MASARYK UNIVERSITY
Faculty of Science
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PhD Thesis

Electronic structure, phase transformations and stability of phases

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Abstract

The present thesis is focused on the calculation of electronic structure, elastic properties and structural behavior of various magnetic phases of iron and two transition metal disilicides, $MoSi_2$ and WSi_2, with $C11_b$ structure. For all ab initio electronic structure calculations, the all-electron full potential linearized augmented plane wave method (FLAPW) within the framework of density functional theory (DFT) implemented in Wien97 package is used.

The first part of the work is devoted to iron and both the local density approximation (LDA) and generalized gradient approximation (GGA) for exchange and correlation energy is employed. Tensile test in ferromagnetic iron for loading along the [001] and [111] directions is simulated and the values of theoretical tensile strengths ($\sigma_{\rm th}^{[001]} = 12.7$ GPa and $\sigma_{\rm th}^{[111]} = 27.3$ GPa within GGA, $\sigma_{\rm th}^{[001]} = 13.2$ GPa and $\sigma_{\rm th}^{[111]} = 34.2$ GPa using LDA) as well as Young moduli ($Y^{[001]} = 155$ GPa and $Y^{[111]} = 285$ GPa within GGA, $Y^{[001]} = 200$ GPa and $Y^{[111]} = 370$ GPa using LDA) are determined and compared with those of other materials. The magnetic and elastic behavior of iron under uniaxial tensile loading is discussed in detail and compared with the results for triaxial loading (theoretical triaxial tensile strength $\sigma_{\rm th}^{\rm tri}$ was found to be 28 GPa within GGA and 36.6 GPa within LDA, very close to the value for uniaxial [111] loading). Marked anisotropy of theoretical tensile strength in [001] and [111] direction is explained in terms of existence of higher-symmetry structures along the deformation paths.

A detailed theoretical study of magnetic behavior of iron along the tetragonal bcc-fcc (Bain's) and trigonal transformation paths at various atomic volumes is presented. The total energies and magnetic moments are calculated within both GGA and LDA and are displayed in contour plots as functions of deformation and volume. The borderlines between the non-magnetic, ferromagnetic and selected antiferromagnetic phases are shown. Stability of tetragonal and trigonal magnetic phases of γ-Fe is discussed.

The calculated phase boundaries are used to predict the lattice parameters and magnetic states of iron overlayers on various (001) and (111) substrates. Detailed comparison of the LDA and GGA results is performed. The theoretical results obtained within the GGA are in a very good agreement with available experimental data verifying our theoretical approach. Further, the instability of the antiferromagnetic fcc γ-Fe with respect to tetragonal distortion is confirmed.

In the second part, the results obtained for elastic properties and electronic structure in transition metal disilicides $MoSi_2$ and WSi_2 with $C11_b$ structure over wide range of tetragonal lattice parameters are presented. Here the LDA for exchange-correlation energy is employed. Similarity in behavior and structural parameters of materials studied is demonstrated.

Also here the uniaxial tensile test along the [001] direction is performed. The theoretical tensile strengths of both disilicides for [001] loading are determined (37 GPa for $MoSi_2$ and 38 GPa for WSi_2) and are compared with those of other materials.

Here full relaxation of both external and internal structural parameters is included and influence of each relaxation process on energetics and elastic properties of materials is studied. The effect of two different relaxation processes on the total energy and interatomic bonds is examined in detail and a new metastable state is found. The analysis of bond lengths variation under uniaxial stress shows that it is possible to distinguish "strong" and "weak" TM-Si bonds. The behavior of Si-Si bonds is more complex and exhibits a tension-compression asymmetry connected with relaxation of internal parameter of $C11_b$ structure that favors cooperative movement of Si atoms.

The epitaxial growth conditions at various (001) substrates are simulated and calculated elastic properties including Young and bulk moduli of single-crystal materials are applied to epitaxial thin films of materials studied with special attention paid to the behavior of the internal parameter.

Finally, the total energies and fully relaxed values of internal parameter connected with the $C11_b$ structure are displayed in contour plots as functions of tetragonal lattice parameters and the influence of internal parameter on the total energy is demonstrated in the form of an analogous contour plot of the total energy. Results for all states are then compared to improve physical and chemical understanding of the behavior of interatomic bonds under various loading conditions.

Publications

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