

# *Ab initio* modelling of mechanical and elastic properties of solids

*Petr Lazar*

CENTER FOR  
COMPUTATIONAL MATERIALS SCIENCE  
<http://www.cms.tuwien.ac.at>



# Motivation

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- 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 → theoretical atomic-level treatment

# Overview

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- PART 1: Mechanical and elastic properties
  - Correlation between elasticity and fracture<sup>1 2</sup>
  - Semirelaxed cleavage<sup>3</sup>
- PART 2: Ductility improvement
  - Microalloying of NiAl<sup>4</sup>
  - Tension-shear coupling<sup>5</sup>

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<sup>1</sup>P. Lazar, R. Podloucky, W. Wolf, *Applied Physics Letters* **87**, 261910 (2005)

<sup>2</sup>P. Lazar, R. Podloucky, W. Wolf, *Progress in Materials Science*, Proceedings, submitted

<sup>3</sup>P. Lazar, R. Podloucky, *Modelling and Simulation in Materials Science and Engineering*, submitted

<sup>4</sup>P. Lazar, R. Podloucky, *Physical Review B*, in print (scheduled 1st March, 2006)

<sup>5</sup>P. Lazar, R. Podloucky, *Physical Review B*, submitted

# Elasticity and fracture

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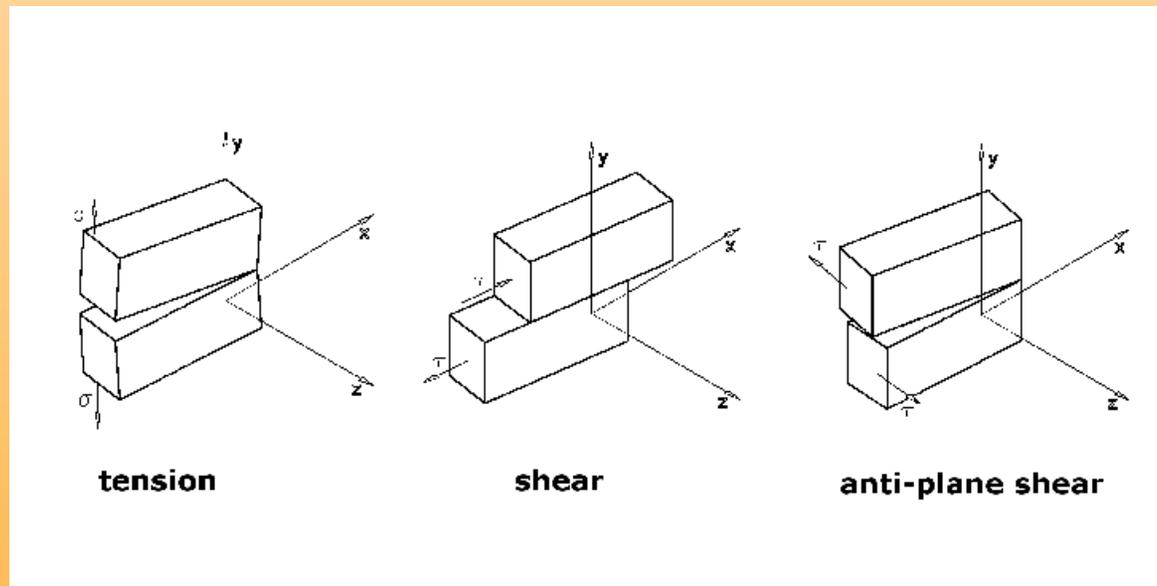
- **ELASTICITY:**
  - response of material to small strains
  - related physical quantities are **elastic constants**
    - easy to measure or calculate
- **FRACTURE:** describes nucleation and propagation of cracks.
  - the processes which contribute to crack energy span over several length scales
  - a description within one general theory impossible

# Correlating fracture and elasticity

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

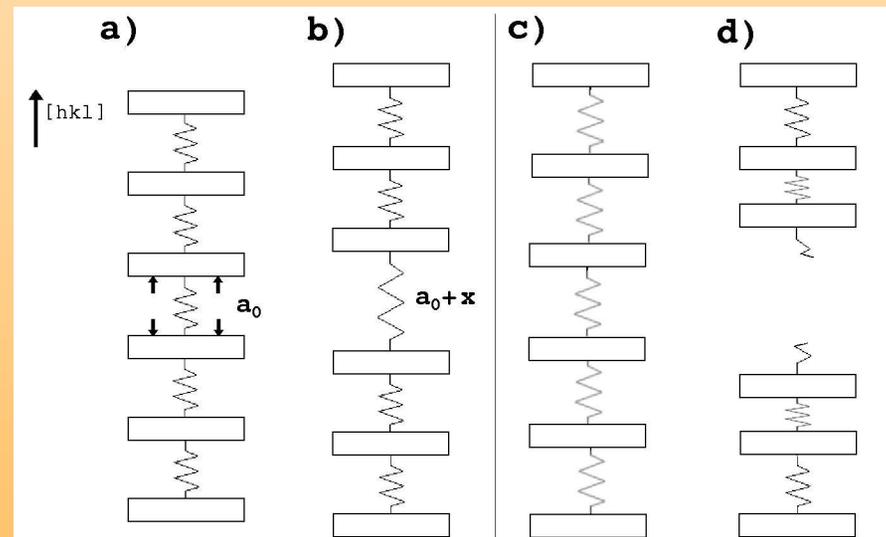
**CRACK / CLEAVAGE** . . . energy localised near to crack  
→ **atomistic level**

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

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*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

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- 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):<sup>6</sup>

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

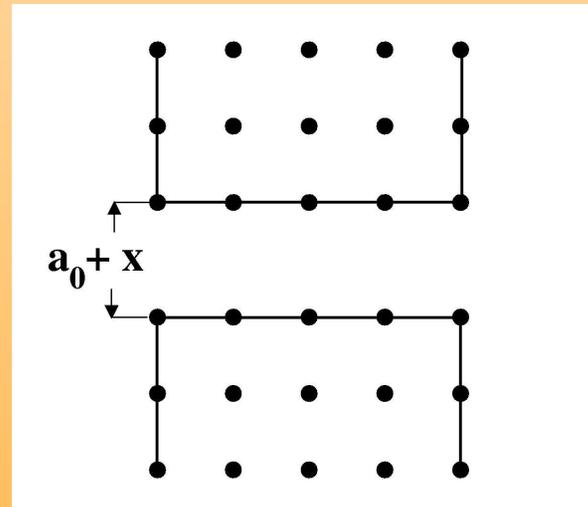
$G_b$  ..... cleavage energy

$l_b$  ..... critical length

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

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

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



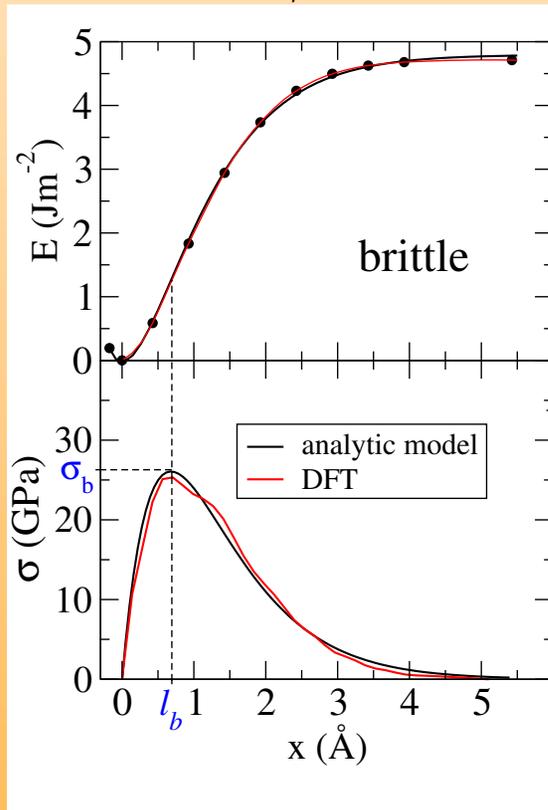
<sup>6</sup>Rose et al. *Phys. Rev. B* **28**, 1835 (1983)

# The UBER

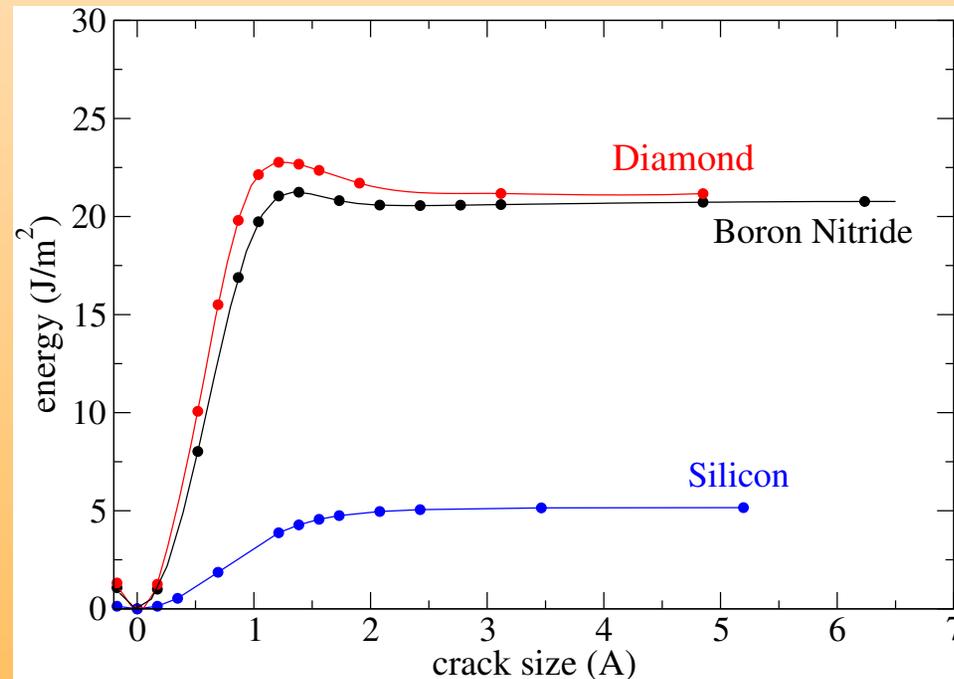
- universal curve, broad classes of materials
- presumably valid for metals, proved for covalent and ionic materials

NiAl (001):

UBER: —; DFT: ●



(111) diamond structure - narrow planes  
(DFT results)



## Historical: estimates of theoretical cleavage stress

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- Orowan-Gilman criterion:<sup>789</sup> model with sinusoidal restraining force

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

$E$ ...rigid or Young's modulus

$\gamma_s$ ...surface energy

$a_0$ ...distance between layers

- Orowan-Gilman criterion often overestimates theoretical cleavage stress
- fit to ab-initio calculations<sup>10</sup>: model not reliable

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<sup>7</sup>M. Polanyi, Z. Phys **7** p. 323 (1921)

<sup>8</sup>E. Orowan, Rep. Prog. Phys. **12** p. 185 (1949)

<sup>9</sup>J. J. Gilman: Proc. symp. on the physics and chemistry of ceramics, p. 240 (1963)

<sup>10</sup>M. H. Yoo and C. L. Fu, Mat. Sci. Eng, **A153**:470 (1992)

## Connecting elasticity and brittle cleavage - key relations

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

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

→ equal to elastic energy with (unknown) fitting parameter<sup>11</sup>  $L_b$ :

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

$A$  . . . area of cleavage plane (known),  $C$  . . . elastic modulus (known)<sup>12</sup>

**$L_b$  . . . new materials parameter of dimension  $[l]$**

”LOCALISATION LENGTH” for brittle cleavage

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<sup>11</sup>for correct physical dimension  $[E]$

<sup>12</sup> $G_b, l_b, C, \sigma_b, L_b$  depend on material and cleavage plane ( $hkl$ )

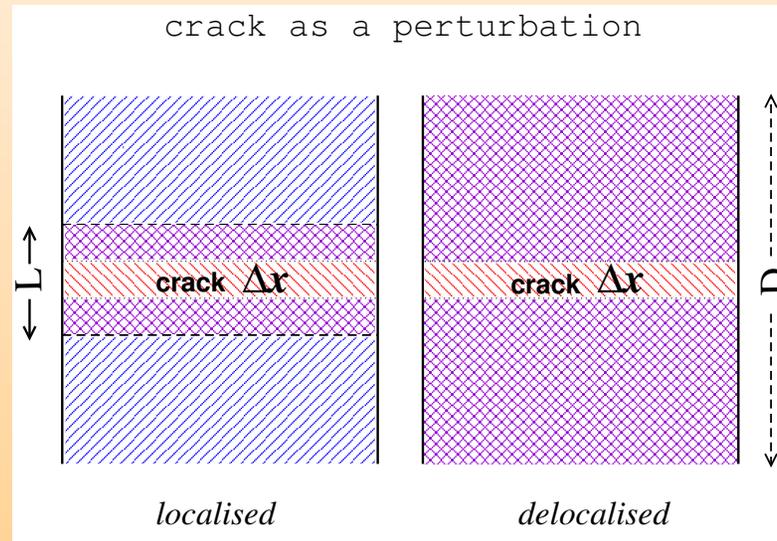
## Calculated values - simple metals

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

	$[hkl]$	$C$	$G_b/A$	$l_b$	$\sigma_b/A$	$a_0$	$L_b$
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  $\rightarrow$  rigid modulus  $C$

$V = AD$  . . . macroscopic volume

$V = AL$  . . . localisation volume

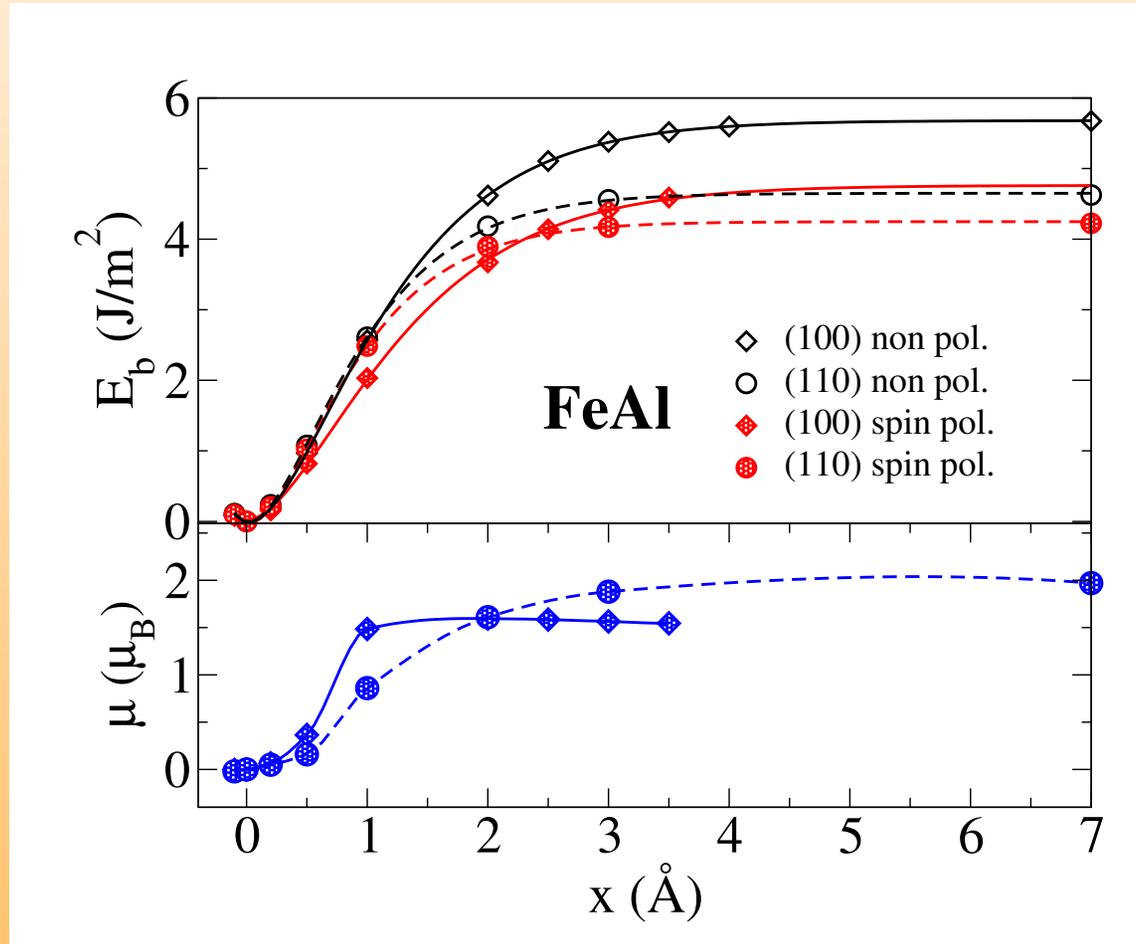
## Calculated values - intermetallic compounds

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

		$[hkl]$	$C$	$G_b/A$	$l_b$	$\sigma_b/A$	$a_0$	$L_b$
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 <sub>3</sub> Al	L1 <sub>2</sub>	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 <sub>0</sub>	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

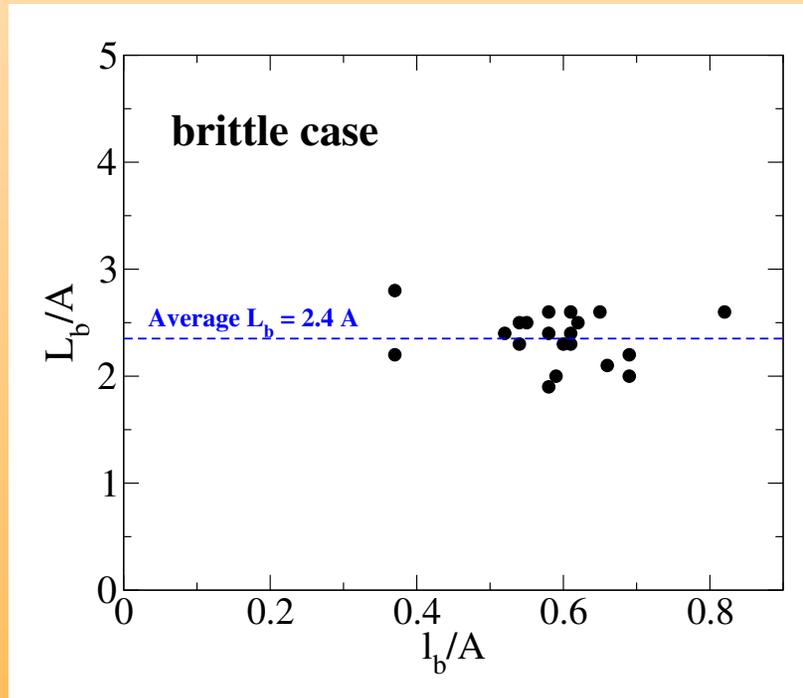
## Calculated values - covalent and ionic compounds

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

		$[hkl]$	$C$	$G_b/A$	$l$	$\sigma_b/A$	$a_0$	$L_b$
VC	B1	100	<b>647</b>	3.2	0.37	32	2.08	2.77
		110	<b>585</b>	7.0	0.55	46	1.47	2.53
		111	<b>564</b>	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	<b>4.16</b>
		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

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

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

"Orowan - type"

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

## Conclusions - brittle cleavage

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- + 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,  $L_b \approx 2.4 \text{ \AA}$** , for all (studied) materials and directions.
- + Model tested for different types of bonding (metallic, ionic, covalent).

## Relaxed cleavage

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*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<sup>13</sup>

Relaxed cleavage energy  $E_r(x)$  quadratic in crack size  $x$ :

$$E_r(x) = G_r \frac{x^2}{l_r^2}$$

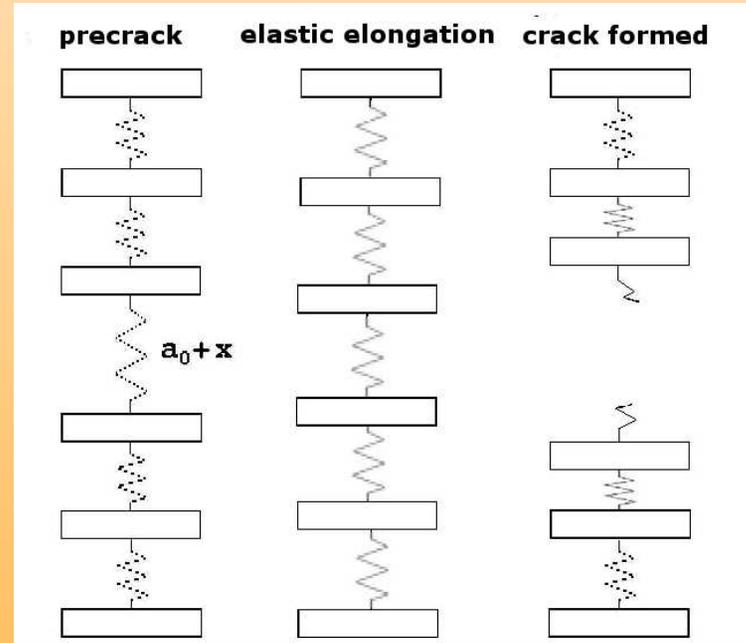
$G_r$  . . . relaxed cleavage energy,  $l_r$  . . . critical length  
 FIT PARAMETERS  $G_r, l_r$ :<sup>14</sup> fit  $E_r(x) \rightarrow E_{\text{DFT}}(x)$

STRESS

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

CRITICAL STRESS

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

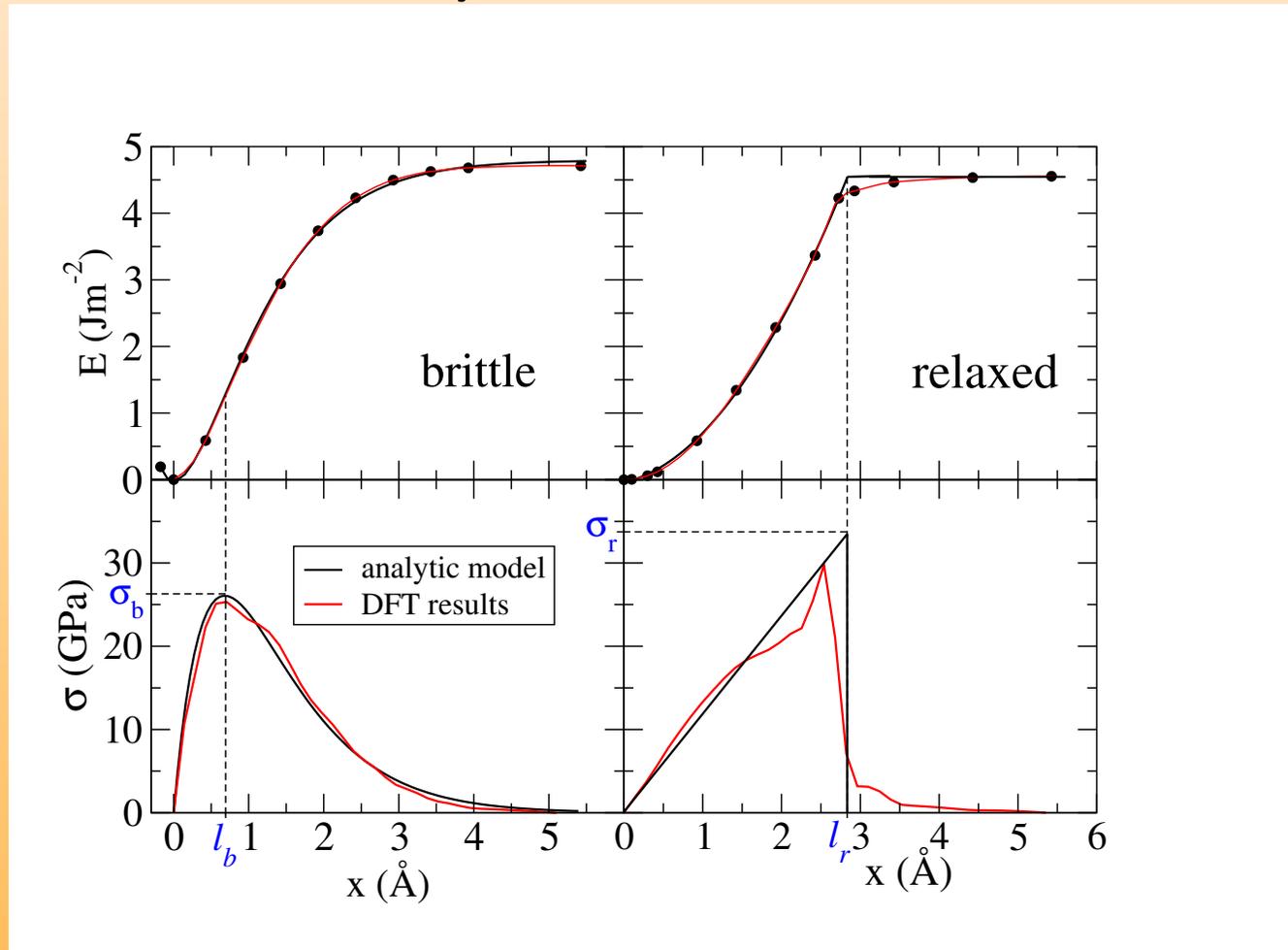


<sup>13</sup>P. Lazar, R. Podloucky, W. Wolf, *Phys. Rev. B*, submitted

<sup>14</sup> $G_r, l_r, C, \sigma_r, L_r$  depend on material and cleavage plane ( $hkl$ )

# DFT vs. analytical models

NiAl (001)  
analytic models —; DFT ●



## The connection for relaxed cleavage

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relaxed cleavage energy  $E_r(x)$  quadratic in  $x$   
→ equal to elastic energy with (unknown) fitting parameter  $L_r$ :<sup>15</sup>

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

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

$L_e$  . . . new materials parameter of dimension  $[l]$

"LOCALISATION LENGTH" for relaxed cleavage

critical stress relation ("Orowan type"):

$$\frac{\sigma_r}{A} = 2 \frac{G_r}{A l_r} = \sqrt{\frac{2}{L_r}} \sqrt{\frac{G_r}{A} C}$$

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<sup>15</sup>for correct physical dimension  $[E]$

## Comparison of brittle and relaxed results

BRITTLE | RELAXED

	$(hkl)$	$C$ GPa	$G_b/A$ J/m <sup>2</sup>	$\sigma_b/A$ GPa	$G_r/A$ J/m <sup>2</sup>	$\sigma_r/A$ 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

## Conclusions - part I.

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- + 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  $L_b \approx 2.4 \text{ \AA}$ : for all (studied) materials and directions
- + models valid for all types of bonding (metallic, ionic, covalent)
- + derivation of model potentials for crack tip simulations

## PART II.

# Microalloying of NiAl

## Microalloying of NiAl modelling

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*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

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- + low density, high melting point, high strength at elevated temperatures  
→ INTERESTING MATERIAL FOR AEROSPACE INDUSTRY
- + wide range of stability in atomic composition
- + site occupancy probability of additions can be varied by chemical composition<sup>16</sup>
- BUT - poor ductility at room temperature

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<sup>16</sup>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 → **cleavage decohesion** (brittle fracture) or **dislocation emission** (ductile fracture).

Preferred fracture mode -

→ *critical energy release rate  $G$*

## (1). CLEAVAGE DECOHESION

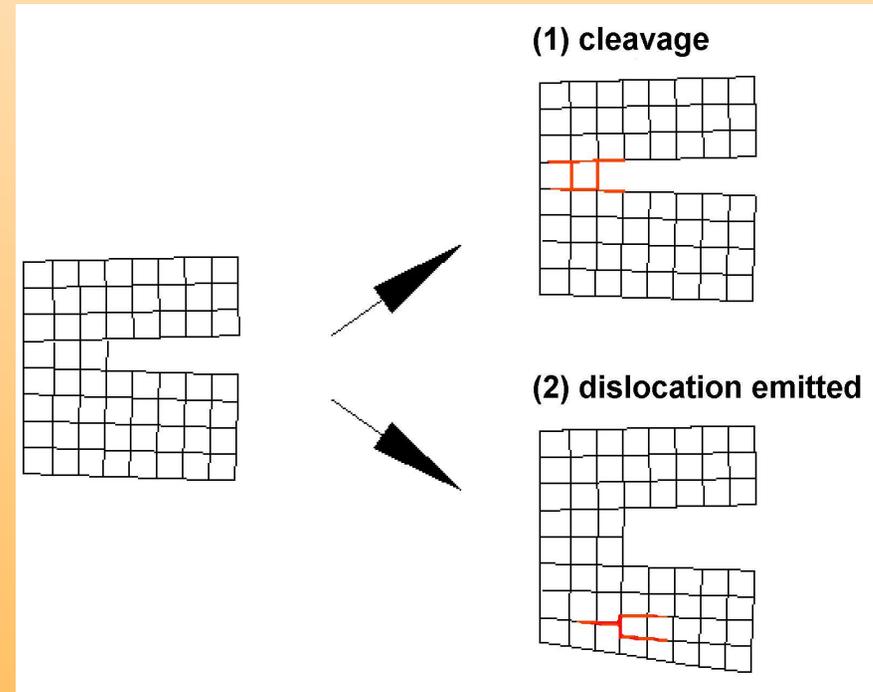
- brittle propagation of crack
- critical energy release rate for cleavage

$$G = G_b$$

$$\gamma_s = G_b/2$$

## (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

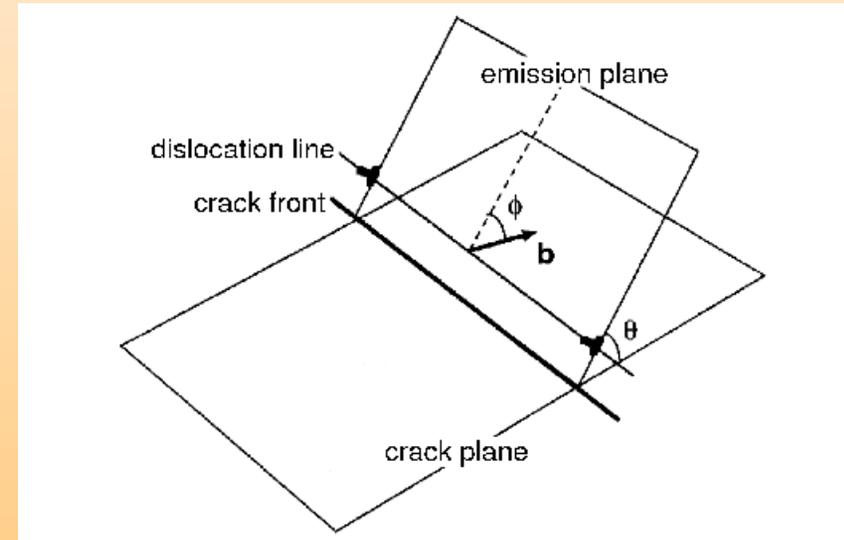
Rice's concept: a new material parameter - unstable stacking fault energy  $\gamma_{us}$

For mode II configuration

$$G_d = \gamma_{us}$$

In mode I configuration

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

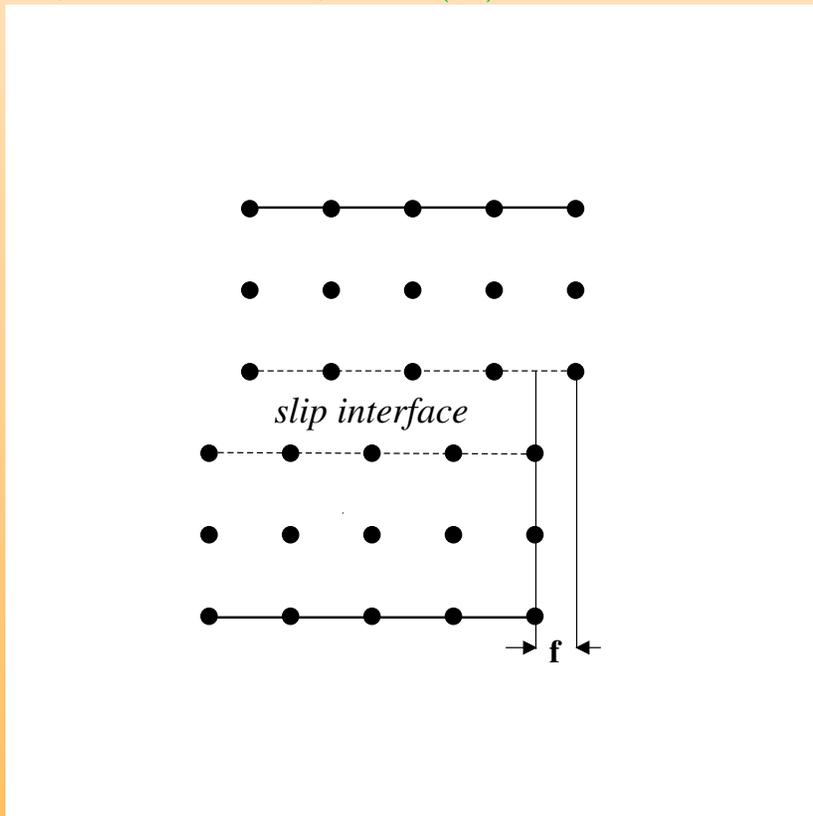


$\gamma_{us}$  may be obtained *ab initio*!

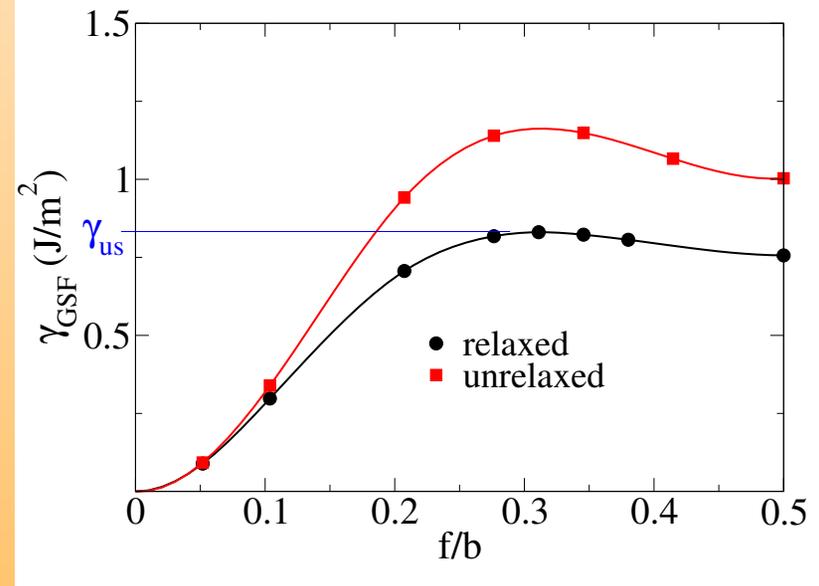
## Calculation of $\gamma_{us}$

- 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

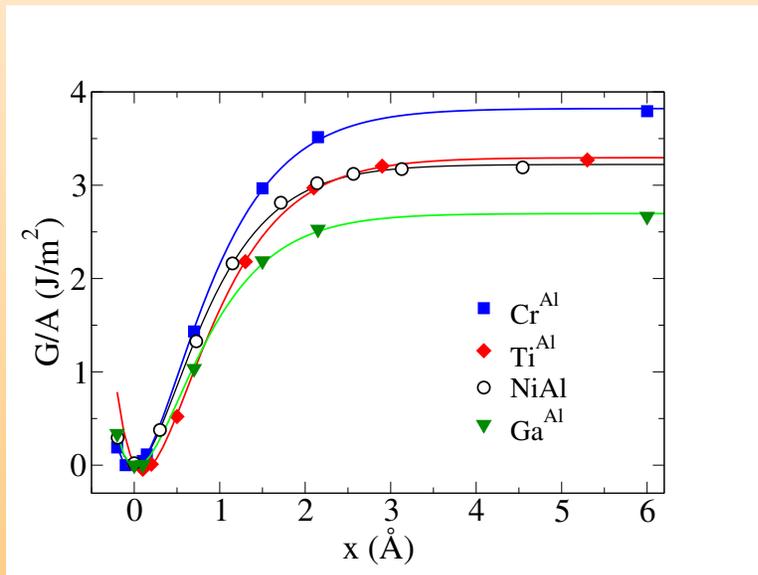
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Slip system	$\gamma_{us}$ [J/m <sup>2</sup> ]	$G_b/G_d$
$\langle 100 \rangle (001)$	1.52	0.53
$\langle 110 \rangle (001)$	2.9	0.28
$\langle 100 \rangle (011)$	1.28	0.63
$\langle 0\bar{1}1 \rangle (011)$	2.09	0.38
$\langle 1\bar{1}1 \rangle (011)$	0.83	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  $\gamma_s/\gamma_{us}$  is small (ductile when  $G_b/G_d > 1$ ) → brittle crack propagation predicted
- the largest value of  $\gamma_s/\gamma_{us}$  found for  $\langle 1\bar{1}1 \rangle$  slips

# (110) plane alloyed

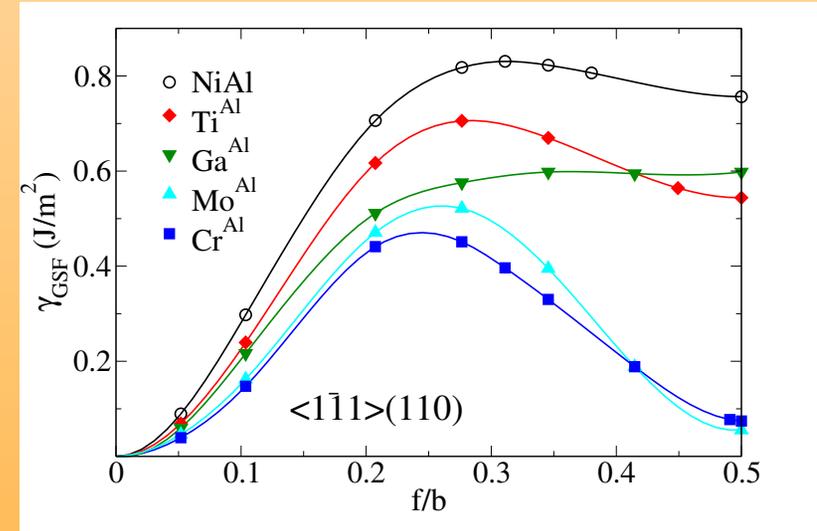
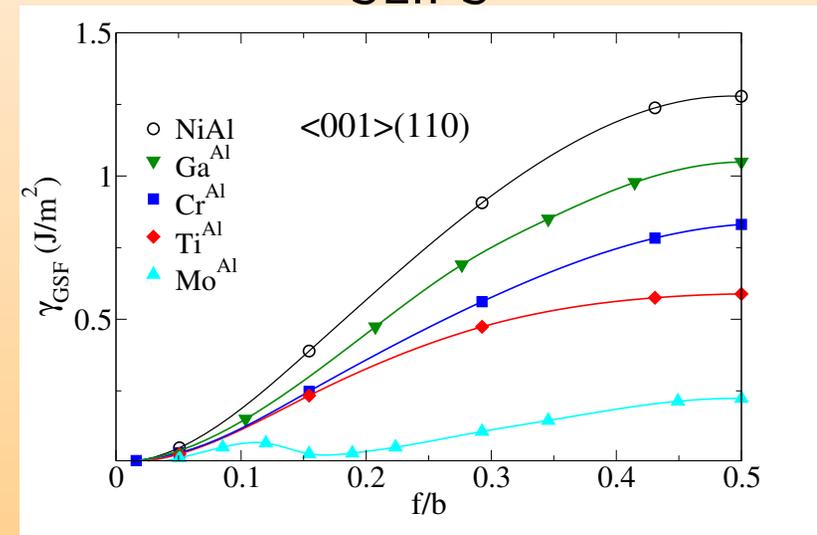
## CLEAVAGE



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

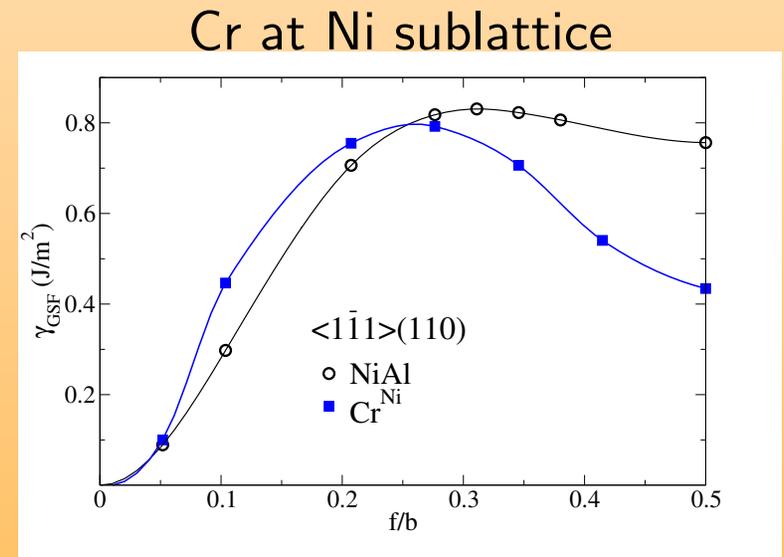
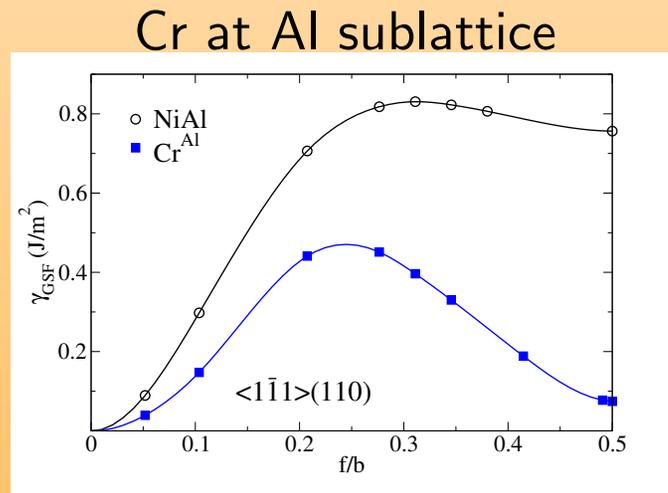
Darolia et al., Scripta Metall. Mater. **26** p. 1007 (1992)

## SLIPS



## "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



COMPOSITION plays role!

## Results - ductility enhancement

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compound	Rice		ZCT <sup>1</sup>	
	$\langle 1\bar{1}1 \rangle$	$\langle 001 \rangle$	$\langle 1\bar{1}1 \rangle$	$\langle 001 \rangle$
NiAl	no	no	no	no
Cr <sup>Al</sup>	?	no	yes	no
Cr <sup>Ni</sup>	no	no	no	no
Mo <sup>Al</sup>	?	yes	?	yes
Mo <sup>Ni</sup>	no	no	no	no
Ti <sup>Al</sup>	no	no	no	no
Ga <sup>Al</sup>	no	no	no	?

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<sup>1</sup>Zhou, Carlsson, Thompson, *Phys. Rev. Lett.* **72**, 852 (1994)

## Conclusions - part II.

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- + 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

# Acknowledgments

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- Calculations were performed on the Schrödinger-2 PC cluster of the University of Vienna.
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