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Study of structural phase transitions in solids by ab initio simulations

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(meno a priezvisko s uvedením titulov a hodností
a presná adresa jeho zamestnávateľa)

Abstract

(English)

Study of structural phase transitions in solids by ab initio simulations

In this thesis we present ab-initio simulations of high-pressure structure and properties of two rather distinct solid materials, Mo and W-based transition metal dichalcogenides and amorphous polymeric nitrogen. Our work is divided into five chapters. In the first one we describe and discuss structure prediction methods used in our thesis with focus on evolutionary algorithms. In the second chapter we provide brief introduction into density functional theory which is our main quantum-mechanical computational scheme. In chapter III we show predictions of high-pressure phase diagrams of selected transition metal dichalcogenides, where we found new stable crystalline high-pressure phases by evolutionary search. In chapter IV we employed evolutionary algorithms to a different problem, preparation of amorphous polymeric nitrogen at high-pressure. This system was already prepared experimentally but its detailed structure is unknown. To our knowledge this is only the second time the evolutionary approach was used in this context and therefore this part of our work represents also methodological development. Finally, in the last chapter, we summarize our findings and sketch our plans for the future. Results from the third chapter were published in Physical Review B in two papers (in April 2015 and February 2017) and one other paper is currently being prepared. The results from chapter IV are currently under review process in Physical Review Materials.

Keywords: density functional theory, structure prediction problem, evolutionary algorithms, transition metal dichalcogenides, amorphous structures, nitrogen;

Abstract

(Slovak)

Štúdium štruktúrnych fázových prechodov v tuhých látkach pmocou ab initio výpočtov

V našej práci prezentujeme výsledky ab-initio simulácií, v ktorých sme skúmali vysokotlakovú štruktúru a vlastnosti dvoch odlišných materiálov, dichalkogenidov prechodných kovov na báze molybdénu a wolfrámu a polymerického amorfného dusíka. Práca pozostáva z piatich kapitol. V prvej sa venujeme popisu metód na predikciu kryštálových štruktúr s dôrazom na evolučné algoritmy, ktoré používame v našej práci. V druhej podávame stručný úvod do teórie hustotového funkcionálu, ktorý je naším najpoužívanejším kvantovomechanickým výpočtovým modelom. V tretej kapitole predstavíme našu predpoveď pre fázový diagram vybraných dichalkogenidov prechodných kovov, kde sme našli nové kryštalické vysokotlakové stabilné fázy pomocou evolučných algoritmov. Vo štvrtej kapitole sme použili evolučné algoritmy na iný problém, prípravu vysokotlakovej polymerickej amorfnej fázy dusíka. Podľa našich vedomostí je to len druhýkrát, čo sa v tomto kontexte používa evolučný prístup, a preto táto časť našej práce predstavuje aj metodologický vývoj. Nakoniec v poslednej kapitole zhrnieme naše zistenia a načrtneme naše plány do budúcna. Výsledky z tretej kapitoly boli publikované v časopise Physical Review B v dvoch článkoch (v apríli 2015 a februári 2017) a ďalší sa pripravuje. Výsledky zo štvrtej kapitoly sú v súčastnosti v recenznom konaní v časopise Physical Review Materials.

Klúčové slová: teória hustotového funkcionálu, problém predikcie kryštálových štruktúr, evolučné algoritmy, dichalkogenidy prechodných kovov, amorfné štruktúry, polymerický dusík;

Autoreferát dizertačnej práce

Introduction

The main goal of this thesis was finding new materials by computer simulations. We employed state-of-the-art evolutionary algorithms in order to search for new high-pressure crystalline phases in the Transition metal dichalcogenides class of materials (Mo and W-based) and we also verified the applicability of this method to amorphous materials, namely high-pressure amorphous polymeric nitrogen. We employed the density functional theory as our main quantum mechanical computational scheme as implemented in the VASP package[1][2][3], as well as, in the Quantum ESPRESSO package[4][5].

Transition Metal Dichalcogenides

Starting with the first case we studied high-pressure behaviour of selected transition metal dichalcogenides, namely: MoS_2 , $MoSe_2$, $MoTe_2$, WS_2 , WSe_2 and WTe_2 . These transition metal dichalcogenides are at abmient pressure well-known layered materials, with strong intra-layer covalent bonds and weak van der Waals inter-layer interactions. Such structures, however, fill the space really poorly. When we start to compress the structure the pV term can easily destabilize the structure in favour of different one with better space filling and therefore with a smaller volume. By employing evolutionary algorithms we tried to find out how these materials behave at high pressures and at which pressure they lose their layered character. As a driver for evolutionary algorithms we used the XtalOpt software[6]. Prior to our research only few structural phase transitions in this class of materials were known, all of them being between two different layered polymorphs. In MoS_2 at low pressures (around 20 GPa) a layer-sliding phase transition between the two different polytypes occurs (2Hc →2Ha) [7][8] and no other phase transition at higher pressures was observed [9]. $MoSe_2$ and $MoTe_2$ were also studied at high-pressure and structural phase transition between thermodynamically stable structures was neither observed nor predicted [10][11][12]. In WS_2 at moderate-pressure (45 Gpa) a structural transition was observed by applying non-hydrostatic pressure [13]. This transition was attributed to layer-sliding phase transition between two polytypes (2Hc →2Ha) [13] (as it was in case of MoS_2). At the beginning of our research no pressure induced phase transitions were reported in case of WSe_2. WTe_2 has, however, richer phase diagram. At ambient pressure WTe_2 adopts orthorhombic T_d structure. When pressure is applied it was

predicted that at 5 GPa it undergoes a phase transition into monoclinic 1T' structure, followed by another phase transition at 10 GPa into $2H_c$ structure[14]. However, only the first phase transition was observed in experiment [15]. In Ref. [15] authors also compressed sample up to 68.5 GPa and no other phase transition was reported.
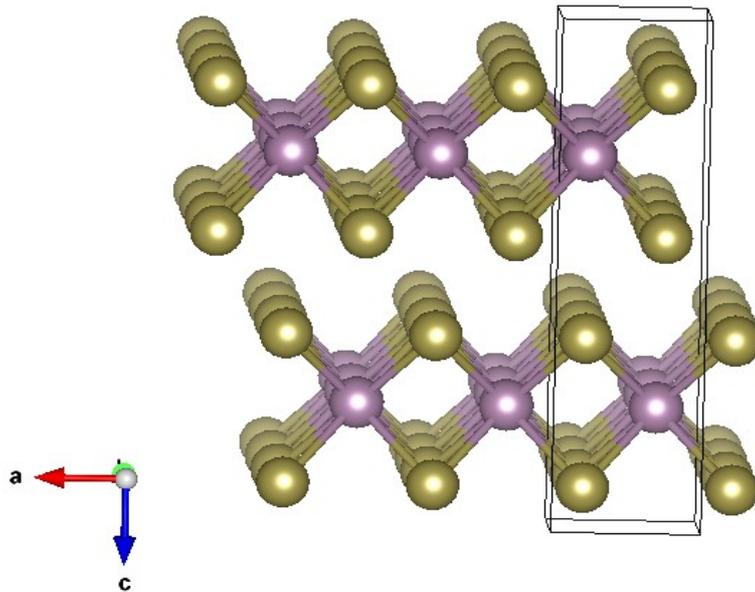

Figure 1: I4/mmm structure of MoTe₂ at 50 GPa. Visualized by VESTA package [16].

Interestingly, as our investigation has shown, these materials stay layered up to remarkably high-pressures. Aside from the well-known 2Hc →2Ha phase transition in sulphur based transition metal dichalcogenides, we do not predict any other structural phase transition between two layered polytypes[1] above 15 GPa. In MoSe₂ , MoTe₂ and WTe₂ at high pressure a new type of layer emerges, where the transition metal atom is 8-coordinated instead of coordination 6 observed in low-pressure layered polymorphs (see Fig. 1). This new tetragonal structure has space group *I4/mmm* and to our knowledge, such structures were neither observed (so far) nor predicted in this family of materials. One of the common characteristics of *I4/mmm* structures through our studied materials is a high density of states at the Fermi level. Moreover, in Mo-based transition metal dichalcogenides we found that this density increases with pressure. According to our electron-phonon calculations, we predict them to be superconducting, but with relatively low transition temperature Tc ≈ 2 K. The *I4/mmm* structure is only metastable for

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1   Excluding transition between two layered polymorphs.

MoSe$_2$ but for Te-based materials there is a pressure range in which it is thermodynamically stable.
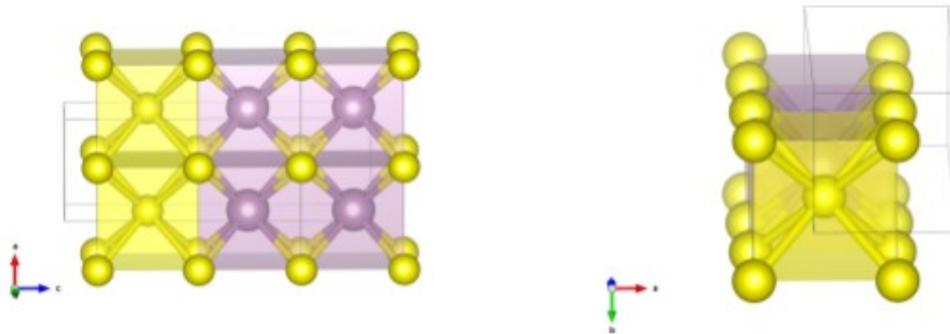

Figure 2: P4/mmm strcture of MoS$_2$ at 160 Gpa. Visualized with VESTA package [16].

Another interesting structure found basically in each of the studied materials is again tetragonal, however, non-layered *P4/mmm*. The structure of this phase is interesting. All atoms are 8-coordinated forming bcc-like crystal, however, on one side of unit cell atoms form binary CsCl-structure and on the other chalcogen atoms form one pure bcc (see Fig. 2). This phase is metallic and in case of MoS$_2$ has an interesting superconducting transition temperature T$_c$ = 16 K at 150 GPa. According to our study, we conclude that within MX$_2$ (M – metal atom Mo and W, and X – chalcogen atom S, Se and Te) stoichiometry the *P4/mmm* structure eventually becomes stable against every layered polymorph.

Finally, leaving fixed stoichiometry, we also checked the possibility of chemical decomposition MX$_2$ → X + MX. Since the high-pressure structure of MX was unknown, additional search within stoichiometry 1:1 was performed. From its results, we predict that the high-pressure structure of MX is the CsCl structure. According to our calculations for Mo-based materials only MoS$_2$ is prone to chemical decomposition into MoS and elemental S. We did not yet check this possibility for W-based transition metal dichalcogenides, but we plan to do so. As for the W-based materials, the research is still ongoing. We did not yet find any new structure, which was not reported or predicted for the Mo family. So far our predictions can be summarized in diagram in Fig. 3.
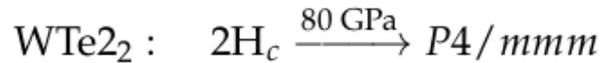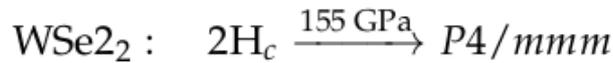
$$\text{MoS}_2: \quad 2H_c \xrightarrow{20\,\text{GPa}} 2H_a \to \begin{cases} \xrightarrow{138\,\text{GPa}} P4/mmm \\[4pt] \xrightarrow{130\,\text{GPa}} \text{chem. decomposition} \end{cases}$$

$$\text{MoSe}_2: \quad 2H_c \to \begin{cases} \xrightarrow{118\,\text{GPa}} P4/mmm \\[4pt] \xrightarrow{150\,\text{GPa}} I4/mmm \\[4pt] \xrightarrow{150\,\text{GPa}} \text{chem. decomposition} \end{cases}$$

$$\text{MoTe}_2: \quad 2H_c \xrightarrow{50\,\text{GPa}} I4/mmm \xrightarrow{110\,\text{GPa}} P4/mmm$$

$$\text{WS}_2: \quad 2H_c \xrightarrow{45\,\text{GPa}} 2H_a \xrightarrow{140\,\text{GPa}} P4/mmm$$

$$\text{WSe2}_2: \quad 2H_c \xrightarrow{155\,\text{GPa}} P4/mmm$$

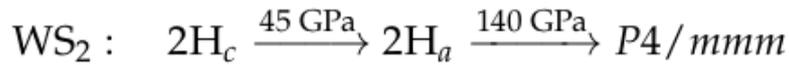$$\text{WTe2}_2: \quad 2H_c \xrightarrow{80\,\text{GPa}} P4/mmm$$
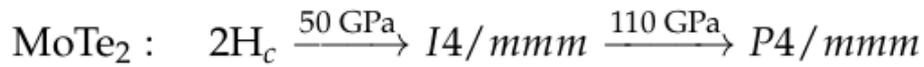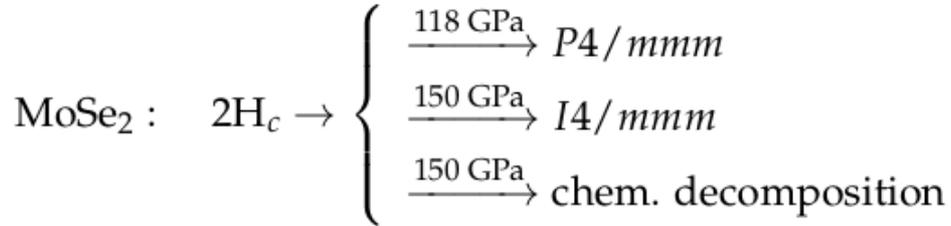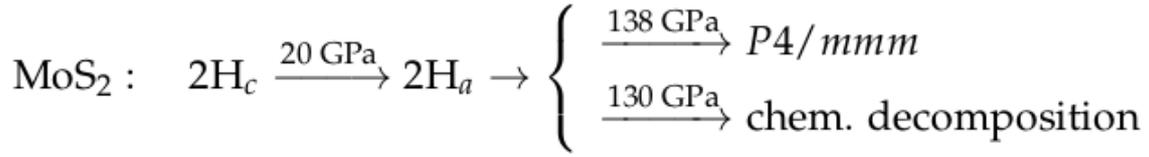
Figure 3: Diagram showing our predictions for high-pressure phase diagram in Mo and W-based transition metal dichalcogenides (neglecting phase transitions below 15 GPa).

Amorphous Polymeric Nitrogen

Our second studied material was high-pressure amorphous polymeric nitrogen. At ambient pressure and room temperature nitrogen forms a diatomic gas with very strong triple bond with binding energy of 4.88 eV [17]. When cooled below 34 K it forms a molecular crystal. By applying pressure and changing the temperature an interesting phase diagram with numerous molecular phases emerges. By increasing the pressure the molecules come closer together and intuitively one can expect that at some pressure the molecular phase would polymerize. Although the first

non-molecular phase is thermodynamically stable above 60 GPa (T = 0 K), due to slow kinetics the polzmerization cannot be observed below 110 GPa and 2000 K [18]. This first polymeric structure is cubic cg-N (sg.: $I2_13$), where all nitrogen atoms are 3-coordinated (3c). This phase is insulating and atoms are arranged in fused N_{10} rings, in such a way that both bond angles and gauche dihedral angles are near their local minima [19][20]. Five valence electrons form three single bonds, while the rest forms a lone pair [21]. The energy difference between one triple bond and three single bonds is interesting, assuming cg-N structure and α-N_2 molecular phase at 0 GPa the difference is as high as 1.4 eV per atom [17]. We have to note that cg-N structure would be a powerful high-energy-density material at 0 GPa. Unfortunately, this phase transforms back to its molecular form during the decompression at 42 GPa according to experiments [18].

Yet another structure can be routinely prepared at pressures above 100 GPa – amorphous polymeric nitrogen. This structure shares with the crystalline forms the absence of molecules and therefore it can be considered as a perspective high-energy-density material. We decided to investigate short and medium-range order in this amorphous phase. We prepared the structure in three different ways in order to be sure that we have correct structure. First two (liquid cooling and pressure-induced amorphization) employed molecular dynamics. The third approach used a novel way to find the atomic structure of amorphous materials: evolutionary algorithms (see Fig. 4). To our knowledge, this is the second time such method was applied to an amorphous system (for the first one see Ref. [22]). We conducted an analysis of evolutionary operators to estimate their efficiency for this particular task. Interestingly, the crossover operator (an operator which mixes two structures into one) was not useful. Nonetheless, we can conclude that all three approaches yielded very similar structure giving us good confidence in correct description of the amorphous system. High-energy density materials are still hot topic and nitrogen is a very promising one and therefore we think that our results can inspire new experiments.

Conclusions

We also hope that our work can trigger a new computational approach to amorphous materials using evolutionary algorithms. All of our results are valid within limitations of structural search given by the number of atoms used in simulation cell and the number of generated structures. Next thing we would like to focus on in this field is how to decompress and stabilize the amorphous form at low and ambient pressure. In order to do

so, we would like to try to add some impurities. We studied two different classes of interesting materials. For the first one (transition metal dichalcogenides) we predict new stable and metastable phases at high pressure and analyze their properties. For the second one (amorphous nitrogen) we predict and analyze the structure of already known phase, using a novel approach.
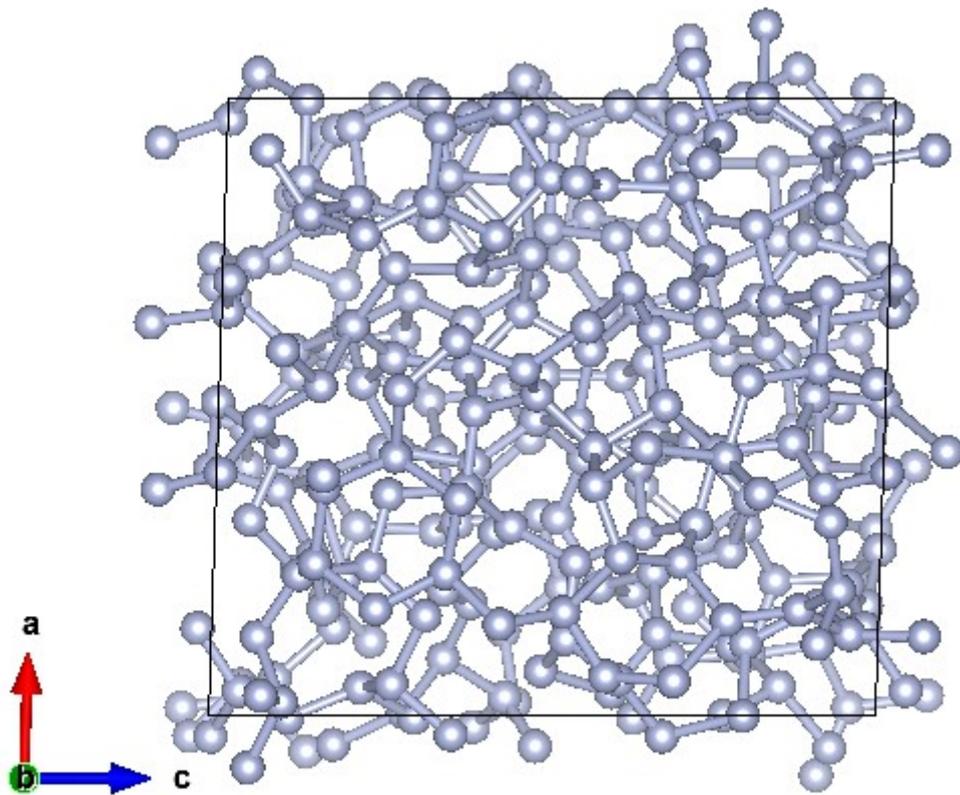

Figure 4: Sample of amourphous nitrogen prepared by evolutionary algorithms at 120 GPa. Visualized with VESTA package [16].

Bibliography

1: G. Kresse and J. Hafner, Ab initio molecular dynamics for liquid metals, 1993
2: G. Kresse and J. Furthmüller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set, 1996
3: G. Kresse and J. Furthmüller, Efficient iterative schemes for ab initiototal-energy calculations using a plane-wave basis set, 1996
4: Paolo Giannozzi et al, QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials, 2009
5: Paolo Giannozzi et al, Advanced capabilities for materials modelling with QUANTUM ESPRESSO, 2017
6: David C. Lonie and Eva Zurek, XtalOpt: An open-source evolutionary algorithm for crystal structure prediction, 2011

7: Liliana Hromadová, Roman Martoňák, and Erio Tosatti., Structure change, layer sliding, and metallization in high-pressure MoS2, 2013

8: Zhenhua Chi et al, Pressure-Induced Metallization of Molybdenum Disulfide,

9: Zhenhua Chi et al., Superconductivity in Pristine 2Ha − MoS2 at Ultrahigh Pressure, 2018

10: Michaela Riflikova, Roman Martoňák, and Erio Tosatti., Pressure-inducedgap closing and metallization of MoSe 2 and MoTe 2, 2014

11: Zhao Zhao et al., Pressure induced metallization with absence of struc-tural transition in layered molybdenum diselenide, 2015

12: Yanpeng Qi et al., Superconductivity in Weyl semimetal candidateMoTe2, 2016

13: Sakun Duwal and Choong-Shik Yoo., Shear-Induced Isostructural PhaseTransition and Metallization of Layered Tungsten Disulfide under Non-hydrostatic Compression, 2016

14: Pengchao Lu et al., Origin of superconductivity in the Weyl semimetalWTe 2 under pressure, 2016

15: Xing-Chen Pan et al., Pressure-driven dome-shaped superconduc-tivity and electronic structural evolution in tungsten ditelluride, 2015

16: Koichi Momma and Fujio Izumi., VESTA3 for three-dimensional vi-sualization of crystal, volumetric and morphology data, 2011

17: Jamal Uddin, Verónica Barone, and Gustavo E. Scuseria., Energy stor-age capacity of polymeric nitrogen, 2006

18: Mikhail Eremets et al., Single-bonded cubic form of nitrogen, 2004

19: C. Mailhiot, L. H. Yang, and A. K. McMahan., Polymeric nitrogen, 1992

20: F. Zahariev et al., Layered single-bonded nonmolecular phase of ni-trogen from first-principles simulation, 2005

21: Xing-Qiu Chen, C. L. Fu, and R. Podloucky, Bonding and strength ofsolid nitrogen in the cubic gauche (cg-N) structure, 2008

22: Suhas Nahas, Anshu Gaur, and Somnath Bhowmick, First principlesprediction of amorphous phases using evolutionary algorithms, 2016

Papers published by the author:

Kohulák, Oto, and Roman Martoňák. "New high-pressure phases of MoSe 2 and MoTe 2." *Physical Review B* 95.5 (2017): 054105.

Kohulák, Oto, Roman Martoňák, and Erio Tosatti. "High-pressure structure, decomposition, and superconductivity of MoS 2." *Physical Review B*91.14 (2015): 144113.