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Študijný program: Theoretical Physics and Mathematical Physics (Single degree study, Ph.D. III. deg., full time form)
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Title: Search for Stable Clathrate Films within Elements from Column XIV of the Periodic Table

Abstrakt: The aim of the thesis is a computer modelling of new stable clathrate structures within the realm of thin films based on pure elements from Column XIV of the Periodic Table, exploiting DFT energy evaluations. Of special importance are clathrates exhibit- ing decagonal and dodecagonal symmetry – composed entirely of one of the Group-IV elements (Sn, Ge, Si) – whose stability and occurrence have not been reliably ascertained yet. The theoretical part of the present work consists of two chapters. Chapter 1 de- scribes numerical methods as a basic instrument of our research: A. current ab initio models of interatomic interaction in condensed matter with emphasis laid on the predic- tive power and relation to experimental results and B. approaches for effective sampling of configurational space (search for the ground-state and thermodynamic equilibrium). A. is undoubtedly represented by Density Functional Theory (DFT), recently upgraded by Machine Learning Force Fields (MLFF). As for the second immense category B. we shall introduce Molecular Dynamics (MD), Parallel Tempering (PT)/Replica Exchange (RE), Lattice Gas (LG) as well as Chemi-Inspired Search. In the world of atomistic ma- terial simulations, models A. serve as an engine of approaches B. in pursuit of new stable materials. Important differences in stability assessment of bulk phases and thin films are pointed out in chapter 2. The experimental part of the thesis compares stability of assorted sp3 tetrahedal phases in bulk (3D variant) with that of thin films. Chapter 3 depicts bulk clathrates in the shadow of the unique stable diamond configuration for each of the elements Si, Ge and Sn. The ranges of coverages (i.e. number of atoms per Å2) of the elemental Column-XIV thin films where clathrates become stable are unraveled in chapter 4. With the exception of section 4.5, concerned with decagonal tin clathrate already deposited on d-Al-Ni-Co substrate in real experiment, the only objective of the thesis are free-standing layers. Last but not least, chapter 5 compensates for the very absence of substrate where a possi- bility of the clathrate stabilization on the diamond (111)-terminated surface is considered. Key words: Clathrates, Column XIV, Structure Prediction, Density Functional Theory, ground state, thin films, surface reconstruction, Molecular Dynamics.

Cieľom práce je počítačové modelovanie nových stabilných klatrátových štruktúr na bá- ze čistých prvkov XIV. skupiny Periodickej tabuľky v oblasti tenkých vrstiev s využitím výpočtov energie pomocou DFT. Mimoriadna pozornosť je venovaná klatrátom s deka- gonálnou a dodekagonálnou symetriou – tvoreným jedným z prvkov XIV. skupiny (Sn, Ge, Si) – ktorých stabilita a výskyt dosiaľ neboli spoľahlivo preukázané. Teoretická časť práce pozostáva

z dvoch kapitol. Prvá kapitola popisuje numerické metódy ako základný aparát nášho výskumu: A. zaužívané ab initio modely medzi- atomárnej interakcie v tuhých látkach s dôrazom na ich predpovednú hodnotu a vzťah k experimentálnym výsledkom a B. prístupy na efektívne vzorkovanie konfiguračného priestoru atómov (hľadanie základného a termodynamicky rovnovážneho stavu). Do prvej kategórie (A.) nepochybne patrí Teória hustotového funkcionálu (Density Functional The- ory, DFT) s modernou nadstavbou na báze umelej inteligencie (Machine Learning Force Fields, MLFF). Z druhej nesmierne širokej kategórie (B.) predstavíme Molekulárnu dy- namiku (Molecular Dynamics, MD), Paralelné žíhanie (Parallel Tempering, PT/Replica Exchange RE), Algoritmus mriežkového plynu (Lattice Gas, LG) či chemicky inšpirované hľadanie nových štruktúr (Chemi-Inspired Search). Modely A. vo svete materiálových simulácií sú hnacím motorom prístupov B. pri predpovedaní nových stabilných mater- iálov. Na významné rozdiely v posudzovaní stability trojrozmerných fáz a tenkých vrstiev upozorníme v druhej kapitole. Experimentálna časť práce porovnáva stabilitu rozmanitých sp3 tetrahedálnych fáz v bulku (trojrozmernej forme) s tenkými vrstvami. Tretia kapitola zachytáva trojrozmerné klatráty v tieni jedinečnej stabilnej diamantovej štruktúry pre každý z trojice prvkov Si, Ge a Sn. Štvrtá kapitola pre tieto prvky odhaľuje rozsahy pokrytí (t.j. počtov atómov pripadajúcich na Å2) tenkých vrstiev, v ktorých sa stabilnými stávajú práve klatrátové fázy. S výnimkou oddielu 4.5, kde analyzujeme dekagonálny cínový klatrát experimentálne pripravený na d-Al-Ni-Co podložke, sa práca zaoberá výlučne tenkými vrstvami vo vákuu. Absenciu substrátu vynahradíme v piatej kapitole, kde preskúmame možnosť stabilizácie klatrátových vrstiev na diamantovom (111)-rezanom povrchu. Kľúčové slová: klatráty, stĺpec XIV, predpovedanie štruktúr, DFT, základný stav, tenké Go to vrstvy, TOC rekonštrukcia TOC TOC TOC povrchu, molekulová dynamika.

The aim of the thesis is a computer modelling of new stable clathrate structures within the realm of thin films based on pure elements from Column XIV of the Periodic Table, exploiting DFT energy evaluations. Of special importance are clathrates exhibit- ing decagonal and dodecagonal symmetry – composed entirely of one of the Group-IV elements (Sn, Ge, Si) – whose stability and occurrence have not been reliably ascertained yet. The theoretical part of the present work consists of two chapters. Chapter 1 de- scribes numerical methods as a basic instrument of our research: A. current ab initio models of interatomic interaction in condensed matter with emphasis laid on the predic- tive power and relation to experimental results and B. approaches for effective sampling of configurational space (search for the ground-state and thermodynamic equilibrium). A. is undoubtedly represented by Density Functional Theory (DFT), recently upgraded by Machine Learning Force Fields (MLFF). As for the second immense category B. we shall introduce Molecular Dynamics (MD), Parallel Tempering (PT)/Replica Exchange (RE), Lattice Gas (LG) as well as Chemi-Inspired Search. In the world of atomistic ma- terial simulations, models A. serve as an engine of approaches B. in pursuit of new stable materials. Important differences in stability assessment of bulk phases and thin films are pointed out in chapter 2. The experimental part of the thesis compares stability of assorted sp3 tetrahedal phases in bulk (3D variant) with

that of thin films. Chapter 3 depicts bulk clathrates in the shadow of the unique stable diamond configuration for each of the elements Si, Ge and Sn. The ranges of coverages (i.e. number of atoms per Å2) of the elemental Column-XIV thin films where clathrates become stable are unraveled in chapter 4. With the exception of section 4.5, concerned with decagonal tin clathrate already deposited on d-Al-Ni-Co substrate in real experiment, the only objective of the thesis are free-standing layers. Last but not least, chapter 5 compensates for the very absence of substrate where a possi- bility of the clathrate stabilization on the diamond (111)-terminated surface is considered. Key words: Clathrates, Column XIV, Structure Prediction, Density Functional Theory, ground state, thin films, surface reconstruction, Molecular Dynamics.

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