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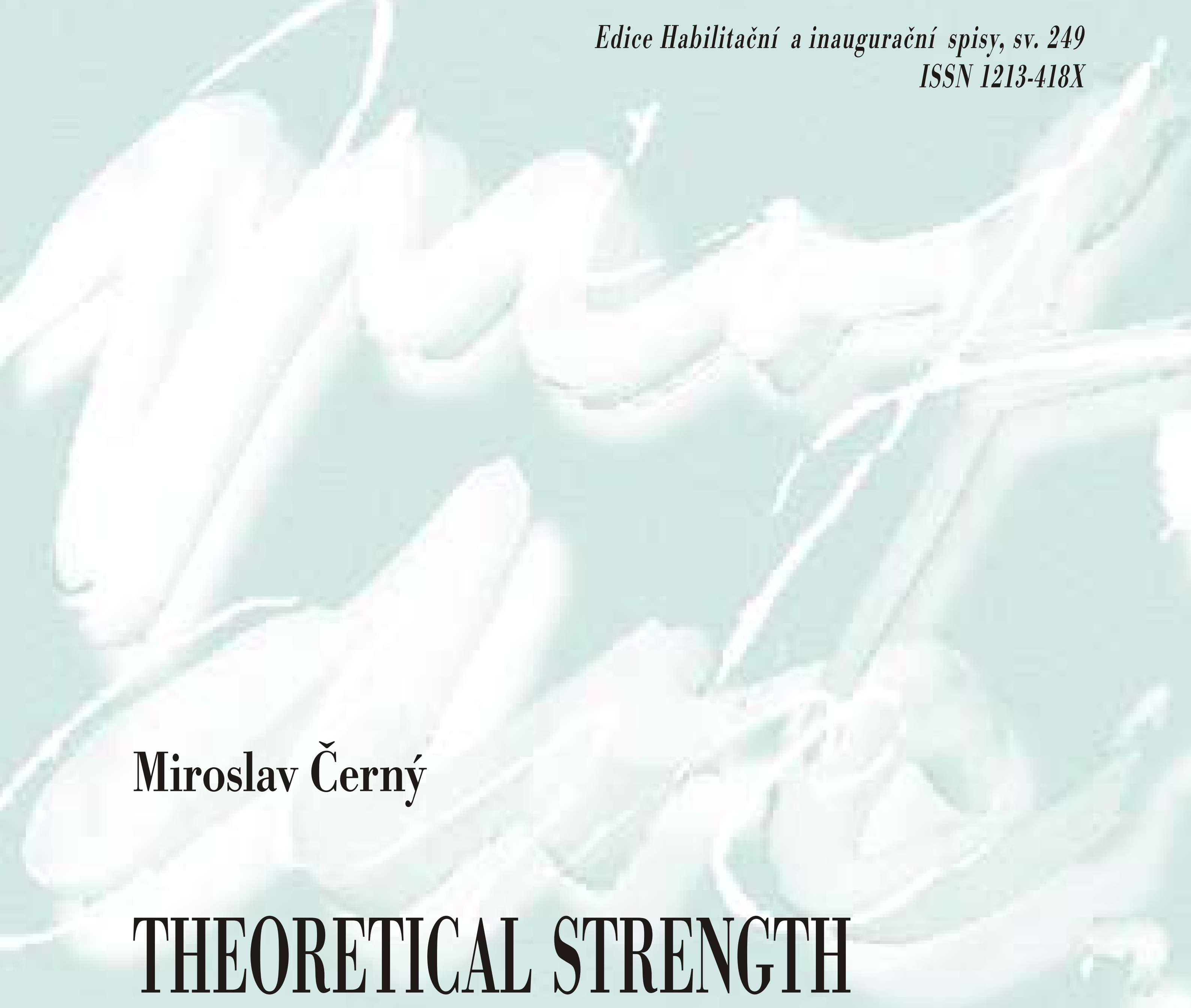

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THEORETICAL STRENGTH AND STABILITY OF CRYSTALS FROM FIRST PRINCIPLES

BRNO UNIVERSITY OF TECHNOLOGY
Faculty of Mechanical Engineering
Institute of Physical Engineering

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THEORETICAL STRENGTH AND STABILITY OF CRYSTALS FROM FIRST PRINCIPLES

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Miroslav Černý obtained his first academic degree Mgr. (MSc.) at Faculty of Education, Masaryk University in Brno in 1996, after finishing his study of "Physics and Technical Education". From 1996 until 2001 he studied Ph.D. course of "Applied Physics" at the Institute of Physical Engineering, Faculty of Mechanical Engineering, Brno University of Technology. There, starting from 1999, he worked as an assistant (junior lecturer). In the years 2000–2001, he was employed also at Institute of Physics of Materials, Academy of Sciences of Czech Republic. He defended his PhD thesis „On the ab initio calculations of ideal strength" (in Czech) in December 2001.

During his Ph.D. study, M. Černý has acquired an experience in condensed matter physics and computer modeling with the main focus on ab initio calculations (based on density functional theory) of electronic structure of solids and related structural and mechanical characteristics. He paid a special attention to the problems of strength and stability of metallic and covalent crystals under various loading types, particularly, the isotropic (hydrostatic) loading, uniaxial tension, simple shear and, later on, a combination of certain loading types. He has also learned to operate several program codes as TB – LMTO – ASA (based on Linear Muffin-Tin Orbital method within the Atomic Sphere Approximation), WIEN97 and w2k (based on Full-Potential Linear Augmented Plain Waves method) and VASP code (Pseudo-Potential Plane Wave method). Although all of his published research activities were based on the above mentioned three computational codes, he has also gained a basic experience with all-electron code EXCITING and pseudo-potential package ABINIT.

The research activities were supported by several grants. After he finished his Ph.D. course, he received a post-doc grant "Ab initio calculation of elastic properties of FeP ordered system" supported by the Czech Science Foundation (project GA 106/02/D101, 2002–2004) and, later, a COST project "Twoscale analysis of stress distribution under nanoindentor tip" (OC 148 – P19, 2006-2009) within the section P19 "Multiscale Materials Modeling". Besides the two, he also participated in several other projects (MSM 0021630518, MSM 262100002, GA106/05/0134, GA106/05/0274, GA106/99/1178, GA101/05/0320). The results achieved were published in impacted international scientific journals (15 publications in last 5 years) and in proceedings of international conferences.

Teaching activities of M. Černý are focused mostly on basic university course of physics. Within the courses of Physics I and Physics II in Masters Study Programs, he teaches labs as well as seminars. Within the course of Physics B in Bachelors Study Programs he presents lectures and teaches labs. He is a supervisor (and sometimes also a teacher) of Selected Topics in Physics (I and II in Masters Study Programs and B in Bachelors Study Programs). He also teaches Physical Laboratory course for Physical Engineers. Starting from 2001, M. Černý participates on preparation of entrance exams to the Faculty of Mechanical Engineering.

1 INTRODUCTION

The strength of any solid has its upper limit called the theoretical (ideal) strength (TS). Although the terms *ideal* strength and *theoretical* strength are often considered to be synonyms, there is a slight difference in "feeling" their definition. While the ideal strength stands for stress value corresponding to the failure of an infinite perfect single crystal (ideal crystal) under zero absolute temperature, the theoretical strength can be assigned also to a system containing defects. Most of the methods for TS calculations based on atomistic simulations use periodic boundary conditions. Therefore, it is much simpler to build a model of an ideal crystal than a crystal structure with lattice imperfections. To make a model of crystal containing a defect, large unit cells (containing many atoms) are necessary even in case of point defects. Because of high computational demands of ab initio methods, the calculations presented in this work were performed for crystals of a perfect symmetry. Therefore, both terms (ideal strength and theoretical strength) are used as synonyms throughout the whole work.

The term TS must be always accompanied by a complete description of the studied system (chemical composition, lattice structure) as well as determination of a loading mode (direction of tension, slip system or other specification in case of a combined loading). It is necessary to describe the applied loading in detail because the computational methods based on atomistic approaches enable us to model sometimes also curious deformation paths, far from reality. From the historical point of view, calculations of theoretical strength became very important issue that made the scientists aware of a significance of crystal defects [1]. First estimates of the tensile strength yielded values of about two orders of magnitude higher then the highest observed ones. This discrepancy led to a conclusion that crystalline solids normally contained imperfections. This became a motivation for deeper studies of various lattice defects, their behaviour under applied load and their mutual interactions. A development of corresponding theories (principally the dislocation theory) moved an attention of materials scientists to this new subject.

However, simultaneous development of materials led to fabrication of almost perfect crystalline fibres (whiskers). In mechanical tests on whiskers of very pure metals and semiconductors [1], the measured strengths approached values of ~10 GPa, very close to theoretical predictions. Nowadays, nanoindentation experiments became used as a new and effective tool for approaching the TS limits and the obtained data contributed to a convergence of theoretical and experimental values [2].

The work is written as a commented collection of nine selected authors articles published in scientific journals or conference proceedings. The papers attempt to map more or less continuous author's effort to penetrate problems of theoretical strength calculations and their application in the field of materials science and engineering. The sequence of the papers was chosen so that it reflects a transition from the simplest analyses of TS of pure crystals to more sophisticated approaches, more complex loading conditions and to atomistic models of composites. The last part of the work is devoted to a multi-scale analysis of the nanoindentation test, where some of the previously obtained results can be directly applied.

Introduction is followed by a chapter containing a brief history of TS calculations as well as their recent development. Chapter 3 describes briefly the methods for ab initio calculations. A particular attention is devoted to three computational codes (TB – LMTO – ASA, VASP, Wien2k) that were employed in all the calculations discussed in the next chapter. Chapter 4 introduces examples of applications of the ab initio computational techniques. This chapter consists of nine sections, each containing individual comments to the selected papers [3–11].

2 THEORETICAL STRENGTH

2.1 APPLICABILITY OF TS CALCULATIONS IN MATERIALS ENGINEERING

The TS values set an upper limit to the envelope of attainable stresses and its knowledge enables us to assess the gap remaining to upper strength values of advanced engineering materials. Another reason for the TS investigation is that it plays a crucial role in the fundamental theory of fracture. For example, the stress necessary for nucleation of a dislocation loop can be identified with the shear TS value and the local stress for nucleation of a cleavage crack should overcome the tensile TS value [12]. The ratio of these values expresses a tendency of the crystal matrix to become brittle or ductile [13, 14]. Moreover, the TS values can be also used for calibration or checking of semi-empirical interatomic potentials that are currently used for study of extended defects.

From the practical point of view, the shear TS appears to control both the onset of fracture and the dislocation nucleation in defect-free thin films and, in particular, in nanostructured materials that are currently being developed. This has been con-firmed most eloquently by nanoindentation experiments [15] which suggest that the onset of yielding at the nanoscale is controlled by homogeneous nucleation of dislocations in a small, dislocation free, volume under the nanoindenter where stresses approach the TS. Therefore, starting from the beginning of the last century, there is a more or less continuous effort expended in order to obtain theoretical and experimental data concerning TS of various solids.

2.2 BRIEF HISTORY OF TS CALCULATIONS

2.2.1 Theoretical shear strength

Historically first calculations of shear strength were made 1926 by Frenkel [1, 16]. Model of a crystal subjected to shear is in Fig. 1 together with the related behaviour of the shear stress τ under applied shear deformation, expressed by the plane shift s. The $\tau(s)$ dependence was assumed to be of a sinusoidal shape.

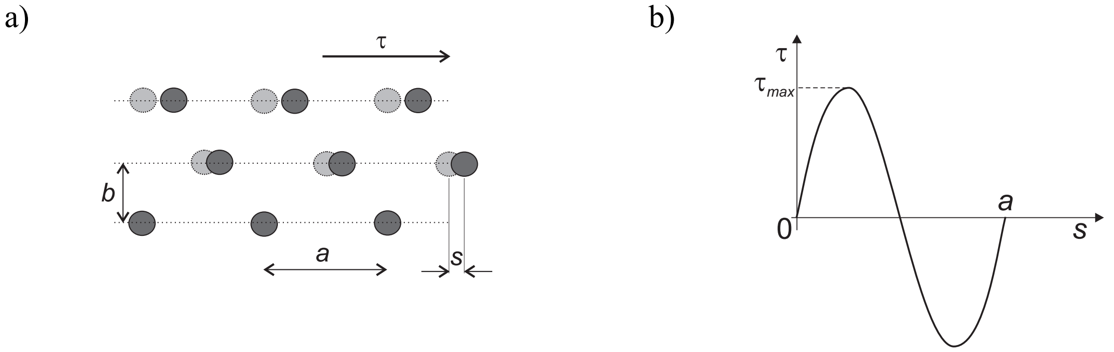

Figure 1: a) Model of a homogeneous shear deformation. Dark spheres represent atomic positions within atomic planes, mutually shifted by *s*, the light spheres show their original positions.
b) Shear stress τ as a function of shift *s* of two adjacent planes.

According to specification of variables in Fig. 1, the stress behaviour can be described by the relation

$$\tau = \tau_{\max} \sin \tfrac{2\pi}{a} s \, .$$

Next step is a calibration of the stress amplitude $\tau_{\max}$ that can be done using the shear modulus G. For a small shift, the shear modulus should be $G = \frac{d\tau}{d\xi}$, where $\xi = \frac{s}{b}$. The shear strength is equal to the derived

$$\tau_{\max} = \frac{Ga}{2\pi b},$$

that yields values $\tau_{\max}$ ~1/9G for $\{111\}\langle 11\bar{2}\rangle$ shear of fcc metals, $\tau_{\max}$ ~1/9G and $\tau_{\max}$ ~1/5G for $\{11\bar{2}\}\langle 111\rangle$ and $\{\bar{1}10\}\langle 111\rangle$ shears of bcc metals, respectively.

Mackenzie presented 1949 a more extended study of theoretical shear strength based on variation of potential energy U per unit area of a shear plane with plane shift s [1, 17]. From this perspective, the above described Frenkel's approach considers only first two terms in the Fourier series for $U(s)$. Mackenzie included further terms into consideration. The shear stress is computed from the energy U as

$$\tau = \frac{dU}{ds}. \tag{1}$$

Mackenzie's theory yielded results $\tau_{\max}$ ~1/30G for $\{11\bar{2}\}\langle 111\rangle$ shear in fcc lattice [1]. However, latter studies on shear strength [18] yielded $\tau_{\max}$ values of about 0.1G.

Further theoretical shear strength (TSS) calculations were performed with various models and methods [19, 20]. Most of them, however, used an analogy to Eq. (1). The potential energy U was calculated via summation of pair-potentials of various types as Morse potential, Lennard-Jones, etc [13, 18, 21, 22]. Nowadays, ab initio approaches enable us to compute the crystal energy in a very accurate manner (for simple crystals) [22, 23] or very sophisticated semi-empirical methods as potentials of Finnis-Sinclair type, embedded atom method or bond-order potentials are used for more complex studies [25–27].

Not just the methods for energy evaluation were upgraded during years, but also models of deformation processes experienced further development. The very first models assuming rigid shear planes in a constant distance [1, 13] were exchanged by more sophisticated models that enable to relax not only interplanar distance but also the arrangement of atomic positions within the planes [28–30].

2.2.2 Theoretical tensile strength

The first attempts to compute the theoretical strength in tension were performed by Polanyi [1, 31] (1921) and Orowan [32]. It was based on an assumption of brittle fracture of a stretched crystal. The basic idea is that when a perfect solid is stretched at absolute zero temperature, forces between two adjacent atomic planes (perpendicular to the loading axis) as well as tensile stress vary with the interplanar distance as in Fig. 2.

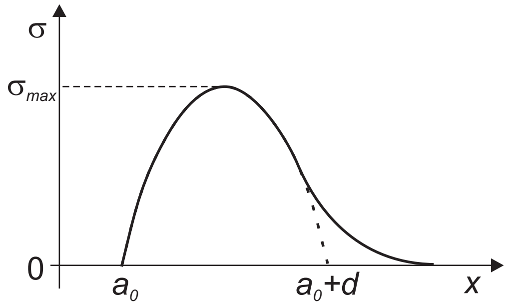

Figure 2: Tensile stress σ as a function of distance x of atomic planes.

The dependence was approximated by a sinusoidal function $\sigma = \sigma_{\max} \sin\frac{x - a_0}{d}\pi$ and the expected deviation from this trend for high strain values was neglected. The function was parameterized according to following two assumptions: i) the work of deformation per unit area corresponds to energy 2γ of the two new surfaces

$$\int_{a_0}^{a_0+d} \sigma dx = 2\gamma$$

and ii) in the vicinity of the equilibrium state ($x = a_0$), the stress is proportional to the Young's modulus and the relation $E = \frac{d\sigma}{d\varepsilon}$ must be valid for the strain $\varepsilon = \frac{x-a_0}{d}$. The maximum value of the tensile stress can be then evaluated as

$$\sigma_{\max} = \sqrt{\frac{E\gamma}{a_0}} .$$

Corresponding cleavage strengths of metals were mostly very high (several tens of GPa).

In the very first studies of TS, it has been assumed that the deformation proceeds in a stable manner until the applied stress reaches its maximum value, i.e. that the crystal fails in the same mode as it was deformed. This assumption was later disputed in many works [20, 33, 34]. Under certain tensile loadings, shear stresses in some slip systems can exceed their critical values (corresponding to the related TSS) well before the tensile stress reaches its maximum. This was observed also in experimental tensile tests on whiskers [1, 19]. Some of the whiskers evidently failed by cleavage across a favourable plane yielding apparently atomically smooth fracture surfaces. Thus, the definition of TS as a maximum attainable stress along the deformation path was assigned to a stress related to the first onset of instability.

Plenty of stability studies were based on analysis of elastic response of crystal subjected to small homogeneous deformations. Such analysis, based on calculations of independent elastic moduli, is often called elastic stability analysis and its application led, in some cases, to a significant decrease in theoretical strengths [7, 35–37].

A further step towards identification of the very first onset of instability was made by studies on phonon spectra of crystal states along investigated deformation paths. This approach has reduced the theoretical strengths even more [38]. The phonons are quasiparticles usually used to express the particle aspect of lattice vibrations. Although they play a major role e.g. in the theory of both thermal and electric conductivities, they can also serve as an indicator of lattice instability at zero absolute temperature.

Instability of the lattice is related to so-called soft phonon modes (at which the phonon frequency becomes an imaginary number). Such instabilities are responsible for various structural transitions [39]. They can be understood as an irreversible non-uniform (inhomogeneous) distortion of a crystal. In this aspect, the phonon analysis represents generalization of the elastic stability analysis because any observed elastic instability corresponds to a soft phonon mode with an infinite wavelength. Once the crystal becomes unstable, it will follow a trajectory in configurational space that will eventually violate the harmonic approximation inherent in the phonon calculation. Therefore, to find such trajectories requires molecular dynamic (MD) methods that can account for variations of the unit cell shape as well as the positions of constituent atoms.

Molecular dynamic methods are probably the most promising tools for investigation of system stability and eventual structure evolution during spontaneous structural transition. They can give sufficient number of degrees of freedom to the studied system and, furthermore, they can also incorporate finite temperatures and bring the simulations closer to reality. However, certain limitations related to computational capacity hinders to their wider distribution and application. Present MD methods are based mostly on empirical or semiempirical interatomic potentials. Quantum ab initio MD simulations [40] are computationally more demanding but, on the other hand, they represent very reliable tool for atomistic simulations.

3 COMPUTATIONAL METHODS

3.1 GENERAL INTRODUCTION

Calculations described in this work were performed with utilization of ab initio (first principles) methods. The fundamental problem of ab initio approaches, based on applied quantum theory, is to calculate stationary states for electrons in the electrostatic field of nuclei, i.e. the electronic structure (ES). The energy of this ground state can then serve as a potential energy for displacements of nuclei. From the point of view of TS calculations, the total energy of the system is the most important output of ab initio methods.

The main advantage of ab initio methods is their independence on experimental data. Unlike the empirical and semi-empirical methods, there is no need for calibration parameters. Thus, they can be used also for calculations of some structural and mechanical characteristics of hypothetical systems (prediction of properties of materials that have not been yet developed) or study of materials behaviour under large deformation (far from the equilibrium state) that can give a better understanding of micromechanisms of materials failure.

First attempts to develop applicable theories were made in late twenties [41], few years after the foundations of modern quantum theory were laid (derivation of the Schrödinger equation). A very successful step forward represented the Hartree-Fock method [42] (also called the self-consistent field method). This method yields very good bond lengths in molecules. On the other hand, the binding energies are generally not in a good agreement with experimentally obtained energies. Moreover, for solids, the Hartree-Fock method has problems with a description of band structures. The density functional theory (DFT) [43, 44] was invented to include correlation effects without using the very costly wave function methods. All the methods used within this work are based on the density functional theory.

In DFT the energy is not obtained as an eigenvalue of a wave function, but rather as a functional of the electron density. The complex problem of many interacting electrons is transformed into much simpler study of a single electron interaction with an effective potential U_{eff} created by other electrons and all nuclei. This is expressed by the Kohn-Sham equation (one-electron Schrödinger equation)

$$\left(-\Delta + U_{eff}(\vec{r}) - \varepsilon_i\right)\psi_i(\vec{r}) = 0 \,,$$

where ε_i represents one-electron energies and ψ_i are the one-electron wave functions.

The wave functions are then occupied in accordance with the Pauli principle and a new field is obtained by solving the Poisson equation for point nuclei shielded by the electronic cloud of the density

$$\rho(\vec{r}) = \sum_{i,occ} \left|\psi_i(\vec{r})\right|^2 \,.$$

In the case of periodic crystalline materials, the one-electron wave functions are expanded into appropriate basis sets and satisfy the Bloch theorem. The Kohn-Sham equation is solved iteratively till the solution becomes self-consistent, i.e., the electron density, determined from the effective one-electron potential, must generate the same effective potential (which is again a functional of the electron density). The self-consistent cycle usually starts with a guess of the effective potential (superposition of atomic-like potentials) and then the input and output potentials are appropriately mixed before starting a new iteration. The quality and speed of the convergence of such calculations is related not only to the choice of a suitable basis, but also to the sophistication of the iterative process. Necessary corrections for exchange and correlation are also included in effective potential U. This seems to be the crucial point of ab initio calculations because the exchange-correlation (XC) functional is not known exactly and must be approximated. The first (and the simplest) attempt to build an approximation of the exchange-correlation (XC) energy functional in the density functional theory is the local-density approximation (LDA) [45]. This approximation uses the XC energy of an electron in a non-interacting homogeneous electron gas of equivalent density as the XC energy of an electron in the system being calculated. The LDA is local in the sense that the electron exchange and correlation energy at any point in space is a functional of the electron density at that point only. As a consequence of this, LDA fails in situations where the density undergoes rapid changes (molecules).

An improvement to this can be made by considering the gradient of the electron density. The density gradient corrections are implemented in the so-called Generalized Gradient Approximation (GGA). While there is only one LDA there are several different parameterizations of the GGA [46]. Some of them are semi-empirical – experimental data (e.g. atomization energies) are used in their derivation. Others are derived entirely from first principles.

Various methods used for the electronic structure calculations may be distinguished according to the choice of the basis functions. The better we choose them (according to the character of the problem), the smaller number of them is needed for the description of one-electron wave functions. The next three chapters describe the basis sets implemented in three computational codes that were employed for all the presented calculations.

3.2 PARTICULAR COMPUTATIONAL CODES

3.2.1 TB – LMTO – ASA code

Linearized ab initio methods have been successfully utilized for solving many problems in solid state physics and materials science [47]. One of the most effective approaches for early first principles calculations was the linear muffin-tin orbital (LMTO) formalism which has been continuously developed since 1980 [48]. This method is very appropriate for the self-consistent calculations.

The TB – LMTO – ASA code was developed in Max-Planck-Institut für Feskörperforschung in Stuttgart and its description can be found in the user's guide [49]. The crystal potential U is approximated by a muffin-tin shape potential which is composed of a set of spherically symmetrical potentials inside slightly overlapping spheres around individual nuclei and a constant potential in the interstitial region outside the spheres (Fig. 3). Atomic-like orbitals derived for the MT potential constitute a suitable basis set. In order to avoid problems arising from an infinite range of conventional solid-state muffin-tin orbitals (MTO's), the tight binding (TB) MTO's [50] were proposed. They represent short-ranged linear combinations of the conventional set.

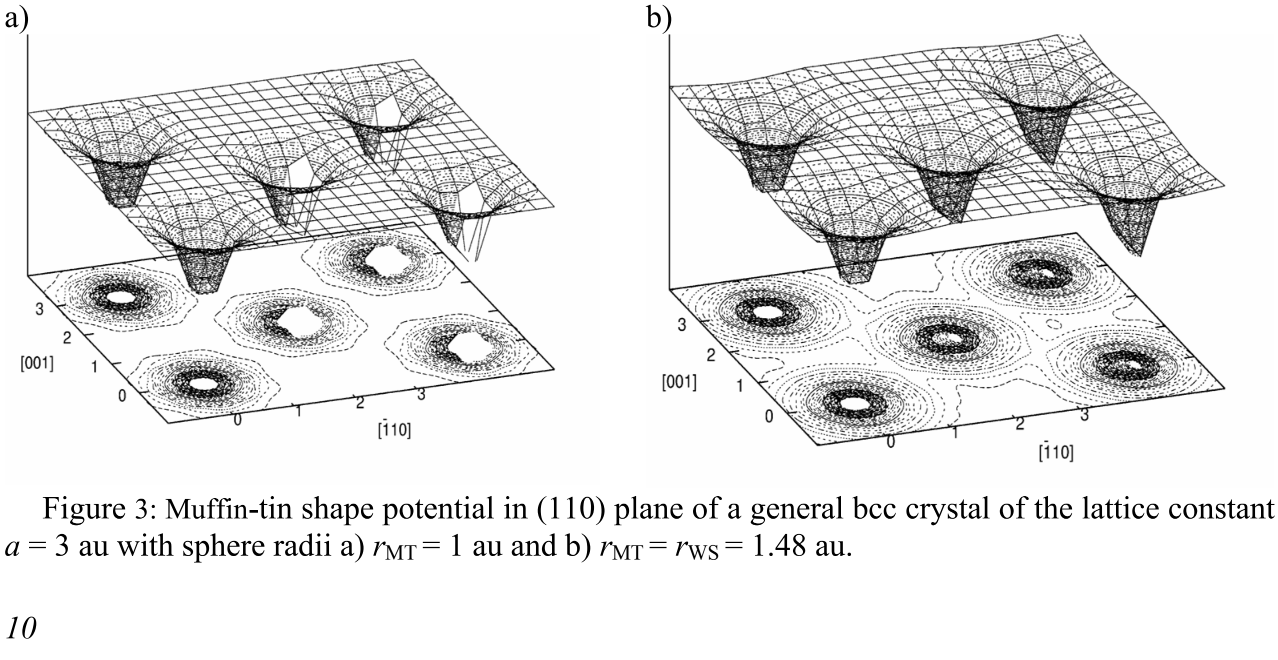

Figure 3: Muffin-tin shape potential in (110) plane of a general bcc crystal of the lattice constant $a = 3$ au with sphere radii a) $r_{\mathrm{MT}} = 1$ au and b) $r_{\mathrm{MT}} = r_{\mathrm{WS}} = 1.48$ au.

In all presented calculations, the LMTO method is used in the framework of an Atomic Sphere Approximation (ASA) which is particularly suitable for closely packed structures like fcc or bcc [47]. The size of a spherically symmetric potential is assumed to be equal to that of the Wigner-Seitz cell (Fig. 3b). It suppresses the interstitial region and neglects the kinetic energy of related free electrons. Owing to the necessary space-filling condition, ASA represents a physically plausible model only for description of an infinite system of atomic spheres.

3.2.2 Wien 95–w2k codes

Computational codes Wien95, Wien97 and w2k (Wien2000) were written at Vienna University of Technology, Institute of Physical and Theoretical Chemistry, Austria. All the codes are individual versions of program package WIEN [51].

This code does not use any shape approximation to the potential. The crystal environment is divided into a region of non-overlapping atomic spheres (centred at individual atomic sites) and an interstitial region as can be seen in Fig. 4. In order to describe ES reliably and effectively, two different basis sets are employed: a product of linear combination of radial functions and spherical harmonics are used inside the spheres whereas the wave functions in the interstitial region are expanded into a linear combination of plane waves. Solution in both regions must be continuous at the sphere boundary. Each basis function is then defined as a plane-wave in the interstitial region connected smoothly to a linear combination of atomic-like functions in the spheres, thus providing an efficient representation throughout the space. A similar representation is used for potentials and charge densities. The method is called Linear Augmented Plane Wave (LAPW) method [47].

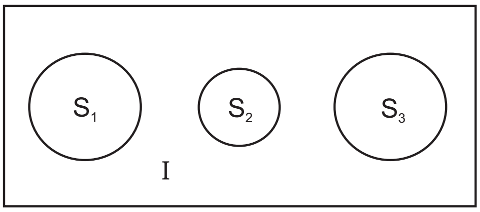

Figure 4: Illustration of a crystal model – three atomic spheres ($S_1 - S_3$) with potential $U_S(r) = \sum_{lm} U_{lm}(r) Y_{lm}(\hat{r})$ embedded in the interstitial region I with $U_I(\vec{r}) = \sum_{K} U_{\vec{K}}(r) e^{i\vec{K}\vec{r}}$.

With respect to the fact that no shape approximation to the potential is made, a method of treating the electronic structure implemented within WIEN code is called full-potential LAPW [52].

In order to increase the flexibility of the basis (to improve upon the linearization of wave functions) and to make possible a consistent treatment of semicore and valence states in one energy window (to ensure orthogonality) additional basis functions can be added. They are called local orbitals [53] and consist of a linear combination of two radial functions at two different energies (e.g. at the 3*s* and 4*s* energy) and one energy derivative (at one of these energies). The local orbitals are normalized and have zero value and slope at the sphere boundary.

3.2.3 VASP code

Another way how to avoid a problem with plane wave basis set in vicinity of atomic nuclei, where number of plane waves would exceed any practical limits (perhaps except for H or Li), is to substitute the exact potential by a pseudopotential.

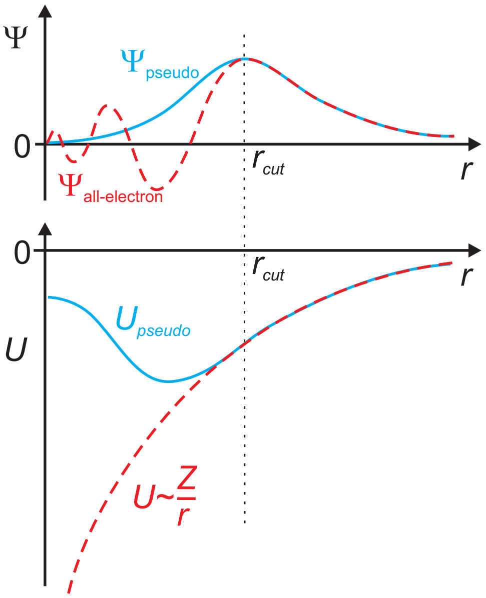

Figure 5: Comparison of a wavefunction in the Coulomb potential of the nucleus (dashed lines) to that in the pseudopotential (solid lines).

Construction of pseudo-wavefunctions is schematically described in Fig. 5 [54]. The Coulomb potential of the nucleus and corresponding wavefunction are represented by dashed line. The solid line displays pseudopotential and pseudo-wavefunction. The real and the pseudo-wavefunction (and also the potentials) match above a certain cutoff radius r_{cut}.

The pseudopotential approach has been implemented in VASP (Vienna Ab initio Simulation Package) code. This code was built at Institut für Materialphysik, Universität Wien. The VASP currently supports three types of pseudopotentials: norm-conserving pseudopotentials [55], ultrasoft pseudopotentials [55] and projector augmented waves pseudopotentials [56]. In all three cases, the core electrons (at lower energy levels than valence electrons) are precalculated in an atomic environment and kept "frozen" in the course of the remaining calculations.

4 APPLICATIONS

4.1 THEORETICAL ISOTROPIC STRENGTH

One of the applications of ab initio methods is calculation of the theoretical strength under isotropic (hydrostatic) loading (TIS). The knowledge of TIS and the theoretical shear strength allows for the assessment of both the ductile/brittle response and the crack stability in solids [14]. On the other hand, there are no experimental data for isotropic strength. The reason lies in difficulties in experimental realization of isotropic tensile loading. Thus, a theoretical assessment remains the only applicable tool to gain such information.

Summary of computed TIS values can be found in Table 1 and in Ref. [3]. The presented isotropic strength values correspond to stresses at the onset of a volumetric instability. The data in Table 1 were taken from LMTO [57, 58] and VASP [9, 29] calculations and semiempirical (polynomial, Morse, sinus) methods [22, 59].

The minor differences between LMTO computed values in Table 1 (and in Table 1 in Ref. [3]) are caused by slightly different computational conditions (different version of computational code, different number of *k*-points).

Table 1: Theoretical isotropic strength σ_{iso} from two ab initio (LMTO – ASA [57, 58], VASP [9, 29]) and several semiempirical (polynomial, Morse and sinus [22] and Discrete Variation Cluster (DVC) [59]) approximations.

crystal		Theoretical strength σ_{iso} (GPa)							
		Ab initio results				Semiempirical results			
		LMTO LDA	LMTO GGA	VASP Ref. [9]	VASP Ref. [29]	poly	Morse	sinus	DVC
Li	bcc	3.53	3.13			5.06	2.49	4.91	1.92
C	dia	66.1	53.2	88.5^a	88.5^a	84.7	69.7	138	
Na	bcc	1.97	1.55			1.87	1.20	1.86	1.77
Al	fcc	13.8	12.0		11.2^b	22.2	11.9	23.0	
Si	dia	15.0	10.4	15.5^a	15.4^a	15.1	13.7	28.2	
K	bcc	0.955	0.701			0.99	0.659	1.28	0.10
V	bcc	39.2	33.2	32.7^b		32.6	23.5	45.4	38.3
Cr	bcc	37.2	21.0			35.2	25.9	50.2	47.4
Fe	bcc	37.7	26.7	27.7^b	28.5^b	33.8	24.1	48.1	
Ni	fcc	39.5	27.4	28.9^b	29.2^b	44.7	26.9	51.2	
Cu	fcc	28.8	20.9	19.8^b	20.4^b	32.7	19.9	38.4	
Ge	dia	11.0	6.46	11.1^a		11.3	10.1	21.4	
Nb	bcc	36.3	31.6	31.6^b		35.5	25.5	49.4	34.1
Mo	bcc	49.3	42.7	42.9^b	43.2^b	48.2	35.0	68.9	42.2
Ag	fcc	19.0	12.6		17.6^a	20.2	13.7	26.7	
Ba	bcc	2.69	1.93			2.36	1.64	3.17	
Ta	bcc	41.3	36.4			39.2	28.5	55.1	41.3
W	bcc	57.0	50.6	50.7^b	50.2^b	56.1	42.2	80.1	53.1
Ir	fcc			40.1^b		61.2	45.6	85.6	
Pt	fcc	42.7	33.6	39.6^a		48.5	35.1	68.0	
Au	fcc	25.5	17.6	23.2^a	23.5^a	28.4	20.9	39.9	
Pb	fcc	8.7	6.98			7.91	5.47	10.6	

^{a}LDA
^{b}GGA

4.2 THEORETICAL ISOTROPIC STRENGTH OF MAGNETIC MATERIALS

Some of elements in the periodic table have a magnetic moment in their atomic ground state. The major role in magnetism plays the spin of electrons that is not included in equations of non-relativistic quantum mechanics. The simplest way how to introduce the electronic spin into ab-initio study is an ad hoc approach called the spin polarization. Heart of the spin-polarized calculations dwells in a separate treatment of self-consistent charge densities for each spin orientation.

With respect to the nature of the participating electrons in solids, we can distinguish two different types of magnetism, itinerant and localized. The localized states are well described by the atomic theory, including the Hund's rules, with corrections due to the influence of the crystal fields. The itinerant magnetism is always a result of the competition of the exchange interaction between valence electrons that favours spin polarization and the hybridization that causes band formation and favours a paramagnetic ground state.

A simple and useful model for the itinerant magnetism is the Stoner model. According to this model, magnetic ordering is energetically favourable for systems with sufficiently high density of states (DOS) at Fermi level. This model correctly predicts magnetism e.g. for 3*d* transition metals. As an example, total DOS for Ni was computed using the VASP code employing the PAW – GGA pseudo-potential with 20x20x20 *k*-points and plane-wave cutoff of 350 eV. The results of magnetic (spin-polarized) as well as non-magnetic calculations at equilibrium lattice parameter a_0=3.52 Å are displayed in Fig. 6.

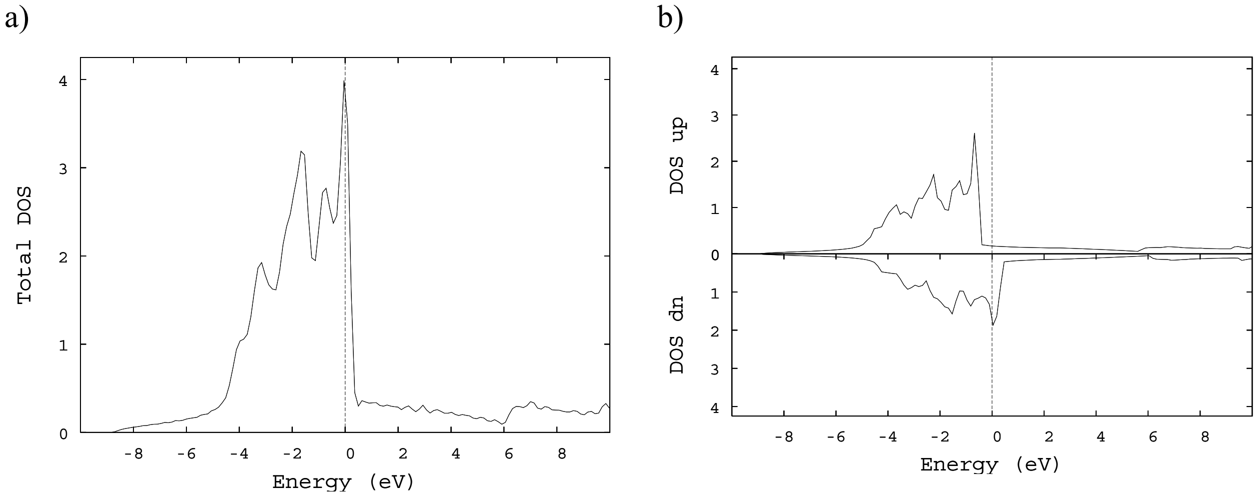

Figure 6: The density of valence states in fcc Ni computed a) without and b) with the spin-polarized approach. The zero energy was assigned to the Fermi level.

The Fermi level in Ni is localized right at the peak in DOS computed without spin-polarization (non-magnetic calculation) (Fig. 6a) and the Stoner model predicts magnetic ordering. The corresponding DOS for both spin orientations are displayed in Fig. 6b. A difference of integrated DOS for both spin orientations up to the Fermi level yields an approximate value of a magnetic moment (in Bohr magnetons) per atom.

Numerous authors [60–62], have shown that neglecting the magnetic ordering in magnetic materials as Fe, Co and Ni leads to an incorrect prediction of the ground-state structure as well as some material properties. The results presented in Ref. [4] for four magnetic crystals lead to the same conclusion. Moreover, it was found that introduction of the magnetism into calculations can also substantially lower the TIS values.

4.3 STABILITY ANALYSIS OF ISOTROPICALLY LOADED CUBIC CRYSTALS

The theoretical isotropic strength (TIS) values of cubic crystals presented in the previous two chapters were identified with the maximum tensile stress along the isotropic deformation path. It was widely believed that in cubic lattices, particularly under such kind of loading, no other instability precedes the moment of reaching the maximum stress value. The main aim of the work presented in Ref. [5] was to verify validity of this presumption.

Elastic stability of crystals can be assessed using so called Wallace matrix [63, 64]. Such matrix corresponding to the cubic system (with 48 symmetry operations) under applied isotropic loading ($\sigma_1 = \sigma_2 = \sigma_3 = \sigma$) has the symmetric form

$$\hat{B} = \begin{vmatrix} C_{11}+\sigma & C_{12}-\sigma & C_{12}-\sigma & 0 & 0 & 0 \\ C_{12}-\sigma & C_{11}+\sigma & C_{12}-\sigma & 0 & 0 & 0 \\ C_{12}-\sigma & C_{12}-\sigma & C_{11}+\sigma & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44}+\sigma & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44}+\sigma & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{44}+\sigma \end{vmatrix}$$

and a requirement of its positive definiteness (all the principal minors must be positive) yields a set of stability conditions

$$\begin{aligned} &i \quad C_{11}+2C_{12}-\sigma>0 \\ &ii \quad C_{11}-C_{12}+2\sigma>0 \\ &iii \quad C_{44}+\sigma>0 \end{aligned} \tag{2}$$

that are in a coincidence with conditions derived for equal definition of elastic moduli elsewhere [63–64].

Each of the criteria can be tested using an energetic response of the crystal to small deviations from the reference state. The condition (2 *i*) expresses the response to the isotropic (hydrostatic) loading. Breaking this criterion can be perceived as reaching the maximum isotropic stress. Basically, this condition was inadvertently tested in all TIS calculations (also in those presented in Refs. [3, 4]). The conditions (2 *ii*) and (2 *iii*) are related to crystal responses the tetragonal and the trigonal deformations, respectively.

The necessary additional deformations from the reference states are described in detail e.g. in Ref. [23]. The atomic configurations corresponding to the deformed structures usually have lower symmetries and, at the strength limit, they are very far from the lowest-energy equilibrium state. Therefore, to obtain reliable structural energy differences, the full-potential methods (i.e. without any shape approximation of the interstitial crystal potential and the valence charge density) have to be utilized in such studies. Wien2k and VASP codes were employed for this purpose.

A proper study of the elastic stability of three fcc metallic crystals (Al, Cu, Ag) under hydrostatic tension that is presented in Ref. [5] shows that aluminium is the only crystal, among those investigated, where the shear instability precedes the moment of reaching the maximum isotropic stress in the region of tensile stresses.

4.4 STABILITY ANALYSIS OF ISOTROPICALLY LOADED MAGNETIC CRYSTALS

The stability of magnetic metals strongly depends on their magnetic ordering. An example of the direct influence of magnetism on structural stability can be found in study of phonon spectra in a fixed-spin-moment scheme performed by Hsueh et al. [65]. Their results for α-Fe, bcc Co and bcc Zr show that an enhancement of the magnetic moment can stabilize the crystal lattice whereas; when it is suppressed, soft phonon modes appear indicating instability.

In Ref. [6], the elastic stability analysis is presented for three magnetic metals (Cr, Fe, and Ni) subjected to isotropic tensile and compressive loading. Unlike the work of Hsueh et al., the magnetic moment was not an adjustable parameter. Its value was computed to correspond to the ground-state electronic structure of any crystal state. In the region of tensile stresses, no instability was found to precede the volume instability related to the inflection point on energy-volume dependence. On the other hand, a kind of shear instability was observed in case of iron in the compressive region. This instability was accompanied by a sharp decrease of the magnetism in bcc ferro-magnetically ordered crystal. The Fig. 7 displays the density of states (DOS) in bcc iron at two relative volumes: the equilibrium volume $v = 1$ and the volume $v = 0.66$ corresponding to the onset of tetragonal shear instability. The magnetic moment in the equilibrium is 2.20 μ_B per atom and decreases to value of 1.22 μ_B per atom when the relative volume decreases to 0.66.

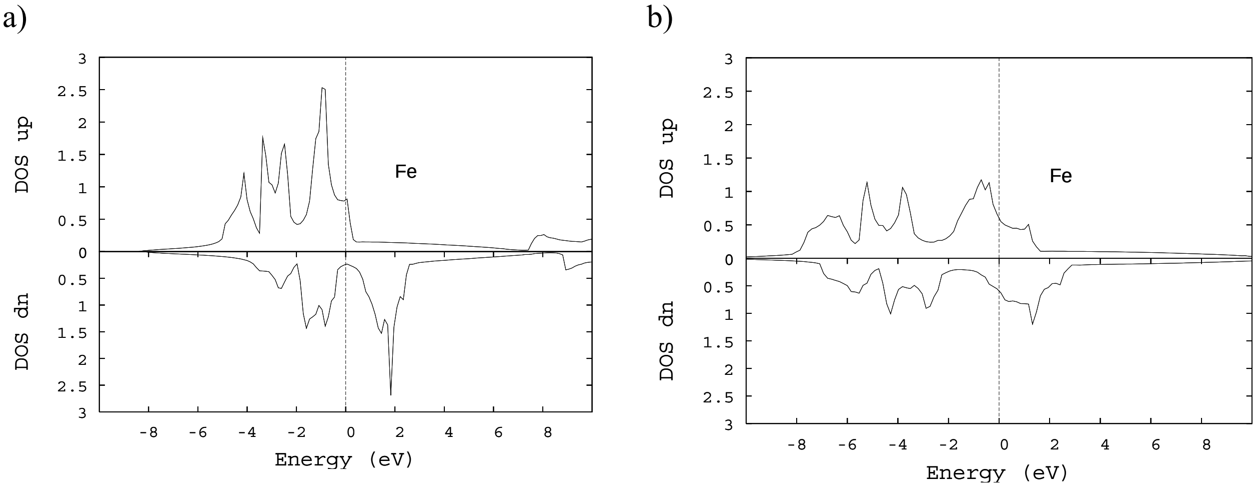

Figure 7: The density of states in iron crystal at a) equilibrium volume ($v = 1.0$, $a_0 = 2.83$ Å and b) at the first onset of instability in the compressive region ($v = 0.66$, $a_0 = 2.46$ Å). The zero energy is set to the Fermi level.

The DOS plot was generated from values computed by the VASP code with settings as described in Ref. [6] (PAW pseudopotential, GGA, 20x20x20 *k*-points).

4.5 UNIAXIAL LOADING OF ELEMENTAL CRYSTAL

When a uniaxial stress is applied to any cubic crystal, its symmetry decreases. In case of the uniaxial loading in [001] direction, the crystal acquires a tetragonal symmetry with 16 symmetry operations. A model of two adjacent cells subjected to [001] loading is displayed in Fig. 8.

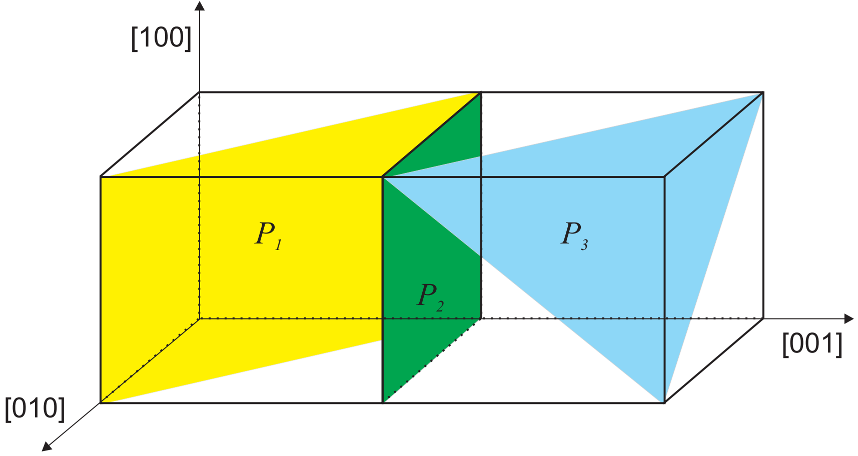

Figure 8: Illustration of a lattice extended in [001] direction with examples of one cleavage (P_2) and two possible shear (P_1 and P_3) planes.

Experiments on whiskers [1, 19, 66] suggested that, under such particular loading, the lattice usually fails by shear in {111} plane (P_3 in Fig. 8) in fcc systems or in {110} plane (P_1 in Fig. 8) in bcc systems rather than by cleavage along {001} plane (P_2 in Fig. 8) as was assumed in the very first calculations of tensile strength [1] or even in some later studies [67–70].

The elastic matrix of such system contains six independent elements and the corresponding stability analysis is presented e.g. in Ref. [7] for a particular case of copper and in Refs. [23, 35]. As was found, the copper crystal is expected to fail in shear (stability condition 3*b* in Ref. [7]) at the tensile stress of 9.4 GPa, well before the tensile instability (condition 3*a* in Ref. [7]) can take place (24.3 GPa).

4.6 UNIAXIAL LOADING OF NANOCOMPOSITES

The perfect single crystalline wires (whiskers) are used as reinforcements in advanced composite materials. A first principles study of metallic nano-fibres in metallic matrix under uniaxial tensile loading applied parallel to the fibres is presented in Ref. [8]. The results reported therein, as well as in Refs. [71] and [72], show that, although quantities as the equilibrium volume or bulk modulus more or less follow a simple linear mixture rule, the theoretical strength of the reinforcing material can be reached (or even exceeded) at certain atomic concentration (60–80 %) of the reinforcement (see Fig. 9). This very interesting result is worth subjecting to further study. A possible explanation can be the fact that, due to the lattice mismatch, fibres are under transversal tensile or compressive stresses that can influence the stress-strain response and, thus, the uniaxial tensile strength of the whole composite.

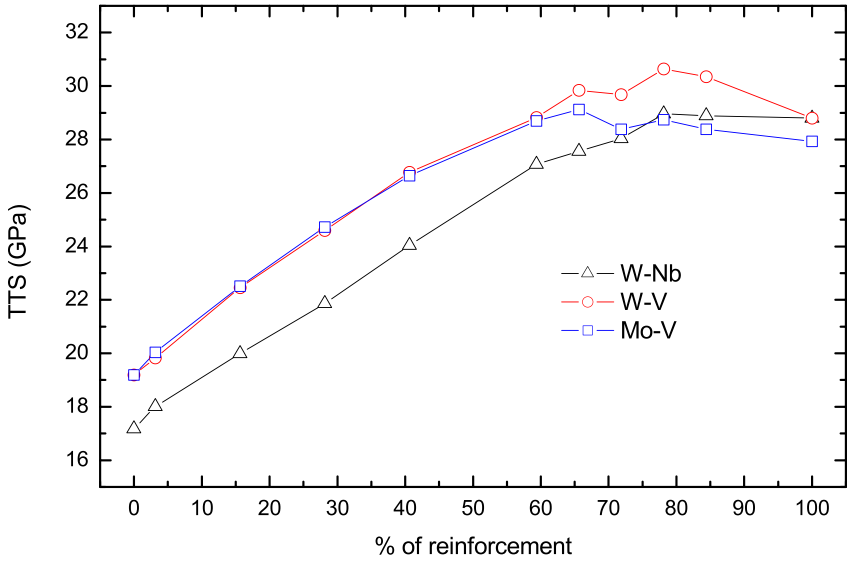

Figure 9: Theoretical tensile strength as a function of atomic concentration of reinforcing fibres for three composites. The fibres are made of W or Mo, whereas the matrix consists of V or Nb atoms.

It should be noted, however, that the crystal model has only limited number of degrees of freedom (given by a size of the supercell composed of 4x4x1 elementary bcc cell) and, thus, its stability is not guaranteed along the whole deformation path.

4.7 COUPLING OF UNIAXIAL AND BIAXIAL STRESS TENSOR COMPONENTS

In order to describe the influence of superimposed transversal biaxial (plane) stress on the theoretical tensile strength of metallic fibres in nanocomposites, a corresponding study was performed for a bulk system representing ideal crystals of several metallic and covalent systems. Results of the analysis are presented in Ref. [9].

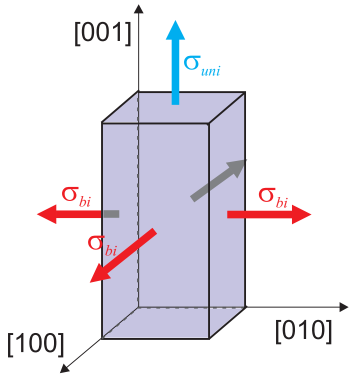

Figure 10: Illustration of a triaxial stress state that comprises a tensile stress in [001] direction σ_{uni} and superimposed transverse biaxial stresses σ_{bi}.

This particular study is focused on cubic (and diamond) structures subjected to a superposition of tensile stress in [001] direction σ_{uni} and transverse biaxial stresses σ_{bi} as can be seen from Fig. 10.

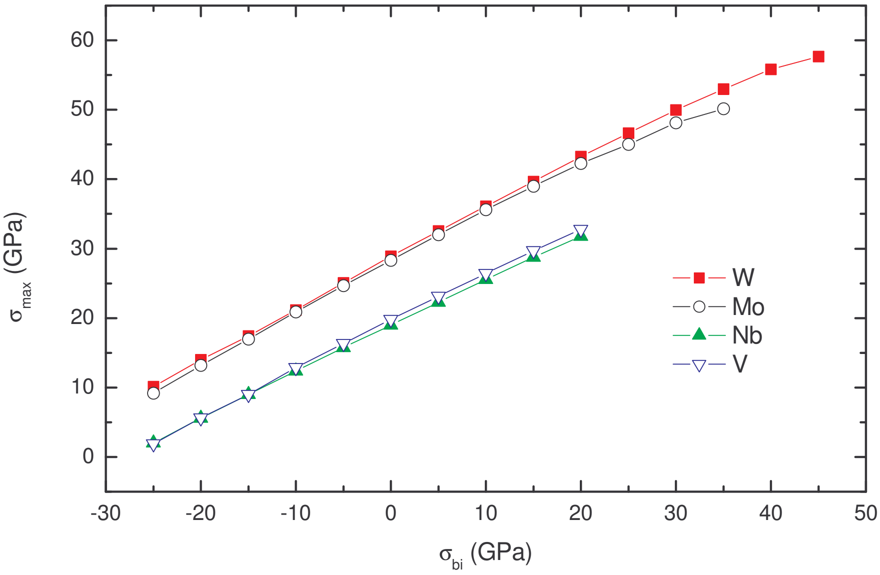

Figure 11: Dependence of the theoretical tensile strength σ_{max} on perpendicularly acting biaxial stresses σ_{bi} for W, Mo, Nb and V.

The results obtained for four metals mentioned in the previous chapter are displayed in Fig. 11. As can be seen from the graph, the tensile strength increases (almost linearly) with the applied biaxial stresses. Thus, the reinforcing fibre (as well as the matrix) subjected to tensile transverse stresses induced by incompatibility strain (lattice mismatch) can exhibit higher strength.

4.8 THE SHEAR STRENGTH UNDER SUPERIMPOSED NORMAL STRESS

Another possible example of coupling between two stress tensor components that can be of a high engineering importance is an influence of the stress acting perpendicularly to slip planes upon the strength during the simple shear as displayed in Fig. 12 for a particular case of $\langle\bar{2}11\rangle\{111\}$ shear in fcc lattice. Results of such analyses are presented in Ref. [10] for three bcc metallic crystals and in Refs. [30, 73] for several fcc ones.

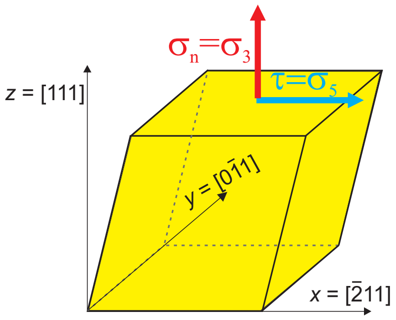

Figure 12: Model of a crystal under superposition of shear τ and normal σ_n stresses.

It should be noted that the relaxation procedure used in Ref. [73] comprised just a relaxation of distances between the slip planes but did not include the relaxation of ionic positions within the planes (in-plane relaxation). On the other hand, the in-plane relaxation was added to the procedure used in Ref. [10] and in recent work [30].

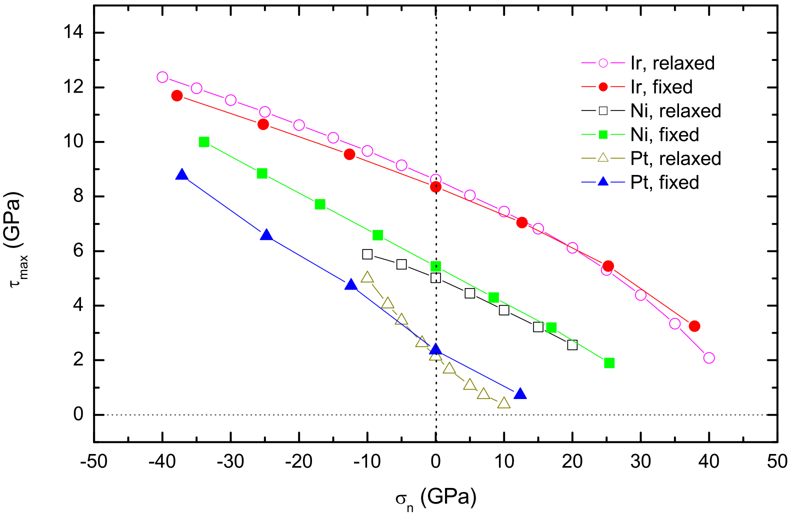

Figure 13: Influence of normal stress σ_n upon the shear strength τ_{max} in Ir, Ni and Pt computed with and without in-plane relaxation.

Few examples of the obtained results are included in Fig. 13. The displayed data correspond to computed values for $\langle\bar{2}11\rangle\{111\}$ shear in three selected crystals with rigid planes (solid symbols) and with full relaxation of transverse stresses (open symbols).

It seems to be apparent that the compressive (tensile) force can substantially increase (decrease) the shear strength of the crystals. The influence can be approximated by a linear function (particularly in the region of compressive normal stresses), in a suitable analogy to the well known relation between the friction and the normal forces exerted to sliding surfaces. As can be also seen from Fig. 16, the in-plane relaxation has only small influence on computed data for Ir.

4.9 TWO-SCALE ANALYSIS OF NANOINDENTATION PROCESS

A particular application of calculations described in the previous section is an analysis of the nanoindentation experiment data that can be found in Ref. [11]. This analysis proceeded at two different levels (two length scales as well as two different approaches). The first level is represented by a finite element analysis of the stress distribution under the nanoindenter. The stress field under frictionless sphero-conical indenter was computed in a fine mesh that was refined in vicinity of the interface to get sufficiently small elements in comparison with the penetration depth.

The other level corresponds to an atomistic scale. Here, the results of ab initio study of the normal stress influence on the theoretical shear strength in Cu [73] were employed. The onset of microplasticity, associated with the pop-in effect identified in experimental nanoindentation tests (creation of first dislocations), is assumed to be related to the moment of achieving the value of the ideal shear strength for the copper crystal. However, the model used in Ref. [11] does not take into account neither crystallography nor the nonlinearity in the stress-strain relation. Subsequently, the calculated critical values of the load and the indenter displacement lie exactly at the lower limit of the range of experimentally observed pop-ins.

Our recent study [74] includes both the above mentioned corrections along with an additional one related to friction forces between the surfaces of indentor and the substrate. Calculated values of the critical indentation depth lie within the range of experimentally observed pop-ins in the copper crystal. The related indentation load is somewhat lower than that observed in the experiment.

5 CONCLUSION

A development of powerful computers and effective computational methods enabled materials scientists to study materials microstructure also on a theoretical basis with unprecedented reliability so far. The ability to simulate various processes in condensed matter yielded a deeper insight into micromechanisms of materials fracture that helps materials engineers in their effort to design materials with required mechanical, magnetic, electrical or optical properties.

This work is focused on computer modelling of electronic structure of materials using first principles approaches. Output of such calculations is used to predict crystal behaviour under applied loading, in particular, to evaluate its elastic response and strength.

It could be seen from the several examples presented here that a proper computational study requires a very careful treatment that includes translation of an engineering problem to the language of atomistic simulations, an application of suitable computational procedures and, finally, a correct interpretation of the obtained data.

The summary of the most important conclusions that can be found in this work and in the selected applications (also reported in the papers [3–11]) is as follows:

- A formulation of elastic stability conditions depends on a definition of elastic moduli and strain variables.
- When the crystals of elemental metals are subjected to the isotropic tensile loading they usually remain elastically stable up to the onset of tensile instability related to the stress maximum. This was proved by calculations assuming zero absolute temperature for particular cases of silver, copper, iron, chromium and nickel. On the contrary, aluminium is expected to fail by shear prior to the onset of the tensile lattice instability.
- A copper single crystal subjected to the uniaxial loading in [100] direction becomes unstable with respect to shear deformation well before a tensile instability (tearing) can occur. The corresponding tensile strength is then reduced to about one third of the tearing stress.
- Ideal fibre-reinforced metallic nanocomposites exhibit maximum strength values when the atomic concentration of the reinforcing material reaches the value of 60–80 %. A possible

explanation of the above mentioned result lies in the fact that the tensile strength of many cubic metals can be influenced by superimposed transverse biaxial stresses. When the reinforcing fibre is subjected to tensile biaxial stresses, its tensile strength usually increases.

- Study of a shear deformation under a superimposed normal stress suggested that the shear strength can be raised by application of a compressive stress to slip planes and lowered by a tensile stress. The corresponding dependence seems to be well approximated by a linear function.
- The increase of the shear strength under superimposed compressive normal stress plays significant role in a model describing deformation processes in the vicinity of a nanoindentor. In this way, the nanoindentation was proved to be an efficient tool for experimental determination of the ideal shear strength.

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SHRNUTÍ

Rozvoj výpočetní techniky a účinných algoritmů umožnil fyzikům, chemikům a materiálovým vědcům studovat mikrostrukturu materiálů s užitím velmi spolehlivých teoretických přístupů. Možnost simulovat různé stavy a procesy v pevných látkách vedla k lepšímu pochopení mikromechanismů porušování materiálů a pomohla materiálovým inženýrům v jejich úsilí vyvíjet materiály s požadovanými mechanickými, magnetickými, elektrickými či optickými vlastnostmi.

Tato práce se zabývá studiem elektronové struktury materiálů pomocí prvoprincipiálních metod. Výstupy provedených výpočtů byly využity k předpovědi chování materiálů za různých podmínek zatěžování, zejména pak k předpovědi elastických odezev a výpočtu teoretických pevností. K úspěšnému využití takových metod je zapotřebí vykonání několika důležitých kroků, které zahrnují zejména převedení inženýrského zadání na problém počítačové simulace na atomární úrovni, výběr a použití vhodných výpočetních metod a postupů a následně správné vyhodnocení a interpretace získaných dat. Toto je demonstrováno v předkládané práci na řadě příkladů. Výpočetní metody, kterých autor při práci využil, jsou založeny na teorii funkcionálu elektronové hustoty. Tato teorie umožňuje výpočetně zvládnutelné přibližné řešení problémů kvantové mechaniky. Pro aplikaci takových metod na konkrétní zadání je však nutné je vhodně zkombinovat např. i s krystalografií či mechanikou kontinua.

Předkládaná práce je koncipována jako komentovaný soubor devíti autorových prací [3–11] publikovaných v odborných časopisech a sbornících mezinárodních vědeckých konferencí. Výběr prací se snaží zmapovat víceméně trvalé autorovo úsilí proniknout do zmíněné problematiky výpočtů teoretické pevnosti a jejího využití v oblasti materiálových věd a inženýrství, jejich pořadí pak odráží přechod od nejjednodušších výpočtů teoretické pevnosti elementárních krystalů k sofistikovanější analýze jejich stability, složitějším zatěžovacím podmínkám a atomárním modelům kompozitů. Poslední z komentovaných prací [11] je věnována víceúrovňovému modelu nanoindentačního testu, který byl vytvořen i na základě výstupů předchozích studií.