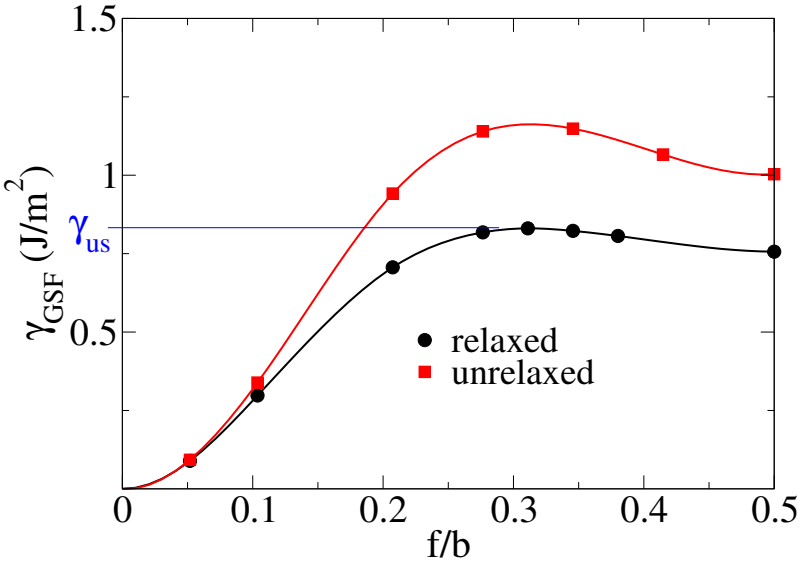
γ_{us} may be obtained *ab initio*!

Calculation of γ_{us}

- slip displacement f applied
- atomic planes relaxed
- maximum of E along f :
  $\gamma_{us} = \max \gamma_{GSF}(f)$



Example: NiAl $\langle 11\bar{1}\rangle(011)$ slip



f/b: slip relative to Burger's vector b

MODEL OF THE GENERALISED STACKING FAULT ENERGY $\gamma_{GSF}(f)$

Slip properties of NiAl

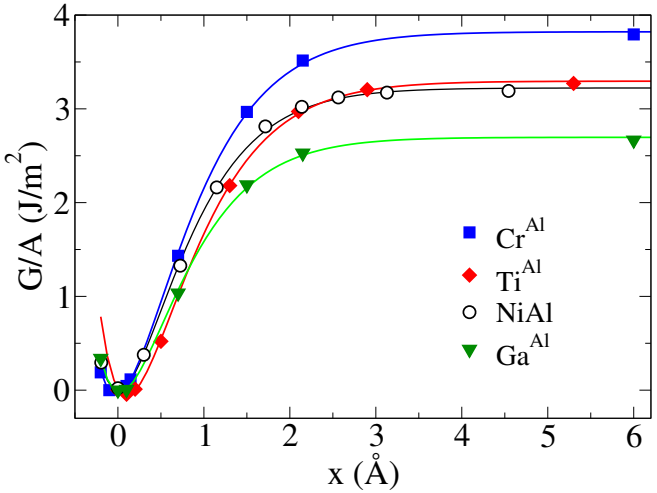
Slip system	γ_{us} [J/m^2]	G_b/G_d
$\langle 100 \rangle (001)$	1.52	0.53
$\langle 110 \rangle (001)$	2.9	0.28
$\langle 100 \rangle (011)$	1.28	0.63
$\langle 0\bar{1}1 \rangle (011)$	2.09	0.38
$\langle 1\bar{1}1 \rangle (011)$	0.83	0.96
$\langle 1\bar{1}0 \rangle (111)$	1.61	0.50
$\langle 1\bar{1}0 \rangle (112)$	2.84	0.35
$\langle 1\bar{1}1 \rangle (112)$	0.96	0.83

- ratio γ_s/γ_{us} is small (ductile when $G_b/G_d > 1$) $\rightarrow$ brittle crack propagation predicted

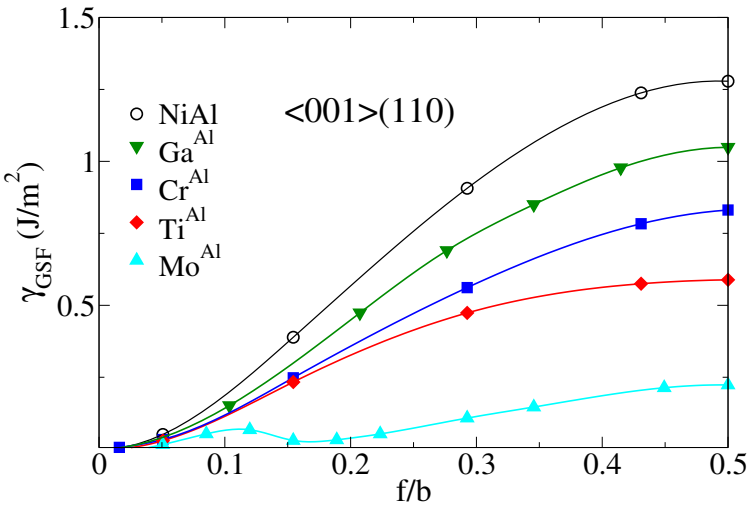
- the largest value of γ_s/γ_{us} found for $\langle 1\bar{1}1 \rangle$ slips

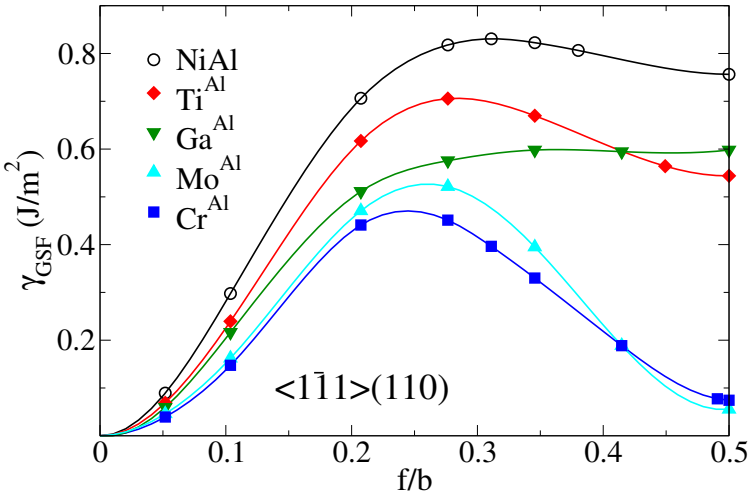
(110) plane alloyed

CLEAVAGE



SLIPS





- weaker effect on cleavage
- change of slip properties direction dependent
- Mo: huge decrease of $\langle 100 \rangle$ γ_{us}

$\longrightarrow$ agreement with experiment

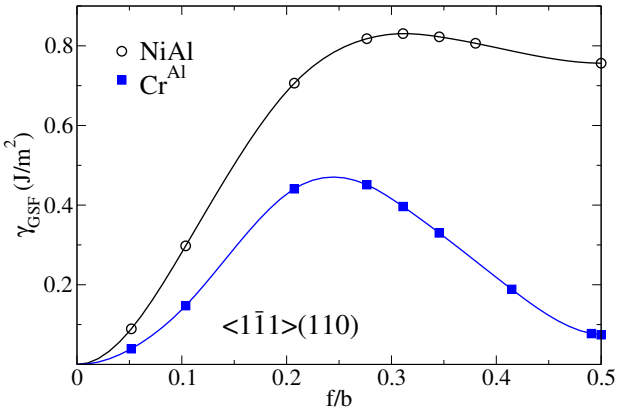
Darolia et al., Scripta Metall. Mater. **26** p. 1007 (1992)

"Mysterious" chromium

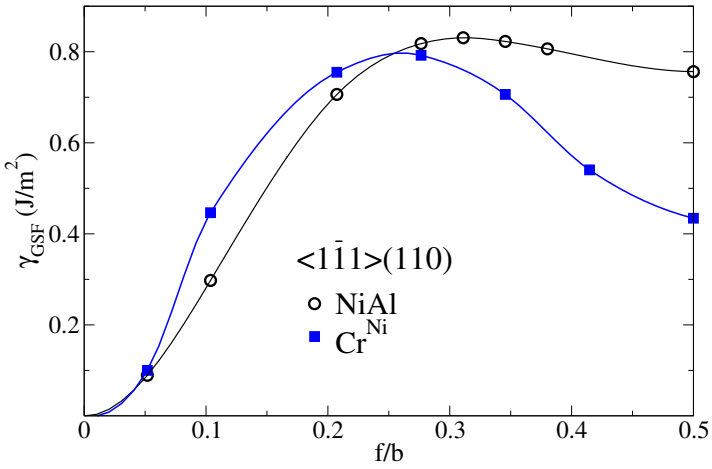
Miracle *et al.:* - *Chromium enhances nucleation and motion of* $\langle 111 \rangle$ *dislocations*
- *Cr alloyed to Al sublattice*

Darolia *et al.:* - $\langle 111 \rangle$ *dislocations are absent*
- *Cr both at Ni and Al sites*

Cr at Al sublattice



Cr at Ni sublattice



COMPOSITION plays role!

Results - ductility enhancement

	Rice		ZCT[1]	
compound	$\langle 1\bar{1}1 \rangle$	$\langle 001 \rangle$	$\langle 1\bar{1}1 \rangle$	$\langle 001 \rangle$
NiAl	no	no	no	no
Cr^{Al}	?	no	yes	no
Cr^{Ni}	no	no	no	no
Mo^{Al}	?	yes	?	yes
Mo^{Ni}	no	no	no	no
Ti^{Al}	no	no	no	no
Ga^{Al}	no	no	no	?

[1] Zhou, Carlsson,Thompson, *Phys. Rev. Lett.* **72**, 852 (1994)

Conclusions - part II.

+ the effect of alloying atoms anisotropic with respect to both plane and slip direction

+ Mo found to promote $\langle 001 \rangle$, Cr $\langle 111 \rangle$ dislocations (dependence on composition)

+ influence of Ti and Ga only moderate

+ calculation agree in trends with experiments, intrinsic effect of additions may be resolved

+ step towards computational material engineering

Outlook

NEAR FUTURE:

+ extension of studies on correlation elasticity - cleavage
  (preparing for submission)
+ influence of tensile-shear coupling on the dislocation emission
  (preparing for submission)

FAR FUTURE:

+ more realistic cleavage modelling $\longrightarrow$ crack tip simulation
+ connection with large scale simulations - derivation of model potentials
+ brittle-ductile transition

Acknowledgments

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