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# Ab initio LDA+U prediction of the tensile properties of chromia across multiple length scales

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## ABSTRACT

Periodic density functional theory (DFT) and DFT+U calculations are used to evaluate various mechanical properties associated with the fracture of chromia ( $\text{Cr}_2\text{O}_3$ ) along the  $[0001]$  and  $[01\bar{1}(3/2)(a/c)^2]$  directions. The properties investigated include the tensile strength, elastic constants, and surface energies. The tensile strengths are evaluated using an ideal tensile test, which provides the theoretical tensile strength, and by fitting the calculated data to universal binding energy relationships (UBER), which permit the extrapolation of the calculated results to arbitrary length scales. The results demonstrate the ability of the UBER to yield a realistic estimate of the tensile strength of a 10- $\mu\text{m}$ -thick sample of  $\text{Cr}_2\text{O}_3$  using data obtained through calculations on nanoscopic systems. We predict that  $\text{Cr}_2\text{O}_3$  will fracture most easily in the  $[01\bar{1}(3/2)(a/c)^2]$  direction, with a best estimate for the tensile strength of 386 MPa for a 10  $\mu\text{m}$  grain, consistent with flexural strength measurements for chromia. The grain becomes considerably stronger at the nanoscale, where we predict a tensile strength along the same direction of 32.1 GPa for 1.45 nm crystallite. The results also provide insight into the origin of the direction dependence of the mechanical properties of  $\text{Cr}_2\text{O}_3$ , with the differences in the behavior along different directions being related to the number of Cr–O bonds supporting the applied tensile load. Additionally, the results shed light on various practical aspects of modeling the mechanical properties of materials with DFT+U calculations and in using UBERs to estimate the mechanical properties of materials across disparate length scales.

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## 1. Introduction

Understanding how materials fail is an important aspect of developing new materials with improved resistance to mechanical failure. Simulation can play an important role in this context by providing a means of predicting the mechanical properties and behavior of novel materials prior to their synthesis. Generally, mechanical engineering models used to simulate the failure of materials employ coarse-grained mesoscopic or continuum models in conjunction with empirical cohesive laws describing the response, e.g. to tensile loading (Dugdale, 1960; Barenblatt, 1962; Langer and Lobkovsky, 1998). Unfortunately, experimental data of complex materials is usually unavailable for the development of such cohesive laws. Moreover, for brittle materials, tensile strength tests are unreliable and instead the tensile strength is estimated from flexural strengths measured in bending tests, typically leading to a wide range of values due to defects.

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First-principles calculations offer an alternative means of developing cohesive laws describing the mechanical response of materials and provide atomic-level insight into the basic processes responsible for the failure of materials. Indeed, fracture and plastic yielding are generally initiated through atomic-level processes such as bond dissociation and dislocation nucleation. Describing directly such processes occurring in brittle materials requires an atomic-level resolution of the finite element mesh, which is not computationally feasible (Camacho and Ortiz, 1996). Developing cohesive laws on the basis of first-principles calculations provides a way to incorporate indirectly these atomic-level details into coarse-grained simulations.

A significant impediment to developing mesoscopic cohesive laws on the basis of first-principles calculations lies in the disparity between the calculated mechanical properties and those measured in experiments. This disparity is due largely to a size dependence of these properties. For example, the cohesive strengths of brittle materials obtained through atomic-scale calculations (Hong et al., 1995; Evans et al., 1999; Gall et al., 2000) differ by several orders of magnitude from those measured experimentally through spallation tests of macroscopic samples (Grady and Kipp, 1993). In order to overcome this limitation, it is thus necessary to have a means of connecting the mechanical properties of a given material across multiple length scales.

The development of strategies for connecting the mechanical (and other) properties of materials across multiple length scales has been the focus of intense research. One particularly useful development in this area was the establishment of Universal binding energy relationships (UBERs) (Rose et al., 1983; Hong et al., 1992; Nguyen and Ortiz, 2002; Hayes et al., 2004), which are effectively renormalized cohesive laws for materials in which all material- and size-dependent quantities are incorporated into the renormalization terms. It has been demonstrated that UBERs can act as a constant between different materials and length scales (Hayes et al., 2004), thereby providing a means of extrapolating the results of atomic-scale calculations to the longer length scales that are relevant to mechanical engineering simulation models, laboratory experiments, and real-world systems.

In the current study, we explore different means of obtaining the tensile strength of ceramics, with a particular emphasis on chromia ( $\text{Cr}_2\text{O}_3$ ). This material is a common component of Cr-based coatings used to protect steel surfaces from wear under extreme conditions (Zeng et al., 2006; Underwood and Vigilante, 2007), and thus understanding its mechanical properties is of significant technological interest. The models used to calculate mechanical properties include two different UBERs, which provide a way to evaluate the tensile strength for samples of arbitrary thickness, as well as two different means of obtaining the theoretical tensile strength. The properties obtained through the work include the uniaxial elastic constants, Young's moduli, theoretical tensile strengths, and tensile strengths of samples  $10\ \mu\text{m}$  thick calculated along the  $[0001]$  and  $[01\bar{1}(3/2)(a/c)^22]$  directions. The results demonstrate an UBER is capable of yielding reasonable values of the tensile strength across multiple length scales. The results also indicate that the mechanical properties of chromia are direction-dependent, with the tensile strength being higher along  $[0001]$  than it is along  $[01\bar{1}(3/2)(a/c)^22]$ . This observation is rationalized in terms of the number of Cr–O bonds that support the load along these two directions.

The calculations were performed using conventional density functional theory (DFT) (Hohenberg and Kohn, 1964; Kohn and Sham, 1965; Bickelhaupt and Baerends, 2000; Gidopoulos, 2003; Kohanoff and Gidopoulos, 2003) and DFT+U methods (Anisimov et al., 1997; Dudarev et al., 1997). The latter method is needed because the intra-atomic interactions between  $3d$  electrons on the Cr atoms of chromia are not described properly by conventional DFT. These errors arise from the inexact treatment of exchange interactions with standard exchange-correlation functionals, which leads to large spurious self-interaction energies between these electrons in DFT calculations and manifests as a significant underestimation of the band gap and incorrect mixing of electronic states. The DFT+U method attempts to overcome this error by applying a parameterized Hartree-Fock (HF)-like potential to the localized states. Since HF methods employ exact exchange, this approach largely reduces the self-interaction errors associated with the localized states. The HF-like potential is dependent on two parameters  $U$  and  $J$ , which correspond to the spherically averaged Coulomb and exchange interactions between electrons localized on the same atom, with the value of  $U-J$  entering the calculation as a single parameter. In this work, we investigate two different values of  $U-J$ . The results indicate that the mechanical properties are relatively insensitive to the value of  $U-J$ , which may be useful in selecting values of  $U-J$  for future studies of mechanical properties of strongly correlated electron materials like mid-to-late transition metal oxides.

In addition to evaluating the mechanical properties, we perform a detailed investigation of the low-energy surfaces of  $\text{Cr}_2\text{O}_3$ . The surface calculations were performed primarily for the purposes of evaluating the surface energies, which are used as parameters in the UBER models, and to identify the directions along which to evaluate the mechanical properties. However, a comparison of the low-energy surfaces of  $\text{Cr}_2\text{O}_3$  has not been reported previously at the DFT+U level, and thus such a study is interesting in its own right. In accordance with experiments (Scarano et al., 1993) and previous periodic HF calculations (Rehbein et al., 1998; Sun et al., 2006), the results indicate that the  $(01\bar{1}2)$  surface is most stable regardless of whether the ionic relaxation is permitted. In addition, the results suggest that the surface energies are relatively insensitive to the precise value of  $U-J$  used in the DFT+U calculations.

The work is presented as follows. In Section 2, the details of UBER models and ideal tensile strength calculations are outlined. The details of the DFT(+U) calculations are given in Section 3. The results are presented in Section 4, and we conclude in Section 5.

## 2. Methodology

The tensile strength,  $\sigma_c$ , is the maximum tensile stress that a material can withstand before failing. For ceramics, failure typically occurs through fracture. The main purposes of this work are to explore different procedures for evaluating  $\sigma_c$  and

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