Correlating elasticity and crack formation

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For solving the longstanding materials science problem of correlating elastic properties of a solid material to the formation of cracks we present a new general concept. This concept is applied to the technologically most important cracks of loading mode I for which we establish exact correlations by introducing a localization length as a new material parameter. We study two limiting cases of crack formation making use of analytic models determining the material and direction dependent parameters by comparison to ab initio density functional results. This is done for a variety of real materials in order to test our approach for different types of bonding. For the most interesting ideal brittle cleavage we find that the localization length is -within a reasonable approximation- of constant value, which results in a simple relation for the critical stress, presumably being useful for materials engineering. Our results confirm that the proposed general concept results in meaningful physical models which -for the first time- allow a rigorous and simple correlation between elastic and mechanical properties.

1. INTRODUCTION

It is a long standing effort in materials science to describe or just to estimate the critical property of crack formation of a solid material in terms of its elastic properties, an objective both of scientific as well as technological interest. Although more than 80 years have been passed since the pioneering work of Griffith [1], it seems that still there is a need for quantitative models on the atomic scale in order to establish a correlation between elastic and mechanical properties. First attempts for cracks of mode I estimating the critical cleavage stress were made by Polanyi [2] and Orowan [3]. Further studies [4, 5] tried to improve Orowan’s approach but the quantitative results were not satisfying. Very recently, Hayes et al. [7] -based on the work of Nguyen and Ortiz [6] -applied a rather complicated concept, which for intrinsic properties on the atomic scale involves a dependency on the macroscopic thickness of the material.

The conceptual problem of correlating elastic and cleavage properties consists in correlating a non-local property to a local property: the elastic response to a perturbation is non-local because the energy of is distributed over a macroscopic volume $V_{mac}$ of the whole material, whereas the energy for the formation of a crack is considered to be localized in some local volume $V_{loc}$ in the vicinity of the crack. Let us now imagine the initialization of an infinitesimally small crack into the solid at equilibrium. This perturbation may either open a finite crack or the solid may respond in a purely elastic way by distributing the energy uniformly over its macroscopic dimensions, which constitutes some kind of unstable equilibrium. Then, one can set equal the elastic response and the crack formation for infinitesimally small crack sizes. Consequently, a correlation between the energies (both, elastic as well as cleavage energies) in the localized volume $V_{loc}$ or -optionally- in the non-local macroscopic volume $V_{mac}$ should exist. This concept of an unstable equilibrium should be suitable for general modes of crack formation and elastic responses. It might, however, be very difficult to derive a correlation in analytic form.

At least for simple crack modes an analytic formulations exists. We demonstrate this for cracks of mode I as sketched in Fig. 1 along a plane with fixed area $A$ and orientation [hkl] a single crystal is cleaved into two blocks. The local volume $V_{loc}$ can then be expressed by

$$V_{loc} = A L,$$

with $L$ being a finite length in which the energy is localized. Consequently, the macroscopic volume $V_{mac}$ is defined as

$$V_{mac} = A D,$$

where $D$ describes the macroscopic thickness of the material. By Eqs. 1 and 2 a simple rescaling condition between the two volumes exists, namely $V_{mac} = V_{loc}(D/L)$. The rescaling factor $D/L$ (or its inverse) transforms local quantities into non-local ones (or vice versa for the inverse factor). We will make use of the conversion factor when we consider two extreme models of crack formation: a) the ideal brittle case modelling cleavage of the material into two rigid blocks, i.e. the atomic positions within the blocks do not relax. This process corresponds to a crack formation which is so fast that the atomic positions do not relax during the process (see panel b of Fig. 1); b) a process we will call ideal elastic crack formation, which is so slow that atoms will always fully relax after a crack with a given size $x$ has been opened. If $x$ is larger than a critical value then the material should abruptly break into two blocks with geometrically relaxed surfaces (as sketched in panels c and d of Fig. 1). For both cases, analytical models for the crack formation energies can be formulated. The yet unknown parameters of these models will be determined by fitting the analytic expressions to energies obtained from density functional theory (DFT) calculations modelling the processes
a) and b). For this purpose we make use of the Vienna Ab initio Simulation Package for calculating the total DFT energies and related quantities for suitably large slabs. Atomic relaxations are determined by minimizing the forces acting on the atoms.

The final goal, the correlation between elastic properties and crack formation, is then formulated for infinitesimally small crack sizes and elastic strains by setting equal crack formation energy and elastic energy, and choosing either a local or non-local description. In order to demonstrate the generality of our concept we apply it to a variety of materials representing different types of bonding, such as metallic, covalent and ionic bonding.

2. IDEAL BRITTLE CLEAVAGE

As an analytical model for ideal brittle cleavage we choose the so-called universal binding relation (UBER) for the energy \( E_b(x) \) depending on the crack size \( x \),

\[
E_b(x) = G_b \left[ \left( 1 + \frac{x}{l_b} \right) \exp \left( -\frac{x}{l_b} \right) - 1 \right],
\]

which represents some kind of interatomic potential. The material and direction dependent parameters are the cleavage energy \( G_b \) and the critical length \( l_b \) at which the stress \( \sigma(x) = dE/dx \) reaches a maximum (the index \( b \) denotes brittle cleavage). The UBER energy behaves quadratically at \( x = 0 \), and for very large separations \( x \) it approaches the energy zero with a negative curvature. It should, however, be mentioned that the UBER is not universal as usually claimed (see e.g. Refs. 9 10) because the curvature for \( E_b(x \to \infty) \) could also be positive 11. Furthermore, the two material parameters \( G_b \) and \( l_b \) might also depend on the actual planes between which the crack is initialized if there are different layer-to-layer distances along the direction \([hkl]\) (e.g. for the diamond lattice in [111] direction).

In the case of ideal brittle fracture the atomic positions remain fixed and do not relax. The electronic states, however, will change due to the change of the atomic environment in the neighbourhood of the crack because potentials at the surface will be different compared to the bulk environment. Directional bonds might be re-ordered which is reflected in the change of the electron distribution and, consequently, the energy of the system. All the electronic relaxation effects are fully taken into account by the self-consistency of the DFT approach which is used to fit the UBER. For this purpose we calculate DFT total energies \( E_{\text{DFT}}(x_i) \) for a suitably large number of different crack sizes \( x_i \) and for sufficiently large slabs.

Studying UBER for a variety of different materials with different types of bonding, we found that for most cases the fit to the DFT values is rather good and therefore the fitted parameters \( G_b \) and \( l_b \) listed in Table I are physically meaningful. Deviations are found for crack sizes \( x > l_b \) which could be particularly large when strong covalent bonds are broken. Anyway, the shortcomings of UBER are not of significant importance for the present study.

If the response to the perturbation is elastic, the energy of the perturbation is expressed by

\[
E_{\text{elast}}(x) = \frac{1}{2} CV x^2,
\]

which comprises the uniaxial modulus \( C \) for straining the material along \([hkl]\) with a fixed area \( A \) of the planes perpendicular to \([hkl]\). The symbol \( V \) denotes the volume over which the energy is uniformly distributed, and \( \delta \) is the dimensionless relative strain. If we decide to refer to a local description then \( V \) is substituted by \( V_{\text{loc}} \), and the relative strain is defined by \( \delta_{\text{loc}} = x/L_b \) with \( x \) being the initial very small crack size. The localization length for brittle cleavage \( L_b \) which is an intrinsic parameter, depends on the material, direction and cleavage planes like \( G_b \) and \( l_b \). For very small \( x \) we set now equal the elastic energy \( E_{\text{elast}} \) and the UBER expression (i.e. the Taylor expansion of \( E_b(x) \) in Eq. 3 in lowest order of \( x \)), which results in the relation

\[
\frac{1}{2} G_b \frac{x^2}{L_b} = \frac{1}{2} AL_b C \frac{x^2}{L_b^2}.
\]

This is the key equation to correlate the ideal brittle cleavage and its material parameters \( G_b, l_b, \) and \( L_b \) to the elastic properties described by the uniaxial modulus \( C \). From Eq. 4 a variety of relations can be derived. For the critical stress, i.e. the maximum \( \sigma_b := \sigma(x = l_b) \), one obtains the equation

\[
\frac{\sigma_b}{A} = \frac{1}{e \frac{A}{l_b}} = \frac{1}{e \frac{L_b}{C}}.
\]

3. IDEAL ELASTIC CLEAVAGE

In contrast to the ideal brittle case we now consider a cleavage process for which the crack formation is so slow that -after opening a crack of size \( x \)- the atoms have sufficient time to fully relax. Furthermore, we require that the material should behave perfectly elastic up to a critical crack size \( x = l_c \), at which it breaks abruptly without any further interaction between the cleaved blocks, as sketched in Fig. 1 (panels c and d). We will call this process ideal elastic cleavage and we characterize the corresponding parameters by the index \( c \). Denoting the corresponding cleavage energy by \( G_c \) we derive the obvious equation

\[
E_c(x) = \frac{G_c}{l_c^2} x^2
\]

for the corresponding cleavage energy \( E_c \) for crack sizes \( x \leq l_c \). For crack sizes \( x > l_c \) we require the condition \( E_c(x) = G_c \). Of course, this is an idealized model because a real material will deviate from the simple ideal elastic behaviour at least close to the critical crack size, as can
be seen in the right panel of Fig. 2 in which the analytic model is compared to a "real" material as calculated by the DFT procedure.

Again, like for the brittle case we establish the correlation between elastic and cleavage properties by setting equal elastic and cleavage energy for very small crack sizes $x$. In order to demonstrate the rescaling feature of our concept (as discussed at the beginning) we want a formulation in terms of a non-local description: the strains are now defined with respect to the macroscopic thickness by $\delta = x/D$ as in standard elastic theory. Doing that, we have to rescale the cleavage energy by the obvious factor $L_e/D$. Now we have again introduced a localisation length as a new material parameter, and we can derive the key equation for correlating elastic and cleavage properties for the ideal elastic case,

$$G_e \frac{L_e}{D} \frac{x^2}{l_e^2} = \frac{1}{2} ADC \frac{x^2}{D^2}. \quad (8)$$

It should be noted that in this equation the macroscopic thickness $D$ cancels out and, because of this cancellation, the relation contains only intrinsic material parameters. In fact, we would have obtained the same relation if the strain would be defined relative to the localization length by $\delta = x/L_e$, similar to treatment of the ideal brittle cleavage.

Exploiting Eq. (8) we derive relations involving the critical stress $\sigma_c := \sigma(x = l_e)$,

$$\frac{\sigma_c}{A} = 2 G_e \frac{1}{A} l_e = \frac{l_e}{L_e} C. \quad (9)$$

The very close formal relationship to Eq. (6) can clearly be seen. However, it should be noted that the material dependent cleavage quantities such as $G, l$ and $L$ are different for both cases (as denoted by the indices $b$ and $e$), and the constant prefactors are also different.

4. RESULTS AND DISCUSSION

In Fig. 2 for the [100] cleavage of NiAl the energies and stresses derived from the analytic models are compared to DFT results. In general for the brittle case (left panels), the agreement is good for smaller $x$ whereas for $x > l_b$ small but characteristic deviations occur (note also the remarks in Ref [11]).

The ideal elastic cleavage energy (right top panel) also fits quite well to the DFT data. Only close to the critical crack size $x \approx l_e$ deviations from the simple analytic model are significant because then atomic relaxations at the crack surfaces are becoming important. The differences are naturally more pronounced for the stress, because it is the first derivative of the cleavage energy.

Studying the results for the new material parameter, the localisation length $L$, we find a rather striking property for the brittle cleavage as shown in Fig. 3 and in Table I namely that -within an error of $\approx 20\%$- the localisation lengths, $L_b \approx 2.4 \text{ Å}$, are rather constant for all studied materials independent of the directions $[hkl]$ and the layer separations $a_0$. Based on this finding we derive from Eq. (9) the simple relation

$$4.21 \frac{\sigma_b}{A} \sqrt{\frac{A}{G_b}} \approx \sqrt{C}, \quad (10)$$

in which cleavage properties (left side) are separated from elastic properties (right side). This equation might serve as a starting point for the development of an "engineering" tool to estimate the critical cleavage properties in terms of the uniaxial modulus $C$ which is a linear combination of the elastic constants $[12,13]$.

For the ideal elastic cleavage the critical lengths $l_e$ and localisation lengths $L_e$ are much larger than for the brittle case, as shown in Table II and Fig. 3. This seems to be obvious because for the ideal elastic cleavage the material is now allowed to relax after the crack initialization and therefore it needs much larger crack sizes to break it. We notice also a strong variation of $L_e$ which is in contrast to the brittle case. Some -but no simple- correlation between $l_e$ and $L_e$ exists because, generally, for larger $l_e$ the values of $L_e$ are also larger. More studies are needed in order to -hopefully- find useful correlations between the material parameters for the ideal elastic cleavage. Also the critical strengths $\sigma_c$ are significantly enhanced from 20% to 100% in comparisons to $\sigma_b$, whereas the cleavage energies $G_e$ -although reduced compared to $G_b$- differ not very strongly from the ideal brittle case (with the exception of VC [100]).

Summarizing, we presented a general concept, which correlates elastic and cleavage properties of a solid. By its application to two different models for cracks of mode I analytic and quantitative correlations were derived by introducing a localization length $L$, a new intrinsic material parameter which proved to be meaningful for a large variety of materials. Future efforts should focus on the fundamental understanding of $L$.

Acknowledgments

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[11] This occurs e.g. when cleaving diamond along [111] because of re-ordering of strong covalent bonds.
[12] e.g. for a cubic structure the uniaxial modulus for the direction \([hkl]\) is given by:

\[
C = \frac{C_{11} - 2(C_{11} - C_{12} - 2C_{44})(h^2k^2 + h^2l^2 + k^2l^2)}{a_0^2}
\]

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### Tables

#### TABLE I: Parameters for brittle cleavage for some selected compounds and directions: uniaxial elastic modulus \(C\) (GPa), cleavage energy per surface area \(G_c/A\) (J/m\(^2\)), critical length \(l_c\) (Å), maximum stress \(\sigma_c/A\) (GPa), interlayer distance between cleaved planes \(a_0\) (Å), and localization length \(L_b\) (Å) for selected compounds and cleavage directions [hkl]. In brackets, the crystal structure is denoted in terms of Pearson’s notation.

| [hkl] | \(C\) (GPa) | \(G_c/A\) (J/m\(^2\)) | \(l_c\) (Å) | \(\sigma_c/A\) (GPa) | \(a_0\) (Å) | \(L_b\) (Å) |
|-------|-----------|----------------|--------|----------------|------|------|
| NiAl  (B2) | 100 | 203 | 4.6 | 2.7 | 34 | 15.8 |
| NiAl  (B2) | 110 | 284 | 3.1 | 2.0 | 32 | 17.7 |
| NiAl  (B2) | 111 | 311 | 3.9 | 2.2 | 36 | 18.4 |
| Ni\(_3\)Al (L1\(_2\)) | 100 | 225 | 3.0 | 2.2 | 27 | 18.2 |
| VC (B1) | 100 | 647 | 2.4 | 0.8 | 60 | 6.5 |
| VC (B1) | 110 | 585 | 6.0 | 1.6 | 75 | 12.5 |
| VC (B1) | 111 | 564 | 8.4 | 1.6 | 105 | 8.6 |
| MgO (B1) | 100 | 299 | 1.7 | 0.8 | 42 | 5.3 |
| MgO (B1) | 111 | 345 | 10.2 | 1.9 | 107 | 6.9 |

#### FIG. 1: Models for cracks of mode I. A solid (sketched as a stacking of interacting layers with a layer distance \(a_0\), panel a) undergoes brittle cleavage as sketched in panel b: a crack of size \(x\) cleaves the material into two rigid blocks without relaxing the atomic geometry of the layers in the blocks. For the ideal elastic cleavage (see text) the material relaxes in a perfectly elastic manner (panel c) up to a critical crack size above which it breaks abruptly into two blocks with atomically relaxed surfaces (panel d).
FIG. 2: Cleavage along [100] of NiAl: energy and stress per surface area vs. crack size $x$ for the ideal brittle (left panel) and ideal elastic (right panel) cleavage model full lines: analytic models, dots: DFT results.

FIG. 3: Localization lengths vs. critical lengths for ideal brittle and elastic cleavage for a variety of materials and directions.