Kinetics of structural transformations in bulk and nano-layered intermetallic systems with $L1_0$ superstructure



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by

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Streszczenie

Celem niniejszej pracy było zbadanie kinetyki procesów porządkowania atomowego zachodzących w litych i cienkowarstwowych układach międzymetalicznych z nadstrukturą L1₀. Szczególny akcent w badaniach był położony na analizę wpływu powierzchni swobodnej układu na stabilność uporządkowania atomowego.

W ramach realizacji pracy doktorskiej wykonano szereg symulacji procesów porządkowania atomowego metodami Monte Carlo (MC) w modelowych układach z nadstrukturą $L1_0$ w postaci próbek litych i cienkowarstwowych na przykładzie układu międzymetalicznego FePt. Obliczenia przeprowadzono w ramach dwóch modeli: model typu Isinga z międzyatomowymi oddziaływaniami parowymi oraz model z oddziaływaniami wielociałowymi Analytic Bond-Order Potentials (ABOP). W obu przypadkach symulacje polegały na przeprowadzeniu izotermicznej relaksacji uporządkowania atomowego od zadanej konfiguracji, najczęściej idealnego uporządkowania atomowego w nadstrukturze $L1_0$, do stanu odpowiadającego równowadze w danej temperaturze.

W pierwszym etapie przeprowadzono szereg obliczeń analitycznych i symulacji MC w modelu typu Isinga z wyznaczonymi dla FePt oddziaływaniami parowymi. W próbkach litych zaobserwowano relaksacje rozporządkowywania/porządkowania atomowego z pojedynczą skalą czasową odpowiadający objętościowo jednorodnej generacji/anihilacji defektów antystrukturalnych. W próbkach cienkowarstwowych badania wykazały tendencje układu do reorientacji nadstruktury z wariantu c (monoatomowe warstwy równoległe do powierzchni (001)) do wariantów a i b (monoatomowe warstwy prostopadłe do powierzchni (001)). Symulacje umożliwiły analizę złożonej kinetyki zjawiska na którą składają się oprócz jednorodnego rozporządkowania, trzy procesy: zarodkowanie domen ze zmienioną orientacją nadstruktury (wariantów a i b) na powierzchni zakończonej monoatomową warstwą Fe, powolny fluktuacyjny wzrost nowo-powstałych domen w głąb próbki oraz powolna relaksacja mikrostruktury domen. Wszystkie wymienione procesy mają charakter relaksacji, wykazując własne unikalne skale czasowe. W przypadku próbek o odpowiednio zmniejszonej grubości zaobserwowano perkolację nowo-powstałych domen do drugiej powierzchni, pokrytej warstwą atomów Pt.

W drugim etapie (ii) wykonano szereg symulacji w modelu opartym o zaawansowane oddziaływania wielociałowe Analytic Bond-Order Potentials (ABOP). Badania te miały na celu uwzględnienie w symulacjach MC zjawisk takich jak ewolucja dystorsji tetragonalnej oraz relaksację powierzchni. W tym celu zastosowano nowatorski algorytm Monte Carlo / Static Relaxation (MC/SR) polegający na połączeniu symulacji MC na sieci krystalicznej z procedurami relaksacji zarówno samej sieci krystalicznej (optymalizacja stałych sieciowych) jak i z relaksacją położeń poszczególnych atomów (Molecular Statics). W próbkach litych wyniki były analogiczne do tych otrzymanych w modelu typu Isinga. W cienkowarstwowych próbkach FePt L1₀ symulowanych z zastosowaniem ABOP charakterystyczną cechą układu było silne przyciąganie wakancji do powierzchni, powodujące efektywnie niejednorodną ich koncentrację (wysoka przy powierzchni, niska we wnętrzu próbki). Zaobserwowano złożony proces kinetyki porządkowania składający się z następujących procesów: częściowe szybkie jednorodne rozporządkowanie próbki, proces powolnego rozporządkowanie powierzchni próbki, oraz proces bardzo powolnego rozporządkowania wnętrza próbki. W badanym modelu przeprowadzono szereg dodatkowych symulacji MC/SR z zastosowaniem algorytmu bezpośredniej wymiany atomów w wyniku których zaobserwowano reorientację nadstruktury analogiczną do tej obserwowanej w modelu typu Isinga.

Głównym wynikiem przeprowadzonych badań jest stwierdzenie, iż równowagową konfiguracją atomową warstw FePt ograniczonych powierzchniami swobodnymi (001) są warianty nadstruktury L1₀ z płaszczyznami monoatomowymi o orientacjach (100) i (010). Osiągnięcie takiej konfiguracji, poprzez transformację początkowej z płaszczyznami monoatomowymi o orientacji (001), wymaga pokonania energii tworzenia domen antyfrazowych pomiędzy wariantami nadstruktury L1₀. Zastosowane modele dają w wyniku różne wartości tej energii i różne przewidywania dotyczące możliwości jej pokonania.

Powyższe wyniki zgadzają się z obserwacjami eksperymentalnymi i stanowią model mechanizmu z jakim w rzeczywistych cienkowarstwowych próbkach FePt z nadstrukturą $L1_0$ zachodzą zarówno reorientacja nadstruktury jak i powierzchniowe rozporządkowanie.

Abstract

The purpose of the hereby thesis is to analyze kinetics of atomic ordering processes in bulk and nano-layered samples of $L1_0$ ordered intermetallics. Special emphasis was put on analysis of mechanism of superstructure stability limitation caused by free surfaces.

Ordering phenomena in $L1_0$ ordered bulk and nano-layered samples were studied by means of Monte Carlo (MC) simulations in two models of FePt intermetallic: Ising-type model with two-body interactions and a model with many-body interactions based on Analytic Bond-Order Potentials (ABOP). In both models the isothermal relaxations of atomic ordering were simulated, starting from a defined atomic arrangement (in most cases perfectly $L1_0$ -long-range ordered) to a configuration corresponding to the equilibrium state at a given temperature. MC simulations were carried out by means of Glauber algorithm with vacancy migration mechanism implemented.

The first part of the study involves simulations of Ising-type L1₀-ordered FePt model with defined pair-interactions. In bulk samples single exponential relaxation of disordering/ordering was observed, related to uniform generation/annihilation of antisites. In the case of layered samples, the study revealed a tendency for L1₀ superstructure transformation from c-variant (monoatomic planes parallel to the (001) free surface) into a- and b-variants (monoatomic planes perpendicular to the (001) free surface). MC simulations allowed to analyze complex kinetics of the transformation which, with the exception of aforementioned uniform (bulk-like) disordering, involved three processes: (i) nucleation of a- and b-variant L1₀ domains at the surface domains inward the layered sample and (iii) relaxation of the microstructure of the surface domains. In sufficiently thin layers, a percolation of the a- or b-variant superstructure domain nucleated at the surface through the layered sample was observed.

The second part of the research consists of simulations carried out in ABOPbased model of $L1_0$ -ordered FePt. This study addressed the allowance of phenomena like evolution of tetragonal distortion and surface relaxations into MC simulations of "order-order" relaxations. In order to meet the above purpose, a novel algorithm Monte Carlo / Static Relaxations was developed. It involves lattice-based MC simulations and relaxations of lattice parameters (lattice optimization) and positions of atoms (Molecular Statics). In bulk samples the results were similar to those obtained in Ising-type model. In the layered samples of $L1_0$ FePt simulated with use of ABOP a significant feature of the system was a strong attraction of vacancies by the surfaces. Complex atomic ordering kinetics were observed involving initially fast partial disordering of an internal part of a layered sample which was continued at extremely low rate and slow surface-induced disordering. Additional MC/SR simulations utilizing directexchange algorithm were carried out in the ABOP-based model, revealing the superstructure transformation similar to the one observed in Ising-type model.

The main result of the present research is the finding that equilibrium configuration of layered $L1_0$ FePt samples with (001) free surfaces are the variants of $L1_0$ superstructure, where monoatomic planes are (100)- or (010)-oriented. The transformation of the configuration from the c- to a-(b-) variant $L1_0$ requires the system to overcome the energy of antiphase domains generation. The applied models, giving different values of this energy, result in particular predictions regarding the transformation mechanism.

The above results are in agreement with experimental results and provide a model mechanism explaining the observed atomic ordering processes in real FePt thin-layers, including disordering and $L1_0$ superstructure transformations.

Chapter 1

Introduction

1.1 $L1_0$ alloys

Intermetallic compounds such as FePt, CoPt, FePd and MnAl chemically ordered in $L1_0$ superstructure are of interest for their uniquely high magnetocrystalline anisotropy which is intrinsic to the tetragonal symmetry of the crystal structure. Those alloys are perceived as potential materials for a wide range of applications from bulk permanent magnets to future nanostructured ultra highdensity magnetic recording media. The most promising among all the mentioned $L1_0$ intermetallics is FePt due to its highest superstructure stability and coercivity. Thus, in this work the author will focus mainly on FePt. However, the model results are valid for all $L1_0$ -ordered intermetallic compounds.

1.1.1 Physical properties of Fe-Pt alloys

The binary intermetallics consisting of Fe and Pt elements have been known for several decades. The Fe-Pt phase diagram [1, 2] (fig. 1.1.1) as well as the magnetic and structural properties are well recognized [3]. In general, Fe-Pt alloys present high superstructure stability, especially for L1₀ (fig. 1.1.2) FePt and L1₂ FePt₃ phases. In L1₀ phase, a tetragonal distortion is observed, which disappears at a discontinuous order-disorder transition at T_t around 1570K. Moreover, the L1₀ phase exhibits an uniaxial magnetocrystalline anisotropy with easy magnetization along the *c*-axis of the L1₀ superstructure (fig. 1.1.2). The coercivity reaches values above $9 \cdot 10^5$ [A/m] [4] which is the same order of magnitude as in the neodymium-based magnets. The ferromagnetic properties disappear at the Curie temperature around 735 K [5].



Figure 1.1.1: Fe-Pt phase diagram



Figure 1.1.2: FePt $L1_0$ superstructure

1.1.2 L1₀ superstructure specific features

The $L1_0$ superstructure is based on FCC crystalline structure. According to the direction of **c** symmetry axis of the superstructure, there are 3 possible $L1_0$ superstructure orientations (variants) (fig.1.1.2). In each considered variant, two antiphase domains are possible, which gives a total of 6 different phases (tab.1.1).

In reality the superstructure of FePt is not strictly FCC-based – it is slightly tetragonally distorted. The experimental values of lattice constants are [6]: a = 0.3861 nm, c = 0.3788 nm and the tetragonality parameter c/a = 0.981.

	a-variant	b-variant	c-variant
c orientation	$oldsymbol{c} \parallel [100]$	$oldsymbol{c} \parallel [010]$	c [001]
basic variant			
antiphase variant			

Table 1.1: 6 particular variants of $L1_0$ superstructure.

1.1.3 Applications of FePt

The high coercivity in the bulk $L1_0$ FePt makes it a good material for permanent magnets, especially for special applications like micro-mechanical systems in aggressive environments [7] due to its chemical durability. The ordered $L1_0$ FePt intermetallic is perceived as a candidate for functional material for future magnetic data storage devices. The above mentioned magnetocrystalline anisotropy [8] together with the high-temperature superstructure stability provide an excellent fixture of the magnetization direction [9, 10]. There are several new technologies that involve $L1_0$ FePt thin layers for improved conventional hard disc drives [11], or monodisperse nanoparticles deposited with a variety of techniques [12, 13] for patterned data storage media [14].

1.1.4 The purpose of this thesis

Although deposition techniques for FePt thin layers and nanoparticles are well developed, there are still several obstacles to overcome¹ before possible technological application of the intermetallic. Recent results obtained from simulations [17], as well as experiments [18], are consistent about the fact that in the ordered FePt nano-layers a free surface causes a decrease of the superstructure stability. However, there is still an open discussion about the atomistic origin of the observed behavior. There are some model results, mostly from MC simulations, that suggest explanation of the superstructure stability limitation by: Pt surface precipitation [19], or surface-induced disorder [17].

This work is dedicated to examine in detail the atomistic mechanism of ordering processes in FePt $L1_0$ intermetallic. Special attention is given to the analysis of the mechanism of superstructure stability limitation caused by free surfaces.

¹In the case of nanoparticles one of the major problems is the lack of long range order (LRO) in the deposited monodisperse FePt particles [15]. Annealing leads to an increase of chemical LRO together with side effects - particles sintering and coalescence [16].

1.2 Thermodynamics of atomic ordering in intermetallics

This is only a very short introduction to thermodynamics of ordering in intermetallics [20, 21]. For the sake of keeping the volume of this dissertation reasonable, the subject is presented only in an abbreviated way.

1.2.1 Parameterizations and approximation models

In statistical thermodynamics a macrostate of the system is defined by a set of macroscopic parameters. However, microstate is a specific, distinct and well-defined condition of a thermodynamic system. In thermodynamics it is assumed that measured observables are equal to the related microstate parameters averaged over all possible microstates (the ensemble) (eq. 2.1.1).

In the case of hereby thesis, it is assumed that the system is represented by a canonical ensemble, the probability of a microstate is given by Boltzmann distribution (2.1.4) and microstates correspond to particular atomic configurations $\{\sigma\}$. The macrostate of interest is represented by a set of observables capable of describing an effective atomic configuration.

Commonly defined observable related to the system configuration is multisite correlation function:

$$\xi = \langle \sigma_{i_1}, \sigma_{i_2} \dots \rangle \tag{1.2.1}$$

where σ_i are so-called occupation variables determining the type of the atom occupying the lattice site *i*. In a rigorous approach ξ covers the entire crystal i.e. all the lattice sites. Due to infeasibility of considering all the exact atomic arrangements of the entire crystal, subsets of the system small enough to allow explicit specification of their configurations, are considered. This approach is the core of the Cluster Variation Method (CVM) [22, 23]. The observable describing the system is then given by a set of correlation functions related to finite clusters α of a size n_{α} :

$$\xi_{\alpha} = \left\langle \sigma_{i_1}^1, \sigma_{i_2}^2 ... \sigma_{i_n}^{n_{\alpha}} \right\rangle \tag{1.2.2}$$

which represent occupation within an α -cluster (composed of n_{α} lattice sites) averaged over the whole system, $\sigma_{i_j}^j$ - are configurational variables represented by integer values for a certain atom residing in the i_j -th site in the lattice that belongs to j-site of the α -cluster. CVM formalism was applied in hereby dissertation for the development of atomic pair-interactions (sec.3.1). The order of the approximation is determined by the largest cluster taken into account (in a rigorous approach the biggest cluster is identical to the whole system). It appears that, once the biggest cluster is chosen, the thermodynamics involves correlation functions of all smaller clusters.

The simplest case of CVM approximation is the case where 1-site cluster is the biggest one. This approach was introduced far before unified CVM by W. L. Bragg and E. J. Williams [24, 25, 26], and is called the Bragg-Williams (B-W) approximation. A basic variable in B-W model is 1-site correlation function $\langle \sigma_i \rangle$ (eq. 1.2.3) averaged over all sites of a certain sublattice² It represents probability of finding certain atoms on a given sublattice.

$$\left\langle \sigma_{i}^{A}\right\rangle _{B}=p_{AB}=\frac{N_{B}^{A}}{N_{B}} \tag{1.2.3}$$

where: $\langle \sigma_i^A \rangle_B$ - value of a correlation function of A-atom in 1-site cluster averaged over B-sublattice, p_{AB} - probability of finding A-atom at the site belonging to B-sublattice, N_B^A - number of A-atoms at B-sublattice, N_B - number of sites in B-sublattice.

The crucial idea behind B-W model is the introduction of auxiliary order parameter to describe the degree of long range order (LRO) in the considered system:

$$\eta = \frac{p_{AB} - c_A}{p_{AB}^0 - c_A} \tag{1.2.4}$$

where: p_{AB}^0 - represents probability of finding A-atom on B-sublattice in the reference (perfectly ordered, T=0 K) superlattice, p_{AB} - probability of finding A-atom on B-sublattice in the considered real (or simulated, T>0K) system, $c_A = N^A/N$ - is the concentration of A-atoms in the sample with N^A -total number of A-atoms in the system and N-total number of sites in the crystal. The parameter equals 1 when the system is perfectly ordered and 0 when completely disordered. The more specific η parameters will be further defined.

1.2.2 Free energy

The equilibrium state of the system corresponds to the minimum of an appropriate thermodynamic potential. One of them is free energy. In thermodynamics, the term free energy refers to the amount of work that can be extracted from a system. Two definitions of free energy are most commonly used in statistical thermodynamics: Helmholtz for NVT-system³ and Gibbs for NpT-system⁴. The content of this dissertation is confined to phenomena in alloys under normal pressure conditions. As pressure-volume work in considered situations is negligibly small in comparison to energy stored in other degrees of freedom, especially in atomic configuration, the Helmholtz free energy is appropriate:

$$F = U - TS \tag{1.2.5}$$

The first component of free energy is internal energy U, which is the total of the potential energy associated with inter-atomic bonds, magnetic and electric fields, and the kinetic energy due to the motion of atoms or molecules, averaged over microstates. In the case of real crystals, we can distinguish two different time scales: a slow time scale of atomic interchanges, and the faster one for lattice vibrations and electronic motions [27]. Consequently, it is possible to formulate internal energy U as configurational energy E_{conf} which is dependent explicitly only on the atomic configuration, including effectively averaged influence of the non configurational degrees of freedom (phonons, electrons). Since

 $^{^{2}}$ A part of the crystal lattice, that presents a favorable occupation of a certain type, and preserve translational symmetry of the original lattice.

 $^{^3\}mathrm{NVT}:$ the system with constant number of particles N, volume V and temperature T.

 $^{^4\}mathrm{NpT}$ the system with constant number of particles N, pressure V and temperature T.

the non-configurational degrees of freedom are taken into account in an effective averaged way, not as a source of different microstates, the entropy S of the system can be also defined based on atomic configurations:

$$S_{conf} = -k \left\langle \ln(P(\sigma)) \right\rangle \tag{1.2.6}$$

where $P(\sigma)$ is the probability of the occurrence of microstate σ - in our case the particular atomic configuration.

Therefore the free energy can be defined solely on the basis of atomic configurations:

$$F = E_{conf} - TS_{conf} \tag{1.2.7}$$

1.2.3 Defects and atomic disordering

Vacancy is an unoccupied (empty) site in a crystal lattice. Vacancies play a basic role in mechanisms providing changes in atomic configuration. They emerge as thermal vacancies or in intermetallic phases as a part of defected solid solutions. Changes of lattice sites occupations proceed mainly through the atomic migrations to the nearest neighboring (NN) vacancies. Other mechanisms of atomic migration, including direct exchange of two atoms, are possible almost only at temperatures near the melting temperature [28]. Therefore, vacancies are essential in all processes based on atomic migration including diffusion.

Antisite defect is an atom residing at an improper site according to the superstructure of the crystal. Antisite concentrations (typical observables) and their descendants (like B-W η parameter) are main parameters that give the measure of disorder in the superstructure.

Ordering energy W is a quite important parameter that gives information about the tendencies in terms of ordering processes in intermetallics. It represents a change in configurational energy caused by the exchange of two different atoms in perfectly ordered structure, causing creation of two antisites. If the W value is negative, at any condition, the intermetallic will tend to disorder or decompose into separate phases. When W is positive, the system has a chance to find itself in a stable ordered equilibrium.

A perfectly ordered crystal ($\eta = 1$) at a real temperature (T > 0 K), from the thermodynamical point of view, is not a stable system and will tend to partially disorder ($\eta \searrow$). Although the creation of defects raises configurational energy, it increases the entropy too, and thus, lowers the total free energy (eq.1.2.7) bringing the system into the equilibrium state. Above the certain critical temperature namely the **order-disorder transition temperature** T_t , the only minimum of the free energy can be found at a complete disorder ($\eta = 0$). It is due to the fact that the entropic part of free energy contains temperature, and above T_t it cannot be balanced by configurational energy.

1.2.4 Activated state rate theory

Let us consider a real crystal lattice. At temperatures above 0 K atoms are slightly oscillating around the crystalline lattice sites which are their equilibrium positions. Due to fluctuations, atom in the lattice can obtain enough kinetic energy to leave the site and migrate towards another (local) equilibrium position in the lattice. Such situation can occur below melting temperature only for single atoms (very rarely for groups of atoms) with a certain probability. As it was mentioned above (subsec.1.2.3), in metals and alloys, atoms migrate virtually only to NN vacancies. In the real system, constantly executed atomic migrations (jumps) are the main mechanism through which the atomic configuration evolves.

Activated state rate theory is a statistical model that provides description of atomic migration phenomena.



Figure 1.2.1: Potential energy evolution during an atomic jump from i to j site.

In general, we can distinguish three characteristic moments during the atomic jump (fig.1.2.1): (i) before the jump (E_{conf}^{i}, S^{i}) , (+) a saddle point - maximum of potential energy during migration (E_{conf}^{+}, S^{+}) , (j) and the moment after the jump (E_{conf}^{j}, S^{j}) . Then, the jump probability can be described as:

$$p_{i-j} = c \exp\left[-\frac{\Delta F}{kT}\right] = c \exp\left[\frac{S^+ - S^i}{k}\right] \exp\left[-\frac{E^+_{conf} - E^i_{conf}}{kT}\right]$$
(1.2.8)

where: ΔF is a change of free energy during the jump, E_{conf}^{i} and S^{i} is energy and entropy before the jump, E_{conf}^{+} and S^{+} are respectively configurational energy and entropy in the saddle point, and c is a rate parameter. When considering the saddle point during the migration, it can be assumed that the entropy is not changed⁵, thus $S^{+} - S^{i} = 0$, and the jump probability formula is the following:

$$p_{i-j} = c \exp\left[-\frac{E_{conf}^+ - E_{conf}^i}{kT}\right]$$
(1.2.9)

After the jump, analogical return jump is possible:

$$p_{j-i} = c \exp\left[-\frac{E_{conf}^+ - E_{conf}^j}{kT}\right]$$
(1.2.10)

 $^{^{5}}$ We can consider one atomic migration in a huge system as a very small change to the value of the entropic component of the free energy which in comparison to the configurational energy component is negligible.

The difference $E_{conf}^{+} - E_{conf}^{i}$ is usually called an activation energy of atomic (or vacancy) migration or simply **migration barrier** and denoted by E^{+} (or E_{m}). Using aforementioned jumps probabilities (eq. 1.2.9and 1.2.10) a detailed balance condition can be written down as:

$$\frac{p_{j-i}}{p_{i-j}} = \frac{p_j^{eq}}{p_i^{eq}} \tag{1.2.11}$$

where $p_{j(i)}^{eq}$ - denotes probability of equilibrium state before i - j jump (or after j - i jump). The detailed balance condition is one of conditions, the fulfillment of which is required in a system relaxing to an equilibrium configuration.

1.2.5 Atomic order relaxation

When considering an intermetallic, the atomic order relaxation is a process of reaching the equilibrium atomic configuration through evolution of this configuration - namely the degree of atomic order in a particular superstructure. Typically, in real or numerical experiments, the relaxation is initiated by a change of temperature, which drives the system away from the equilibrium state. The relaxation advances in time leading the system towards the minimum of free energy. The transitions between atomic configurations proceed through atomic migrations causing generation or elimination of antisites. Depending on the phase (ordered or disordered) at which the relaxation begins and ends, a few kinds of relaxations can be distinguished. In this work the main concern is put to "order-order"⁶ relaxations performed at constant temperatures (isotherms), however in some cases, like tests of interatomic potentials, "order-disorder" relaxations are also considered.

 $^{^{\}rm 6}{\rm The}$ beginning as well as final atomic configurations are ordered phases, below order-disorder transition temperature.

Chapter 2

Methodology

All the methods presented in this section were applied in an universal framework elaborated within this thesis: Alphard (A-dvanced L-attice-based P-latform with H-ybrid A-algorithms and configurable R-esult D-ata output) [29] which is an object oriented program with an adaptable simulation schedule, easily configurable data output and lots of additional options.

2.1 Stochastic methods

Numerical methods that are known as stochastic are defined in general terms as any method that utilizes sequences of random numbers to perform an estimation of the desired result. Stochastic methods have been used for centuries, but only in the past several decades (thanks to tremendous progress in availability of computational resources) has the technique gained the status of a full-fledged numerical method capable of addressing the most complex applications. The name "Monte Carlo", which is a popular alias for stochastic methods, was given by Metropolis (inspired by Ulam's interest in gambling) during the Manhattan Project of World War II, because of the similarity of statistical simulation to games of chance, and because the capital of Monaco was a center for gambling and similar pursuits.

Monte Carlo simulation methods[30] are especially useful in studying systems with a large number of coupled degrees of freedom, such as fluids, disordered materials, strongly coupled solids, and cellular structures. More broadly, Monte Carlo methods are useful for modeling phenomena with significant uncertainty in inputs, such as the calculation of risk in business. It is classically used for evaluation of definite integrals, particularly multidimensional integrals with complicated boundary conditions. Nevertheless, in this work the Monte Carlo methods have been applied to perform efficient, yet precise, simulations of atomic ordering kinetics.

2.1.1 Monte Carlo method in NVT ensemble

Let us consider the statistical mechanics of NVT (canonical) ensemble. Each particle has an index *i*, and a set of dynamic variables α_i , The microstate of the system is described by the complete set:{ $\alpha_1, \alpha_2, ..., \alpha_N$ } which describes the position of a Γ point in the Ω phase space. The system is described by Hamiltonian $H_N(\Gamma)$. A thermodynamic average over an observable A has a following formula:

$$\langle A \rangle = \frac{\int_{\Omega} d\Gamma A(\Gamma) \exp\left(\frac{-H_N(\Gamma)}{k_b T}\right)}{\int_{\Omega} d\Gamma \exp\left(\frac{-H_N(\Gamma)}{k_b T}\right)}$$
 (2.1.1)

where k_b is a Boltzmann constant.

The average $\langle A \rangle$ can be estimated replacing the integrals by finite summations over a finite set of points M within the Ω space:

$$\langle A \rangle = \frac{\sum_{m}^{M} A\left(\Gamma_{m}\right) \exp\left(\frac{-H_{N}\left(\Gamma_{m}\right)}{k_{b}T}\right)}{\sum_{m}^{M} \exp\left(\frac{-H_{N}\left(\Gamma_{m}\right)}{k_{b}T}\right)}$$
(2.1.2)

In most cases, Ω space is highly multidimensional and quantization of such a space by equidistant Γ_m points would fail because of their extremely large quantity. To avoid this problem, only randomly chosen Γ_m points from Ω space are taken into summations. This simple sampling method is the most basic among Monte Carlo methods.

Unfortunately, because of extensive use of exponential functions in the simple sampling formula (2.1.2), values of calculated samples can vary to a very great extent. This causes that many of them have an insignificant contribution to the result and the algorithm becomes inefficient. The problem may be solved by choosing Γ_m points with appropriate probabilities $P(\Gamma_m)$ - this is called the importance sampling method. The improved formula would state as:

$$\langle A \rangle \approx \bar{A} = \frac{\sum_{m}^{M} P(\Gamma_m) A(\Gamma_m) \exp\left(\frac{-H_N(\Gamma_m)}{k_b T}\right)}{\sum_{m}^{M} P(\Gamma_m) \exp\left(\frac{-H_N(\Gamma_m)}{k_b T}\right)}$$
(2.1.3)

A natural choice for the probability function in NVT ensemble would be:

$$P(\Gamma_m) = P_{eq}(\Gamma_m) \alpha \exp\left(\frac{-H_N(\Gamma_m)}{k_b T}\right)$$
(2.1.4)

thus, the states are chosen for summation according to the Boltzmann probability. With such a choice of probability, the bias sampling average formula (2.1.3) becomes a regular arithmetic average:

$$\bar{A} = \frac{1}{M} \sum_{m}^{M} A\left(\Gamma_{m}\right) \tag{2.1.5}$$

The series of Γ_m points in the Ω space showing the distribution (2.1.4) may be generated by simulating Markov chain convergent to canonical ensemble $P(\Gamma_m) \stackrel{M \to \infty}{=} P_{eq}(\Gamma_m)$. The proper Markov chain must be featured by :

• Normalized transition probability $W(\Gamma_m \to \Gamma_n)$:

$$\sum_{\Gamma_n} W\left(\Gamma_m \to \Gamma_n\right) = 1 \tag{2.1.6}$$

- All states in Ω space are accessible
- Detailed balance condition of microscopic reversibility:

$$P_{eq}(\Gamma_m) W(\Gamma_m \to \Gamma_n) = P_{eq}(\Gamma_n) W(\Gamma_n \to \Gamma_m)$$
(2.1.7)

Considering the detailed balance formula (2.1.7), it is easy to notice that the relation between transition probabilities is exponentially proportional to the energy change in the system during the transition:

$$\frac{W\left(\Gamma_m \to \Gamma_n\right)}{W\left(\Gamma_n \to \Gamma_m\right)} = \frac{P\left(\Gamma_n\right)}{P\left(\Gamma_m\right)} = \frac{\exp\left(\frac{-H_N\left(\Gamma_n\right)}{k_bT}\right)}{\exp\left(\frac{-H_N\left(\Gamma_m\right)}{k_bT}\right)} = \exp\left(\frac{-\left(H_{\Gamma_n} - H_{\Gamma_m}\right)}{k_bT}\right)$$
(2.1.8)

The fact that the explicit form of the transition probability is not set, allows quite a few possible solutions. Among many possibilities, Metropolis and Glauber formulas are the most popular:

• Asymmetric Metropolis solution[31]:

$$W\left(\Gamma_m \to \Gamma_n\right) = \begin{cases} \frac{1}{\tau} \exp\left(\frac{-\Delta E}{k_b T}\right) & \text{for } \Delta E > 0\\ \frac{1}{\tau} & \text{for } \Delta E \le 0 \end{cases}$$
(2.1.9)

• Symmetric Glauber solution[32]:

$$W\left(\Gamma_m \to \Gamma_n\right) = \frac{1}{\tau} \frac{\exp\left(\frac{-\Delta E}{k_b T}\right)}{1 + \exp\left(\frac{-\Delta E}{k_b T}\right)}$$
(2.1.10)

where τ is a time constant, and $\Delta E = H_{\Gamma_n} - H_{\Gamma_m}$ is the energy change during the transition from Γ_m to Γ_n .

2.1.2 Stochastic algorithms for structural relaxations

The presented study concerns mainly kinetics of structural transformations in FePt $L1_0$ intermetallic. The kinetics are obtained by simulations of atomic "order-order" isothermal relaxations using Monte Carlo algorithms appropriate for structural relaxations.

When assuming that each transition between the states $\Gamma_m \to \Gamma_n$ has a physical meaning, it is possible to interpret the process of reaching the equilibrium state, i.e. the simulated Markov chain, as a physical one. In the case of atomistic Monte Carlo simulations, based on a rigid lattice, transitions between the Γ states refer to changes in an atomic configuration - lattice occupations. The more detailed physics is applied in the procedure of transition between configurations (direct exchange of atoms, vacancy mechanism etc.), the deeper physical meaning has the obtained model result.

The procedures of simulation, among other operations, consist mainly of iterative execution of a certain algorithm. The routine is repetitively executed until the desired final state of the simulated system is achieved. Usually it is an equilibrium state. In the following overview, common Monte Carlo algorithms are presented (more in-depth explanation can be found in [30]).

2.1.2.1 Direct exchange algorithm

In direct exchange (DE) algorithm, the transition between the states is performed through the exchange of two randomly chosen atoms in the volume. The algorithm is as follows:

- 1. two atoms are chosen at random
- 2. the energy change ΔE following from the exchange of their positions and transition probability W (according to Glauber or Metropolis formula) are calculated
- 3. the probability test is performed and according to its result the atom positions are either exchanged or not exchanged
- 4. back to No. 1

Since the exchange of positions of random atoms has no physical meaning the algorithm is used mainly for preliminary tests of the simulated models or to roughly determine the equilibrium state.

2.1.2.2 Vacancy-migration algorithm

In this work, a particular application of an algorithm, based on atomic jumps to the vacancy, was used. The algorithm is as follows:

- 1. one atom in the vicinity of any of the vacancies is chosen at random
- 2. the migration barrier E^+ or ΔE in Quasi-Kinetic Monte Carlo approach (fig.1.2.1) and transition probability W (according to Glauber or Metropolis formula) are calculated
- 3. a test of transition probability W is performed and, according to its result, the atom is either moved to the vacancy or stays in its site
- 4. back to No. 1

As atomic jumps to the vacancy are considered to be the process responsible for almost all changes in atomic configuration in solid intermetallics [28], this algorithm has a strong physical background. Thus the relaxations obtained with it are interpreted as simulations of a physical process.

2.1.2.3 Residence time algorithm

Basically, this method, as well as the previous one, may involve the vacancy migration mechanism. The migration barrier between the states of the system is taken into account in a way which allows calculation of physical residence time of the system in a certain state. The popular name for this algorithm is "residence time" (RT) [33].

1. a list of all N possible events (jumps to the NN vacancy) is composed with corresponding migration barriers E_i^+ (*i*-th event), transition rates:

$$r_i = \exp\left(\frac{E_i^+}{k_B T}\right) \tag{2.1.11}$$

as well as cumulative rates:

$$R_i = \sum_{j=1}^{i} r_j \tag{2.1.12}$$

2. a random number $u_1 \in (0, 1]$ is set and the corresponding *i*-th event which fulfills the condition:

$$R_{i-1} < u_1 * R_N < R_i \tag{2.1.13}$$

is executed.

3. time is incremented by Δt calculated with use of another random number $u_2 \in (0, 1]$:

$$\Delta t = -\frac{\log\left(u_2\right)}{R_N} \tag{2.1.14}$$

4. back to No. 1

Note that r_i/R_N which is *de facto* a transition probability, fulfills all the conditions set for a proper Markov chain (eq. 2.1.6 and eq. 2.1.7).

This algorithm is slightly more complex than the simple vacancy-migration MC, however, in some cases, it allows faster (in terms of number of MC steps) convergence to equilibrium state¹. In comparison to the previous one it is much more effective in simulations where many attempted jumps would not be executed due to low transition probability (low temperature, high energy barriers). On the other hand, it is less effective than the previous one when the system exhibits a high variation between transition probabilities; especially when there are high probabilities for transitions which are neutral for evolution of the system.

2.1.2.4 Kinetic and quasi-kinetic algorithms

In general, MC algorithms that involve migration barriers are called Kinetic Monte Carlo (KMC), because knowing the value of an energy barrier (E^+) between states it is possible to estimate real time scale, namely the kinetics, of a process (in a similar way to residence time algorithm). Whereas algorithms which utilize constant barriers or simple transition energy (ΔE) , do not allow estimation of a process real time scale, thus they are called quasi-kinetic or pseudo-kinetic (QKMC).

2.2 Deterministic methods

Deterministic methods are based on an attempt to calculate detailed evolution of the system, in contrast to stochastic methods, which are based on random numbers and average estimations.

¹Note that equilibrium state is independent on the used algorithm.

2.2.1 Molecular Dynamics

The Molecular Dynamics [34] technique was developed just after the Monte Carlo methods, around the mid-fifties. Originating from theoretical physics, the method of MD gained popularity in materials science, and since the 1970s also in biochemistry and biophysics. It has also been applied with limited success as a method of refining protein structure predictions. In physics, MD is used to examine the dynamics of atomic-level phenomena that cannot be observed directly. This particular work is an example of such studies.

Molecular Dynamics suits the calculation of trajectory in the phase space of a set of particles, where each particle is subjected to classical equations of motion. It is virtually non-dissipative deterministic algorithm. The algorithm is based on the numerical solution of Newton's equations of motion for each particle in the system. The differential Newton's equations:

$$m_i \frac{d^2 \mathbf{r}_i(t)}{dt^2} = \mathbf{F}_i(t) = -\sum_{j \neq i}^N \nabla_i V(\mathbf{r}_i(t), \mathbf{r}_j(t), ..)$$
(2.2.1)

where \mathbf{r}_i is the coordinate, m_i is the mass of particle, V is the interatomic potential. To compute the solution of a differential equation one must convert it from a continuous time form into a discrete time form of a differential equation with a certain finite time step Δt . It must be at least one order of magnitude smaller than the natural microscopic time scale. For the time scale of atomistic processes in a solid state, the reasonable value of Δt is around 10^{-15} second. The computation time necessary to calculate a particular simulation is mostly spent on force calculations, which are dependent on the complexity of potentials. The time is also proportional to the number of particles in the system N.

2.2.1.1 Calculations of forces: Velocity-Verlet algorithm

There is a huge choice of MD algorithms (methods of integration of differential equations), nevertheless, in this work the Velocity-Verlet (or "leap frog") algorithm was used. This widely known algorithm is easy to apply and sufficiently accurate for the purpose of the hereby study. It can be derived by writing two Taylor expansions of the position vector $\mathbf{r}(t)$ in different time directions. In contrast to the basic Verlet algorithm[35] it uses velocity explicitly².

The implementation scheme of this algorithm is following:

1. Calculate new positions of atoms:

$$\mathbf{r}(t + \Delta t) = \mathbf{r}(t) + \mathbf{v}(t)\Delta t + \frac{1}{2}\mathbf{a}(t)(\Delta t)^{2}$$
(2.2.2)

2. Calculate velocities between positions:

$$\mathbf{v}\left(t+\frac{\Delta t}{2}\right) = \mathbf{v}(t) + \frac{\mathbf{a}(t)\Delta t}{2}$$
(2.2.3)

²An in-depth description of the Velocity-Verlet algorithm can be found in R. Feynman's physics lectures [36].

3. Move particles to their new coordinates $\mathbf{r}(t + \Delta t)$ and calculate accelerations $\mathbf{a}(t + \Delta t)$ from the interaction potentials V:

$$\mathbf{a} = \frac{\mathbf{F}}{m} = -\frac{\vec{\nabla}V}{m} \tag{2.2.4}$$

4. Calculate velocities at new positions:

$$\mathbf{v}(t+\Delta t) = \mathbf{v}\left(t+\frac{\Delta t}{2}\right) + \frac{\mathbf{a}(t+\Delta t)\Delta t}{2}$$
(2.2.5)

5. Set new time $t = t + \Delta t$ and return to point 1

2.2.1.2 Energy and temperature stabilization

Straightforward application of an integration algorithm (like the one described above in subsec. 2.2.1.1) with a proper time step³, theoretically yields the system with a constant total energy. This is because the applied force field is conservative⁴ and no energy dissipation is assumed. However, due to a large number of iterations, a cumulation of small computational errors and fluctuations may cause instability of the system energy. The problem is solved by application of special algorithms, popularly named thermostats, into the basic MD routines. Such algorithm checks the system temperature⁵ and provides small corrections to the kinetic energy of atoms.

In the hereby work, the Gunsteren-Berendsen [37] (G-B) or "velocity scaling" thermostat was used; easy in application, yet sufficiently effective⁶. To reduce the effect of energy fluctuations and guarantee stable temperature, each atomic velocity in each MD step is multiplied by the factor λ :

$$\mathbf{v}_i' = \mathbf{v}_i \lambda \tag{2.2.6}$$

$$\lambda = \sqrt{1 + \frac{\Delta t}{\tau_T} \left(\frac{T_0}{T} - 1\right)} \tag{2.2.7}$$

which is dependent on the relation between the targeted temperature T_0 and the temperature T present in the simulated system. The λ factor contains the τ_T time constant which theoretically causes the system to achieve the desired temperature T_0 after $(\tau_T/\Delta t)$ MD steps. However, in practice, this prevents the effect of jumping around the targeted temperature, which would result in even bigger fluctuations.

 $^{^3 \, {\}rm The}$ sufficiently small time step Δt should not result in divergence of the system energy during MD simulation.

⁴The formulas of Analytic Bond-Order Potentials applied in hereby thesis are smooth in derivatives, independent on the time and history of interacting atoms, thus the potential is conservative. For details see eq. 3.2.1..3.2.8.

 $^{^5\}mathrm{Thermostat},$ as well as the temperature, can stabilize the total energy of the system.

⁶Due to the artificial suppression of the fluctuations, the velocity scaling scheme does not strictly follow the canonical ensemble (particles trajectories are modified). Though in practice, for big systems (containing more than 10^3 atoms), where the fluctuations are inconsiderable, the amount it deviates is small and can be neglected.

2.2.2 Molecular Statics

The Molecular Statics [38, 39] (or Quenched Molecular Dynamics) method was used to calculate energy barriers (E^+) for atomic migrations (fig. 1.2.1), as well as for Static Relaxations during ABOP-based MC simulations. Molecular Statics, in contrast to Molecular Dynamics, is a dissipative method. This means that during the simulation the energy of the system is not conserved, but decreases with time. Such an approach allows the atoms to move according to MD algorithm, however, with a continuous loss of kinetic energy, which causes slowing down. After a certain time all atoms will finally (almost) stop in the positions of their lowest potential energy.

In general the same routines for force calculations are used as in classical MD, however, a kind of "friction" is added. The basic idea underlying in the MS algorithm, which was used in the present studies, was to rescale velocities at each iteration according to the following formula:

$$\mathbf{v}' = \begin{cases} \mathbf{v} - \gamma \frac{\mathbf{F}}{|\mathbf{F}|} |\mathbf{v}| & \text{for } \mathbf{F} \cdot \mathbf{v} < 0\\ \mathbf{v} & \text{for } \mathbf{F} \cdot \mathbf{v} \ge 0 \end{cases}$$
(2.2.8)

where γ is a parameter between 0 and 1. It means that only the component of the velocity that is parallel to the force is altered, and only when the atom moves against the force. When $\gamma = 0$ it means no energy dissipation, whereas $\gamma = 1$ means maximum dissipation and atoms will only slide down along gradients of potentials.

In some cases, during MS simulations, additional constrains have been used together with the above formula. To calculate values of migration barriers during atomic jumps, the base of the sample, as well as the jumping atom's velocity component parallel to the jump direction had to be fixed. This protected the migrating atom from sliding back to its original site (or to the vacancy). This procedure will be explained in detail in sec.5.3.1.

2.3 Monte Carlo / Static Relaxation (MC/SR) algorithm

The combination of methods originating from both MD (interatomic potentials, relaxations) and MC (fast algorithm for atomic interchanges) is not a novel idea. Several particular approaches can be distinguished. Quasi-Harmonic Lattice Dynamics (Q-HLD) [40, 41] - allowing calculation of free energy regarding phonons, pressure and defects in crystalline lattice. Hybrid Monte Carlo [42, 41] (HMC) - allows execution of sets of MD steps together with atomic migration procedures (MC). This method can be virtually applied to simulate ordering processes in FePt thin layers, however it is extremely demanding in terms of necessary computational resources, hence time consuming. In the hereby dissertation a simplified Hybrid Monte Carlo algorithm MC/SR is proposed (similar to the one published by Purton et. al [42]), as a compromise between an attempt to apply the most detailed physical model and available computational resources.

The simultaneous application of both MC and MS simulation methods allows observations of some physical effects that are not available for any of the methods used separately. The MC implemented with vacancy mechanism algorithm provides atomic order relaxation. The MS steps allow localized lattice relaxation. The pressure control algorithms allow relaxations of global lattice parameters affected by long range order. Typical sequence of MC/SR algorithm consists of:

- $10^3..10^5$ steps of MC algorithm (subsec. 2.1.2)
- Static Relaxation including:
 - a lattice constants relaxation in each (x,y,z) direction (subsec. A.3)
 - a partial (up to 500 MS steps) or full Molecular Statics relaxation (subsec. 2.2.2)

In the original HMC MC/SR [42] algorithm the Static Relaxation is one of possible events as well as MC steps, executed with a certain probability. In our simplified approach, the SR sequence is performed in constant MC-time intervals and its acceptance is granted according to the assumption (subsec. 1.2.2) that the crystal lattice relaxations are the result of evolution of the atomic configuration.

Two problems are addressed with this approach:

- The relation between lattice parameters and LRO. The tetragonality of a $L1_0$ structure affects defect formation energies. Different values of antisite formation energy cause changes in order-disorder transition temperature, as well as a minor effect on ordering kinetics. In real system demise of tetragonal distortion is a result of decreasing LRO. To model this process in simulated system, it is necessary to include lattice constants relaxation routines in the schedule of the simulation.
- Surface relaxation. In a real system atoms in the surface region, except deviated coordination, usually exhibit a change in atomic positions with respect to bulk. It is important to take this effect into account since it causes different defect formation energies, and locally may cause significant changes in ordering kinetics. The effect of local relaxations is simulated by Molecular Statics sequences included in the schedule of the simulation.

2.4 Atomic migration barriers - interpolation scheme

The energy barriers used in Kinetic Monte Carlo simulations can be calculated on the basis of atomic migration energy profiles obtained by a sequence of Molecular Statics simulations (subsec. 2.2.2). For the sake of economization of computational time, the barriers can be calculated, tabulated, and afterwards recalled during a simulation.

Let us consider an atom migrating to a NN vacancy in a crystalline lattice. On the way to the vacancy, the atom will have to cross a saddle point (with the highest potential energy)(1.2.1). At this point the atom is in the closest distance to a set of neighboring atoms, in most cases there are four atoms (fig.2.4.1). This set of atoms composes the migration window, through which the migrating atom must pass.



Figure 2.4.1: An example of a migration window \mathbf{W} .

Preliminary sampling of the migration barriers was performed for particular atomic arrangement as well as for a few selected sets of lattice parameters. During data analysis it appeared that there are three important factors which influence the migration barrier energy:

• The atomic arrangement of the migration window (fig.2.4.1). In the case of migrations to NN site in $L1_0$ superstructure, the migration window is composed of 4 atoms - in the bulk, or 2 atoms- when migration proceeds at the surface:

$$\mathbf{W} = \begin{cases} \{\sigma_1, \sigma_2, \sigma_3, \sigma_4\} & - \text{ for bulk} \\ \{\sigma_1, \sigma_2\} & - \text{ for surface} \end{cases}$$
(2.4.1)

where each σ_i corresponds to particular occupation (Fe or Pt in the case of L1₀ FePt)

- The size of the migration window \mathbf{W} , dependent on the lattice parameters in the sample, parametrized by the (minimal average) distance $r_{\mathbf{w}}$ between the migrating atom and the atoms from the window \mathbf{W} (fig.2.4.1).
- A distance of the migrating atom from the surface. This aspect of the migrating atom can be estimated by N_n the number of NN and NNN atoms around the migrating atom and the targeted vacancy.

The above observations have been used to develop a general formula interpolating the value of migration barrier $E_{i,\mathbf{W}}^+$ from sampled data:

$$E_{i,\mathbf{W}}^{+}(r_{\mathbf{W}}, N_{n}) = \frac{E_{0} + E_{1}}{2} + f_{i,\mathbf{W}}(r_{\mathbf{W}})g_{i,\mathbf{W}}(N_{n})$$
(2.4.2)

where: *i* is the type of the migrating atom; **W** is the set of atoms of which the migration window is composed; E_0 and E_1 are respectively the energy before and after the execution of the atomic jump; $f_{i,\mathbf{W}}(r_{\mathbf{W}})$ is the function that gives the value of the migration barrier according to the migration window configuration **W** and the window size $r_{\mathbf{W}}$ (fig.2.4.1), $g_{i,\mathbf{W}}(N_n)$ is the function that modifies the value of the migration barrier with respect to the distance of the migrating atom from the surface. The function, besides being dependent on **W**, is effectively parametrized by N_n the number of NN and NNN neighbors around the migrating atom.

Due to the fact that changes of the value of migration barrier energy caused by the window size (mainly by different lattice constants), are relatively small in the regarded range of lattice constant values (range determined by tetragonal distortion and surface relaxations), linear dependency was assumed:

$$f_{i,\mathbf{W}}(r_w) = (A_{i,\mathbf{W}} \cdot r_w + B_{i,\mathbf{W}}) \tag{2.4.3}$$

The dependence of the migration barrier on the number of neighbors (distance from the surface) $g_{i,\mathbf{W}}(N_n)$ after simulating preliminary migration energy profiles appeared to be well estimatable by linear function:

$$g_{i,\mathbf{W}}(N_n) = (C_{i,\mathbf{W}} \cdot N_n + D_{i,\mathbf{W}}) \tag{2.4.4}$$

Assuming linear dependencies of the aforementioned functions (eq.2.4.3 and eq.2.4.4), the formula estimating migration barrier has the following form:

$$E_{i,\mathbf{W}}^{+} = \frac{E_0 + E_1}{2} + (A_{i,\mathbf{W}} \cdot r_w + B_{i,\mathbf{W}}) \cdot (C_{i,\mathbf{W}} \cdot N_n + D_{i,\mathbf{W}})$$
(2.4.5)

On the basis of the simulated atomic migration energy profiles, the parameters A,B,C and D must be fitted or calculated⁷ separately for each i - type of migrating atom, and W - migration window composition. The particular results are presented in the subsection containing migration barriers evaluation for the ABOP-based system (subsec.5.3.1).

 $^{^7\}mathrm{At}$ the surface C=0 and D=1.

Chapter 3

Models

3.1 Two-body interaction model

The configurational energy of the system based on two-body interactions is represented by the following formula:

$$E_{conf} = \sum_{i \neq j} V_{ij}(r_{ij}) \tag{3.1.1}$$

where *i* and *j* denotes sites in the lattice, V_{ij} is effective pair interaction energy between atoms in sites *i* and *j*, and r_{ij} is a distance between the sites. When considering the model based on the rigid lattice the distances between sites are discrete. The model is isomorphic with the Ising model¹ [45], thus the name Ising-type model will be used interchangeably with the two-body interaction model. When a finite range of interaction is assumed (cutoff distance), only a certain number of coordination shells can be taken into account, which significantly reduces the number of parameters. In this work the interactions up to NNN are considered.

3.1.1 Two-body potentials development for FePt system

3.1.1.1 Ab-initio parametric with Cluster Expansion Method

Ising-type two-body potentials for FePt were developed on the basis of Cluster Expansion Method² (CEM). The formalism was proposed by T.Mohri, Y. Chen et al. for Fe-Pt and Fe-Pd intermetallics [46, 47].

Full-potential linearized augmented-plane-wave (FLAPW) method within the generalized gradient approximation (GGA) was applied to obtain the total energies $E_{Fe_{4-n}Pt_n}(r)$ for $Fe_{4-n}Pt_n$ alloys, where n is an integer value denoting the intermetallic composition and r is a lattice constant parameter. Following

¹Descriptions of the Ising model and the atomistic model based on rigid lattice and twobody interaction are isomorphic, however, the dynamics of the atomistic model differs substantially from the Ising one. The approach which makes Ising model closer to the atomistic one in terms of the system dynamics, was proposed by K. Kawasaki [43]. The Ising-Kawasaki dynamics and the vacancy mechanism gives similar results [44].

 $^{^{2}}$ CEM is a method that combines Ab-initio calculations and CVM to obtain particular system parameters, in this case interatomic potentials.

	m = 0	m = 1	m = 2	m = 3	m = 4
	null	point	pair	${ m triangle}$	tetrahedron
Fe	1	1	1	1	1
Fe_3Pt	1	1/2	0	-1/2	-1
FePt	1	0	-1/3	0	1
$FePt_3$	1	-1/2	0	1/2	-1
Pt	1	-1	1	-1	1

Table 3.1: Values of the correlation functions ξ_m^n

atomic arrangements were studied: pure Fe or Pt FCC for respectively n = 0 or 4, L1₂ superstructure for n = 1 and 3 and L1₀ superstructure for n = 2. Additionally, $E_{Fe_4}^{BCC}$ for pure BCC Fe was also calculated. With total energies $E_{Fe_4-nPt_n}(r)$, the corresponding intermetallic formation energies are obtained as:

$$\Delta E_n(r) = E_{Fe_{4-n}Pt_n}(r) - \frac{4-n}{4} E_{Fe_4}^{BCC}(r_{BCC}) - \frac{n}{4} E_{Pt_4}(r_4)$$
(3.1.2)

where: r_4 and r_{BCC} denote equilibrium lattice constants for particular structures.

Chen and Mohri used Lennard-Johnes type potential and fitted it to the results (Universal Equation of State could be used instead as well), to enable continuous parametrization of the results with regard to lattice constants:

$$\Delta E_n(r) = \frac{a_n}{r^7} - \frac{b_n}{r^{3.5}} + c_n \tag{3.1.3}$$

It is important to note that r in this representation denotes average lattice constant³ and not the individual interatomic distance, thus, the parameter should not be (in further calculations) a variable in the distance dependent pair interaction, but it should be fixed and kept constant during simulations. Moreover, this representation involves tetragonality only in an effective constant way, without the possibility to alter the c/a relation.

Then, the CVM was applied to extract effective cluster energies $v_m(r)$, up to the NN tetrahedron cluster. According to the principles of CVM, the total configurational energy of the system can be described by a set of correlation functions as follows:

$$\Delta E_n(r) = \sum_{m=0}^{m_{max}} v_m(r) \xi_m^n$$
(3.1.4)

where v_m specifies cluster energies and ξ_m^n is the correlation function defined as:

$$\xi_m^n = <\sigma_{p_1}\sigma_{p_2}\sigma_{p_3}...\sigma_{p_k}...\sigma_{p_m}>$$
(3.1.5)

where σ_{p_k} is the spin operator, which is equal to either +1 or -1 depending upon the A or B atom is located at the lattice site specified by p_k in the m-point

 $^{{}^{3}}r$ should be considered as $r = \sqrt[3]{V_{u.c.}}$ the parameter related to the volume of the system unit cell rather than interatomic distance.

cluster of the phase n, and the brackets $\langle \rangle$ denote the ensemble average. Let us assume that x_i and y_{ij} denote point and pair cluster probabilities, the following relationships hold[46]:

$$x_i = \frac{1}{2}(1 + i * \xi_1) \tag{3.1.6}$$

$$y_{ij} = \frac{1}{2^2} \left[1 + (i+j)\xi_1 + ij\xi_2 \right]$$
(3.1.7)

where i and j equal +1 or -1 for A and B atoms, respectively.

The values of correlation functions for the particular phases are provided in tab.3.1. The matrix of $\{\xi_m^n\}$ is 5x5 regular, non-singular, and can be inverted. Then, the matrix inversion of equation (3.1.4) yields the effective cluster interaction energies:

$$v_m(r) = \sum_{n=0}^{4} \left\{ \xi_m^n \right\}^{-1} \Delta E_n(r)$$
(3.1.8)

whose the formula can be represented in the following explicit matrix form:

$$\begin{bmatrix} v_{0}(r) \\ v_{1}(r) \\ v_{2}(r) \\ v_{3}(r) \\ v_{4}(r) \end{bmatrix} = \begin{bmatrix} 1 & 4 & 6 & 4 & 1 \\ 4 & 8 & 0 & -8 & -4 \\ -6 & 0 & -12 & 0 & 1 \\ 4 & -8 & 0 & 8 & -4 \\ -1 & -4 & 6 & -4 & -1 \end{bmatrix} \begin{bmatrix} \Delta E_{0}(r) \\ \Delta E_{1}(r) \\ \Delta E_{2}(r) \\ \Delta E_{3}(r) \\ \Delta E_{4}(r) \end{bmatrix}$$
(3.1.9)

After estimation of cluster energy values, it appears that v_3 and v_4 are negligibly small, thus the simplified energy formula can be written as:

$$\Delta E_n(r) = v_0(r) + v_1(r)\xi_1^n + v_2(r)\xi_2^n \qquad (3.1.10)$$

Within NN pair-interaction estimation, the energy of the system can be rewritten as:

$$\Delta E = \omega \sum_{i,j} V_{ij}^I y_{ij} \tag{3.1.11}$$

where: ω - the NN co-ordination number ⁴, V_{ij}^{I} - effective pair interaction energy. Note that ΔE is a vector with certain values for the particular intermetallics $Fe_{4-n}Pt_n$. By comparison of equations (3.1.10) (3.1.11), and separation of their elements, following equations for cluster energies for Fe-Pt system are derived:

$$v_0(r) = 3\left(V_{FeFe}^I(r) + V_{FePt}^I(r) + V_{PtPt}^I(r)\right)$$
(3.1.12)

$$v_1(r) = 3 \left(2V_{FeFe}^I(r) - 2V_{PtPt}^I(r) \right)$$
(3.1.13)

$$v_2(r) = 3\left(V_{FeFe}^I(r) + V_{PtPt}^I(r) - V_{FePt}^I(r)\right)$$
(3.1.14)

⁴For FCC lattice $\omega = 12$.

3.1.1.2 The nearest neighbor pair-interactions

From equations (3.1.12), (3.1.13) and (3.1.14) it is easy to obtain NN pair interaction energies for the nearest neighbors:

$$V_{FePt}^{I}(r) = \frac{1}{6} \left(v_0(r) - v_2(r) \right)$$
(3.1.15)

$$V_{FeFe}^{I}(r) = \frac{1}{12} \left(v_0(r) - v_1(r) + v_2(r) \right)$$
(3.1.16)

$$V_{PtPt}^{I}(r) = \frac{1}{12} \left(v_0(r) + v_1(r) + v_2(r) \right)$$
(3.1.17)

It is important to note that values obtained in this way are dependent on the lattice constant. However, as it was mentioned (eq.3.1.3) the lattice parameter used in this context refers to the average interatomic distance (unit cell volume). $V_{ij}^{I}(r)$ should not be interpreted as interatomic potentials dependent on the distance. For the sake of the consistency, the lattice parameter must be set the same for all interactions.

3.1.1.3 Second nearest neighbor extension

To expand the model for the next nearest neighbor (NNN) interactions 3 more parameters were necessary. However, to reduce number of free parameters the same proportions between Fe-Fe and Pt-Pt, and between Fe-Fe and Fe-Pt interactions in the first and second coordination shell were assumed:

$$\frac{V_{FeFe}^{I}}{V_{PtPt}^{I}} = \frac{V_{FeFe}^{II}}{V_{PtPt}^{II}}$$
(3.1.18)

$$\frac{V_{FeFe}^{I}}{V_{FePt}^{I}} = \frac{V_{FeFe}^{II}}{V_{FePt}^{II}}$$
(3.1.19)

A free parameter was chosen to set the relation between the interaction values in the first and second coordination shell α :

$$\alpha = \frac{V_{FeFe}^{I}}{V_{FeFe}^{II}} \tag{3.1.20}$$

A set of MC simulations was performed to find the order-disorder transition temperature of of the simulated FePt L1₀ alloy. The values of α and r (lattice constant) parameters were adjusted to fit the simulated order-disorder temperature to the experimental value. Temperature dependencies of η parameter were obtained by MC simulations. Detailed description of the procedure may be found in the section 4.2 devoted to results of two-body interactions model.

The definitely chosen set of interaction parameters, displayed in table 3.2, corresponded to r=0.3862 nm (the experimental value of FePt L1₀ parameter) and $\alpha = -0.1$. The parameters yielded the best approximation of the experimental value of the order-disorder transition temperature $T_t = 1575$ K for FePt.



Figure 3.1.1: $\eta(T)$ curves resulting from MC simulations of L1₀ FePt for r=0.3862 nm (a) rough curves obtained for various values of α parameter; (b) the curve obtained for $\alpha = -0.1$.

i-k	$V^{I}_{ik}[\text{meV}]$	V_{ik}^{II} [meV]
Fe-Fe	11.45	-1.145
Fe-Pt	-67.05	6.705
Pt-Pt	85.63	-8.563

Table 3.2: Values of Fe-Pt two-body interactions used in the simulations of $L1_0$ FePt.

3.2 Analytical Bond-Order Potentials

Analytic Bond-Order Potentials (ABOP) were originally developed to describe semiconducting, covalent-bounded systems like silicon [48, 49] and carbon [50, 51]. In such systems bindings are directionally dependent, which is taken into account by the inclusion of three-body angular terms. It is possible to show that ABOP formalism is formally an expansion of the Second Momentum Approximation (Tight-Biding) model [52, 53] and, at certain assumptions, can be equivalent to Embedded Atom Method (EAM) formalism [54]. This fact justifies the straightforward application of ABOP to metals [55, 17] and metalsemiconductor systems [56]

3.2.1 Bond-order formalism

The potential energy of the system can be described as a sum of individual bond energies including the many-body terms $(b_{ij} (r_{ij}, ..))$:

$$E = \sum_{i}^{N} \sum_{j>i}^{N} f_{ij}^{c}(r_{ij}) \left[V_{ij}^{R}(r_{ij}) - \frac{b_{ij}(r_{ij},..) + b_{ji}(r_{ji},..)}{2} V_{ij}^{A}(r_{ij}) \right]$$
(3.2.1)

where N is a number of all atoms in the system, i and j iterate the interacting atoms. The pair-interactions V^R - repulsive and V^A - attractive terms have the form of Morse potential (for the sake of clear notation, the ij subscript was



Figure 3.2.1: θ_{ijk} angle in a configuration of the interacting *i* and *j* atoms with the neighboring *k* atom

omitted):

$$V^{R}(r) = \frac{D_{0}}{S-1} \exp\left(-\beta \sqrt{2S} (r-r_{0})\right)$$
(3.2.2)

$$V^{A}(r) = \frac{SD_{0}}{S-1} \exp\left(-\beta \sqrt{2/S} \left(r - r_{0}\right)\right)$$
(3.2.3)

where D_0 is the dimer bond energy, r_0 the dimer bond length, β is related to dimer ground state oscillation frequency (k - oscillation wave vector number)

$$\beta = k \frac{2\pi c}{\sqrt{2D_0/\mu}} \tag{3.2.4}$$

and parameter S is a parameter adjustable on the basis of Pauling criterion and to obtain proper r_0 value. The cutoff function f^c is constructed to be smooth in derivatives:

$$f^{c}(r) = \begin{cases} 1 & for \ r \leq R - D \\ \frac{1}{2} - \frac{1}{2} \sin\left(\frac{\pi}{2} (r - R) / D\right) & for \ |R - r| \leq D \\ 0 & for \ r \geq R + D \end{cases}$$
(3.2.5)

R is the cutoff distance and D is the width of the smoothing area. Many-body terms have the following form:

$$b_{ij}(r_{ij},..) = (1 + \chi_{ij}(r_{ij},..))^{-\frac{1}{2}}$$
(3.2.6)

$$\chi_{ij}(r_{ij},..) = \sum_{k \neq i,j} f_{ij}^c(r_{ik}) g_{ik}(\theta_{ijk}) \exp\left[2\mu_{ik}(r_{ij} - r_{ik})\right]$$
(3.2.7)

where μ_{ik} is a three-body interaction coefficient, and $g_{ik}(\theta_{ijk})$ is a three-body angular dependent term:

$$g(\theta) = \gamma \left(1 + \frac{c^2}{d^2} - \frac{c^2}{d^2 + [h + \cos\theta]^2} \right)$$
(3.2.8)

 γ , c, h and d are adjustable parameters.

	$\operatorname{Fe-Fe}$	Pt-Pt	Fe-Pt
$D_0[eV]$	1.5	3.2	2.65
$r_0[0.1 {\rm nm}]$	2.29	2.42	2.36
β [0.1nm ⁻¹]	1.4	1.61	1.46
S	2.07	2.30	2.26
γ	0.0116	0.185	0.0563
С	1.29	0.0609	0.351
d	0.341	0.08	0.169
h	-0.26	0.455	0.450
$2\mu[0.1{\rm nm^{-1}}]$	0.0	1.58	0.958
$R[0.1\mathrm{nm}]$	3.15	3.75	4.20
$D[0.1\mathrm{nm}]$	0.2	0.2	0.2

Table 3.3: ABOP Fe-Pt parameters [17].

3.2.2 Analytic Bond-Order Potentials for Fe-Pt systems

The ABOP model parameters for Fe-Pt were evaluated by Muller et al [17].

In order to test the ABOP model application some of the physical parameters were calculated. The results together with original, experimental and other modeled data are presented in table 3.4.

	Experi-	GGA	EAM and	MEAM	ABOP	ABOP
	mental	[57]	other	[58, 59, 60]	[17]	$\operatorname{present}$
	data		models			work[29]
Fe bcc						
a	2.860[61]	2.832	2.860[62]	2.86^{*}	2.860	2.860
E_{coh}	-4.28 [63]	-4.28	-4.28[62]	-4.29^{*}	-4.28	-4.28
B	173[64]	189	178 [62]	173	169	170
Pt fcc						
a	3.923[65]	3.176	3.92[66]	3.91^{*}	3.917	3.917
E_{coh}	-5.84 [63]	3.986	-5.77 [66]	-5.77^{*}	-5.77	-5.77
B	286[67]	244	283[66]	288	286	289
FePt L1 ₀						
a	3.861[6]	3.872	3.85[68]	3.81	3.862	3.862
c/a	0.981 [6]	0.973	0.964[68]	0.963	0.963	0.963
ΔE_f		-0.224	-0.287 [46]	-0.604	-0.32	-0.32
E_{coh}		-5.249	-5.345 [17]	-5.634	-5.345	-5.345
B		200	217 [17]	232	217	217

Table 3.4: Basic physical properties of Fe, Pt and L1₀ FePt obtained from experiments and various models. *a*- lattice constant [0.1nm] ([A]), E_{coh} - cohesive energy [eV], *B* - bulk modulus [GPa], c/a - tetragonality, ΔE_f - intermetallic formation energy, * - indicates rather input parameter than a resulting value.

Chapter 4

Atomic ordering kinetics in Ising-type FePt model

A substantial part of the thesis consists of the results obtained within two numerical models of interatomic potentials either two-body Ising-type interactions or many-body ABOP interactions. In both cases the same procedure was applied. After the development and application of the particular model to the software (Alphard) and basic parameter tests, the overall configuration energy of the system was analyzed, especially surface configurational energies and defects formation energies. Afterwards, a detailed study was devoted to ordering kinetics in bulk and layered systems. In this chapter, the Ising-type model study results are presented [69, 70].

4.1 Heuristic clues

Before the analysis of the simulation results, some general aspects of atomic configuration and related energetics were studied. Since the configurational energy is composed of the simple two-body energies it was possible (straightforward, however, laborious) to calculate it analytically.



Figure 4.1.1: $L1_0$ A-B superstructure

4.1.1 Comparison of perfectly ordered $L1_0$ a- and c-variant thin layers

Samples in the form of thin layers with two (001)-oriented surfaces (on the upper and lower side of the sample) were considered. In the simulated layered samples, in comparison to the bulk ones, a considerable increase of the system configurational energy is observed. The increase is due to broken interatomic bonds. Depending on the superstructure orientation with respect to the surface, namely the particular $L1_0$ variant (tab. 1.1), the configurational energy of the systems differs.



Figure 4.1.2: Two basic $L1_0$ -ordered thin layer variants: (a) a(b)-variant (b) c-variant

Let us consider two superstructure variants at the (001) surface: a(b)-variant¹ with monoatomic planes perpendicular to the surface, and c-variant with monoatomic planes parallel to the surface (fig. 4.1.2). Firstly, let us consider interactions only among NN atoms. It will appear later in this subsection that the NNN interactions do not influence the considered situation. In general, a difference in configurational (surface) energy among the particular variants of the L1₀-ordered superstructure in the layers can be denoted as:

$$\Delta E_{a-c} = \Delta E_a - \Delta E_c = (E_a - E_{bulk}) - (E_c - E_{bulk}) = (4.1.1)$$
$$E_a - E_c$$

where E_{bulk} is configurational energy of the perfectly ordered L1₀ bulk sample (periodic boundary conditions in all directions), E_c is configurational energy of the perfectly ordered in L1₀ c-variant layered sample with (001) surfaces (fig. 4.1.3) (periodic boundary conditions in [100], [010]), and E_a is configurational energy of the perfectly ordered in L1₀ a-variant layered sample with (001) surfaces.

According to eq. 3.1.1, the Ising-type configurational energy may be expressed by a sum of contributions corresponding to pair-interactions in consecutive coordination zones. Hence, ΔE_{a-c} may be analyzed separately for NN and NNN interactions.

 $^{^{1}}a$ - and b- variants are equivalent when considering (001) surface, due to the 4-fold rotational symmetry around the [001] axis.


Figure 4.1.3: The scheme of (001)-surface generation in $L1_0$ c-variant sample; due to the cut of PBC each atom at the surface loses 4 NN atoms.

Let us consider the NN configurational energy of the bulk system:

$$E_{bulk}^{NN} = \frac{N_A}{2} (4V_{AA}^I + 8V_{AB}^I) + \frac{N_B}{2} (4V_{BB}^I + 8V_{AB}^I)$$
(4.1.2)

where $N_A{}^2$ is the number of A-type atoms in the whole sample, per analogy the same for B-atoms; V_{AA}^I , V_{BB}^I and V_{AB}^I are respectively NN pair-interactions of two A-atoms, two B-atoms and in mixed pair A- and B-atoms.

Now, the configurational energy of the layer limited by a surface can be represented as the one for the bulk with particular number of bonds broken (fig. 4.1.3):

$$E_c^{NN} = E_{bulk}^{NN} - \frac{N_{A_{surf}}}{2} \cdot 4V_{AB}^I - \frac{N_{B_{surf}}}{2} \cdot 4V_{AB}^I$$
(4.1.3)

$$E_a^{NN} = E_{bulk}^{NN} - \frac{N_{A_{surf}}}{2} \left(2V_{AB}^I + 2V_{AA}^I \right) - \frac{N_{B_{surf}}}{2} \cdot \left(2V_{AB}^I + 2V_{BB}^I \right) \quad (4.1.4)$$

where $N_{A_{surf}}$ is the number of A-type atoms at the sample's surface, per analogy the same for B-atoms. There are 4 bonds broken around each surface atom. In the case of c-variant layers, there are only A-B bonds broken (fig. 4.1.3), in the a-variant layers the situation is more complex.

With the assumption: $N_A = N_B = N/2$ and $N_{A_{surf}} = N_{B_{surf}} = N_{surf}/2$, the formula for ΔE_{a-c}^{NN} is found:

$$E_{bulk}^{NN} = N(V_{AA}^{I} + V_{BB}^{I} + 4V_{AB}^{I})$$
(4.1.5)

$$E_c^{NN} = E_{bulk}^{NN} - 2 \cdot N_{surf} \cdot V_{AB}^I \tag{4.1.6}$$

$$E_{a}^{NN} = E_{bulk}^{NN} - \frac{N_{surf}}{2} \left(2V_{AB}^{I} + V_{AA}^{I} + V_{BB}^{I} \right)$$
(4.1.7)

$$\Delta E_{a-c}^{NN} = 2 \cdot N_{surf} \cdot V_{AB}^{I} - \frac{1}{2} N_{surf} \left(2V_{AB}^{I} + V_{AA}^{I} + V_{BB}^{I} \right)$$
(4.1.8)

$$\Delta E_{a-c}^{NN} = \frac{N_{surf}}{2} \left(2V_{AB}^{I} - V_{AA}^{I} - V_{BB}^{I} \right) \sim W_{AB}^{I}$$
(4.1.9)



Figure 4.1.4: An example of NNN co-ordinations around Fe atom in two basic $L1_0$ surface variants: (a) a(b)-variant (b) c-variant.

where W_{AB}^{I} is NN ordering energy of the A-B intermetallic.

Interatomic NNN co-ordinations do not differ among a- and c-variant layers (fig.4.1.4). This can be explained when considering first layer of unit cells at the surface³ (first two monoatomic layers). Each atom of the certain type in the considered volume lacks one NNN of the same type. Moreover, the overall concentration of particular atoms in the considered area is not changing among a- and c- variants. Thus consequently, the number of NNN interactions in the a- and c- variant layers is exactly the same, and $\Delta E_{a-c}^{NNN} = 0$.

The above result (4.1.9) is very important and indicates a general feature of ordered $L1_0$ systems that the a(b)-variant layer is energetically more stable than the c-variant layer.

For the defined values of Ising-type FePt interactions (sec. 3.1) the value of the energy change after c-variant to a-variant $L1_0$ superstructure (001) surface transformation is equal to:

$$\Delta E_{a-c} = N_{surf} (-0.1156) \, [eV] \tag{4.1.10}$$

4.1.2 Surface domains analysis

Now let us analyze the potential mechanism that might lead to the phase transformation from c-variant to a-variant. The fact that the energy difference between a- and c- variants exists at the surface, indicates that the surface is a place where the possible transition would begin. When considering the superstructure transition, it should be noted that the concentration of both A and B atoms is constant. Thus, without losing the generality of this particular study, we can assume that the transition of the superstructure is based on the unit cells rotation, which makes the image of the process easier to imagine. There are several possible definitions of unit cells in ordered $L1_0$ superstructure, however, for the simplicity of geometric construction, let us define the unit cell composed of four atoms, as in figure 4.1.5.

²Because the interactions are represented by pair energies, the numbers of atoms are divided by 2 (like $\left(\frac{N_A}{2}\right)$).

³In the considered Ising-type model based on the rigid FCC lattice, the bulk configurational energy is invariant with respect to 4-fold rotation around each of the symmetry axis.



Figure 4.1.5: L10 unit cell and 010 cross-section view of a sample's surface part.

Now, when the unit cell is defined, let us consider two situations that can occur on one (side) surface of the layered sample: a perfectly ordered c-variant layer with a surface , and a sample consisting of two domains: a-variant at the surface and c-variant in the bulk separated by a flat antiphase boundary (APB) (fig.4.1.6).



Figure 4.1.6: (a) Pure c-variant L10 surface, and (b) a-variant surface domain on c-variant bulk.

Now, let us study the energy differences between those two samples. In the analyzed situation both NN and NNN atoms are acting, however, for the sake of a clear notation let us start with the first coordination shell, and afterwards continue the calculation with the second. In the sample presented in fig.4.1.6a) the configurational energy can be stated as:

$$\Delta E_{c_{surf}}^{NN} = E_{bulk}^{NN} - E_{c_{surf}}^{NN} = E_{bulk}^{NN} - 4 \cdot N_{A(a)_{surf}} V_{AB}^{I}$$
(4.1.11)

whereas in the sample presented in fig.4.1.6b) the situation is more complex:

$$\Delta E_{a_{surf}}^{NN} = E_{bulk}^{NN} - E_{a_{surf}}^{NN} + \Delta E_{interface}^{NN}$$
(4.1.12)

$$\Delta E_{a_{surf}}^{NN} = E_{bulk}^{NN} - \frac{N_{A(b)_{surf}}}{2} \left(2V_{AB}^{I} + 2V_{AA}^{I} \right) - \frac{N_{B(b)_{surf}}}{2} \cdot \left(2V_{AB}^{I} + 2V_{BB}^{I} \right) + \Delta E_{interface}^{NN}$$

$$(4.1.13)$$

where $N_{A(a)_{surf}}$ denotes the number of A-atoms at the surface in the sample as in figure 4.1.6(a); $N_{A(b)_{surf}}$ and $N_{B(b)_{surf}}$ are respectively numbers of A-atoms and B-atoms at the surface as in fig.4.1.6(b). Because both pictures refer to the same sample, the surface area is constant and: $N_{A(a)_{surf}} = N_{A(b)_{surf}} + N_{B(b)_{surf}} = N_{surf}$.

$$\Delta E_{a_{surf}}^{NN} = E_{bulk}^{NN} - \frac{N_{surf}}{2} \left(4V_{AB}^{I} + 2V_{AA}^{I} + 2V_{BB}^{I} \right) + \Delta E_{interface}^{NN}$$
(4.1.14)

Calculation of $\Delta E_{interface}$ which is the energy of an interface between A-atom monoatomic layer and a-variant domain requires more attention. Let us consider four sites at the interface, marked and numbered in fig.4.1.6(b). Their NN energies given by the following formulas:

$$E_1^{(b)} = 10V_{AB}^I + 2V_{BB}^I \tag{4.1.15}$$

$$E_2^{(b)} = 6V_{AB}^I + 6V_{AA}^I \tag{4.1.16}$$

$$E_3^{(b)} = 6V_{AB}^I + 6V_{AA}^I \tag{4.1.17}$$

$$E_4^{(b)} = 6V_{AB}^I + 6V_{AA}^I \tag{4.1.18}$$

whereas in the c-variant bulk the same sites would have NN energies:

$$E_1^{(a)} = 8V_{AB}^I + 4V_{BB}^I \tag{4.1.19}$$

$$E_2^{(a)} = 8V_{AB}^I + 4V_{BB}^I \tag{4.1.20}$$

$$E_3^{(a)} = 8V_{AB}^I + 4V_{AA}^I \tag{4.1.21}$$

$$E_4^{(a)} = 8V_{AB}^I + 4V_{AA}^I \tag{4.1.22}$$

The NN energy of the interface can be calculated as follows:

$$\Delta E_{interface}^{NN} = \frac{N_{surf}}{2} \sum_{i=1}^{4} \left(E_i^{(b)} - E_i^{(a)} \right)$$
(4.1.23)

$$\Delta E_{interface}^{NN} = \frac{N_{surf}}{2} \left(28V_{AB}^{I} + 2V_{BB}^{I} + 18V_{AA}^{I} \right) - \frac{N_{surf}}{2} \left(32V_{AB}^{I} + 8V_{BB}^{I} + 8V_{AA}^{I} \right)$$

$$\Delta E_{interface}^{NN} = \frac{N_{surf}}{2} \left(-4V_{AB}^{I} - 6V_{BB}^{I} + 10V_{AA}^{I} \right)$$
(4.1.24)

The change of configurational energy that appears due to the surface a-variant domain creation (surface transition energy), can be analyzed by subtraction

of interface energy and the energy of the surface transition (c- to a- variant) from the energy of the initial pure c-variant surface:

$$\Delta E_{surface_{a\leftarrow c}} = \Delta E_{a_{surf}} - \Delta E_{c_{surf}} = (E_{bulk} - E_{a_{surf}} + \Delta E_{interface}) - (4.1.25) (E_{bulk} - E_{c_{surf}})$$

When applying equations 4.1.11, 4.1.14 and 4.1.24 to the above formula, NN surface transition energy can be stated as:

$$\Delta E_{surface_{a \leftarrow c}}^{NN} = E_{bulk}^{NN} - \frac{N_{surf}}{2} \left(4V_{AB}^{I} + 2V_{AA}^{I} + 2V_{BB}^{I} \right) + \frac{N_{surf}}{2} \left(-4V_{AB}^{I} - 6V_{BB}^{I} + 10V_{AA}^{I} \right) - (4.1.26)$$
$$E_{bulk}^{NN} + 4 \cdot N_{surf} V_{AB}^{I}$$

and consequently reduced to:

$$\Delta E_{surface_{a\leftarrow c}}^{NN} = -4N_{surf} \left(V_{BB}^{I} - V_{AA}^{I} \right) \tag{4.1.27}$$

The above analysis takes into account only NN interactions, however, the extension of this study to the NNN shell brings only minor change, since only one atom (fig. 4.1.6 atom No. 2) per unit cell in the interface layer has exchanged one next nearest neighbor. The relation that includes NNN interactions would be the following:

$$\Delta E_{surface_{a\leftarrow c}} = -4N_{surf} \left(V_{BB}^{I} - V_{AA}^{I} \right) - \frac{N_{surf}}{2} \left(V_{AA}^{II} - V_{BB}^{II} \right)$$
(4.1.28)

Because the above formula depends only on the differences between pairinteractions among the same types of atoms (A-A or B-B) it indicates that on the surface covered with A-atoms (as in this heuristic approach) the surface transition energy $\Delta E_{surface_{a\leftarrow c}}$ will have exactly opposite value regarding the surface covered with B-atoms. Thus, in all models of L1₀ superstructure based on pair-interactions⁴, there will be a tendency for the superstructure reorientation at the surface covered by either A or B atoms depending on the sign of $\Delta E_{surface_{a\leftarrow c}}$. It also points out to the fact that when the reorientation starts at the surface covered with A(Fe) atoms, an A-atoms rich antiphase domain boundary (APB) will be created during the reorientation.

It is crucial to note that the energy of the surface $a \rightarrow c$ -variant transformation is independent on the depth⁵ of a- or b-variant domain penetrating the layered sample. It is because the energy of the a-variant surface domain (eq.4.1.28) depends only on the free surface and APB energies.

The values of potentials developed for Fe-Pt systems (table 3.2) imply:

$$\Delta E_{surface_{a\leftarrow c}} = (-4N_{surf}(0,0785) - N_{surf}/2(0,00785)) \text{ [eV]} (4.1.29)$$

= $N_{surf}(-0,318) \text{ [eV]}$

⁴Except the situations when $\Delta E_{surface_{a \leftarrow c}} = 0$. ⁵The position where the (001)-oriented APB is located inside the layered sample.

This result clearly indicates possible c- to a-variant superstructure reorientation at the surface covered by Fe-atoms, and suggest no reorientation when the surface is covered with Pt-atoms.

4.1.3 Structural defect energetics

A defect formation energy can be calculated as a difference between the configurational energies of the system with and without a defect :

$$\Delta E_{def} = E_{def} - E_0 \tag{4.1.30}$$

where ΔE_{def} is the defect formation energy, E_{def} is the configurational energy of the system with the defect and E_0 is the configurational energy of the perfectly ordered system. Eq. 4.1.30 actually applies to system with very low defects concentration ($c_{def} \ll 1$). The results of heuristic calculations for vacancies and antisites in various arrangements are presented in table 4.1.

Atom	Occ.	Surface	ΔE_{def}^{NN}	ΔE_{def}^{NNN}	ΔE_{def}
type	sublat.	variant	(NN)	(NNŇ)	[eV]
B (Pt)	A (Fe)	bulk	$8V^I_{BB} - 4V^I_{AA} - 4V^I_{AB}$	$6V_{AB}^{II} - 6V_{BB}^{II}$	0,999
A (Fe)	B (Pt)	bulk	$8V_{AA}^I - 4V_{BB}^I - 4V_{AB}^I$	$6V_{AB}^{II} - 6V_{AA}^{II}$	0,064
V	A (Fe)	bulk	$-4V^I_{AA} - 8V^I_{AB}$	$-6V_{AA}^{II}$	0,497
V	B (Pt)	bulk	$-4V^I_{BB} - 8V^I_{AB}$	$-6V_{BB}^{II}$	$0,\!245$
B (Pt)	A (Fe)	a	$6V^I_{BB} - 2V^I_{AA} - 4V^I_{AB}$	$5V_{AB}^{II} - 5V_{BB}^{II}$	0,835
A (Fe)	B (Pt)	а	$6V_{AA}^I - 2V_{BB}^I - 4V_{AB}^I$	$5V_{AB}^{II} - 5V_{AA}^{II}$	$0,\!205$
V	A (Fe)	a	$-2V^I_{AA}-6V^I_{AB}$	$-5V_{AA}^{II}$	0,385
V	B (Pt)	a	$-2V^I_{BB}-6V^I_{AB}$	$-5V_{BB}^{II}$	$0,\!274$
B (Pt)	A (Fe)	с	$4V^I_{BB} - 4V^I_{AA}$	$5V_{AB}^{II} - 5V_{AA}^{II}$	0,336
A (Fe)	B (Pt)	с	$4V_{AA}^I - 4V_{BB}^I$	$5V_{AB}^{II} - 5V_{BB}^{II}$	-0,220
V	A (Fe)	с	$-4V^I_{AA}-4V^I_{AB}$	$-5V_{AA}^{II}$	$0,\!228$
V	B (Pt)	с	$-4V^I_{BB} - 4V^I_{AB}$	$-5V_{BB}^{II}$	-0,031

Table 4.1: Defect formation energies in two-body interaction $L1_0$ superstructure model, recalculated for Fe-Pt interactions.

4.2 "Order-order" kinetics in $L1_0$ bulk

4.2.1 Bulk samples

Details of the methodology used in thin thesis stem from previous works concerning MC simulation of ordering kinetics in bulk Ni_3Al with $L1_2$ [71] and in other model superstructures [28].

Cubic bulk samples were built of 40x40x40 unit cells, with periodic boundary conditions imposed. The simulated samples consisted of 256000 FCC crystalline lattice sites. One vacancy was introduced into the system by emptying a randomly chosen site. The simulations were performed using Glauber dynamics implemented with vacancy mechanism (sec.2.1). Ising model allowed to perform Quasi Kinetic Monte Carlo simulations.

4.2.2 Monitored parameters

The following set of parameters was monitored during the MC simulations in the Ising-type model:

• Long Range Order Bragg-Williams η parameter, in general defined as in eq. 1.2.4, however, in the case of finite, stoichiometric FePt L1₀ sample, it can be formulated as⁶:

$$\eta = 1 - 2\frac{N_{Pt}^{Fe}}{N^{Fe}} = 2\frac{N_{Pt}^{Pt}}{N^{Pt}} - 1$$
(4.2.1)

where N^{Fe} is number of Fe-type sublattice sites, N_{Pt}^{Fe} is number of Ptatoms occupying Fe-sublattice, or simply number of Pt antisites.

• Short Range Order occupation correlation parameters C_{AB} defined as the average correlations of NN B-atoms around A-atoms:

$$C_{AB} = \sum_{i}^{N_A} \frac{N_{A_i NNB}}{N_A} \tag{4.2.2}$$

where N_A is a number of A-atoms in the sample, and $N_{A_i NN B}$ is a number of B atoms in the NN coordination shell of a selected A_i atom.

• Short Range Order antisites correlation parameters A defined as the average correlations of NN antisites:

$$A = \sum_{i}^{N_{A}} \frac{N_{X_{i} NN X}}{N^{X}}$$
(4.2.3)

where N^X is a number of antisites in the sample, and $N_{X_i NNX}$ is a number of NN antisites around a selected *i*th-antisite.

• Atomic jump statistics defined as: $Nj(t, \Delta t)_A^{C \to D}$ - number of jumps performed by A-atoms from sublattice C to sublattice D executed during Δt starting from moment t. When such data is monitored, it is straightforward to calculate the effective probability of certain jump types:

$$P(t,\Delta t)_A^{C\to D} = \frac{Nj(t,\Delta t)_A^{C\to D}}{Nj(t,\Delta t)_{all}^{all}}$$
(4.2.4)

where $Nj(t, \Delta t)^{all}_{all}$ is a number of all jumps executed during Δt starting from moment t.

Consequently, the number of effective disordering jumps calculated as effectively created Fe antisites during Δt starting from moment t can be monitored as well:

$$P_{dis}(t,\Delta t) = P(t,\Delta t)_{Fe}^{Fe \to Pt} - P(t,\Delta t)_{Fe}^{Pt \to Fe}$$
(4.2.5)

where $P(t, \Delta t)_{Fe}^{Fe \to Pt}$ and $P(t, \Delta t)_{Fe}^{Pt \to Fe}$ are defined by eq. 4.2.4.

• Total configurational energy of the system eq.3.1.1.

⁶Similar to $L1_2$ formulation as in [71]

4.2.3 Simulations series

Three sets of simulations were carried out at a range of temperatures $T_{eq} < T_t$, yielding isothermal "order-order" relaxations: 3.1.1

- Isothermal disordering relaxations of the system originally perfectly longrange ordered (configuration corresponding to equilibrium at 0 K)
- Isothermal disordering and ordering relaxations: (a) initially equilibrated at $T_0 = T_{eq} + 50$ K (ordering) and (b) initially equilibrated at $T_0 = T_{eq} 100$ K (disordering). T_0 was always lower than T_t .

A simulation with the temperature step -50K together with the one performed at the same T_{eq} but with the temperature step +100K produced two nearly symmetric "order-order" relaxations, and allowed comparative analysis of ordering and disordering processes.

4.2.4 LRO and SRO evolution

The experimental results of FePt and FePd atomic ordering kinetics [72], as well as previous MC simulations of the ordering kinetics in the $L1_0$ and superstructure with model interactions [28], suggested possibility of a complex structure of the "order-order" relaxations in $L1_0$ FePt intermetallic. Thus, Laplace transform (sub.A.1) of the $\eta(t)$ curves was applied to check how many time scales contribute to the relaxation. Afterwards, the relaxation times τ were more precisely estimated by fitting the simulated $\eta(t)$ isotherm, according to results of the Laplace transformation, either with a single exponent function:

$$\eta(t) = \eta_{eq} + (\eta_0 - \eta_{eq}) \exp\left(-\frac{t}{\tau}\right)$$
(4.2.6)

where: η_{eq} is the equilibrium value of the LRO parameter, $\eta_0 = \eta \ (t = 0), \tau$ is a relaxation time; or with a weighted sum of two or more exponential functions:

$$\eta(t) = \eta_{eq} + (\eta_0 - \eta_{eq}) \sum_i c_i \cdot \exp\left(-\frac{t}{\tau_i}\right)$$
(4.2.7)

where: c_i is a weight factor of the *i*-th exponential component ($\Sigma_i c_i = 1$), and τ_i is a relaxation time of the *i*-th (exponential) relaxation component.

It is noteworthy that fitting of the above formulas to the result of simulation produces a reasonable outcome only when the simulated "order-order" relaxation is fully saturated. It is especially important when analyzing relaxations close to the order-disorder transition temperature T_t .

Moreover, the "order-order" relaxations analysis appeared to be quite demanding in terms of good data statistics. The first analysis performed on results averaged over 32 independent simulation runs was misleading indicating complex time structure of the $\eta(t)$ relaxations. Only after substantial increase of the number of simulation runs up to 128, the averaged relaxations showed clearly one time scale (fig.4.2.1). This result is corroborated by Phase Field Method (PFM) findings [21, 73] showing that only one time scale in the ordering kinetics in FePt corresponds to homogeneous ordering. Other possible processes in FePt L1₀ "order-order" relaxations, being related to phenomena connected with



Figure 4.2.1: Time evolution of LRO η parameter in simulated "order-order" relaxation in FePt $L1_0$ samples at 1200 K, averaged over 128 samples. (a) disordering from 0 K to 1200 K, (b) disordering from 1100K to 1200K and ordering from 1250K to 1200K.



Figure 4.2.2: Time evolution of antisites correlation parameter A in simulated "order-order" relaxation in FePt $L1_0$ samples at 1200 K, averaged over 128 samples, disordering from 0 K to 1200 K.

antiphase boundaries, were not observed in the simulations carried out in the homogeneous bulk.

The inspiration for the SRO analysis in $L1_0$ bulk FePt system were processes observed in the Ni₃Al intermetallic with the $L1_2$ superstructure [71]. In Ni₃Al two processes played an important role in the ordering kinetics: (i) (fast) a creation and an annihilation of NN antisites and (ii) (slow) a diffusion of Al antisites that broke apart (or joined) NN antisite pairs associated with slow LRO evolution.

The simulated evolution of SRO antisite correlations (eq.4.2.3) in $L1_0$ bulk FePt (fig.4.2.2) indicated that from the very beginning of the simulations, the value of the antisites correlation A was around 0.6 which suggests that antisites are created both as separated defects and as NN pairs. The two attainable ways of antisites creation are allowed as a vacancy can migrate along both Fe and Pt sublattices without antisites generation. In contrast to $L1_2$ superstructure

		$T_{beg} = 0[\mathbf{K}]$	$T_{beg} = T_{end} - 100 [\mathrm{K}]$	$T_{beg} = T_{end} + 50[\mathrm{K}]$
$T_{end}[\mathbf{K}]$	η_{eq}	τ [MC steps]	τ [MC steps]	τ [MC steps]
800	0.9990	$4.26 \cdot 10^{7}$	$3.16\cdot 10^7$	$1.17 \cdot 10^{7}$
850	0.9984	$1.84 \cdot 10^{7}$	$1.35 \cdot 10^{7}$	$6.17 \cdot 10^{6}$
900	0.9975	$7.23 \cdot 10^{6}$	$7.41 \cdot 10^{6}$	$5.89 \cdot 10^{6}$
950	0.9962	$8.70 \cdot 10^{6}$	$4.68 \cdot 10^{6}$	$3.24 \cdot 10^{6}$
1000	0.9945	$5.63 \cdot 10^{6}$	$3.55 \cdot 10^6$	$1.91 \cdot 10^{6}$
1050	0.9923	$4.10 \cdot 10^{6}$	$2.51 \cdot 10^{6}$	$1.95 \cdot 10^{6}$
1100	0.9893	$3.17 \cdot 10^{6}$	$2.14 \cdot 10^{6}$	$1.38 \cdot 10^{6}$
1150	0.9854	$2.86 \cdot 10^{6}$	$1.78 \cdot 10^{6}$	$1.82 \cdot 10^{6}$
1200	0.9804	$2.49 \cdot 10^{6}$	$1.51 \cdot 10^{6}$	$1.41 \cdot 10^{6}$
1250	0.9739	$2.15 \cdot 10^{6}$	$1.58 \cdot 10^{6}$	$1.49 \cdot 10^{6}$
1300	0.9653	$2.08 \cdot 10^{6}$	$1.26 \cdot 10^{6}$	$1.66 \cdot 10^{6}$
1350	0.9540	$2.01 \cdot 10^{6}$	$1.48 \cdot 10^{6}$	$1.48 \cdot 10^{6}$
1400	0.9387	$2.11 \cdot 10^{6}$	$1.70 \cdot 10^{6}$	$1.55 \cdot 10^{6}$
1450	0.9387	$2.26 \cdot 10^{6}$	$2.14\cdot 10^6$	$2.09 \cdot 10^{6}$
1500	0.8837	$2.64 \cdot 10^{6}$	$3.02 \cdot 10^{6}$	$3.63 \cdot 10^{6}$
1550	0.8214	$3.89 \cdot 10^6$	$5.01 \cdot 10^{6}$	
1600	0	_	_	_

Table 4.2: Parameters of simulated relaxations in bulk $L1_0$ FePt samples.

[71], in the examined $L1_0$ system, correlated antisite generation does not seem to influence the ordering kinetics.

4.2.5 Arrhenius plots



Figure 4.2.3: Arrhenius plot of atomic order relaxation times obtained from MC simulations in the Ising-type model of $L1_0$ FePt bulk.

The relaxations showed a wide temperature-domain of the slowing-down effect near T_t , so that the Arrhenius behavior of the relaxation times was observed only at $T_t/T > 1.2$ (fig. 4.2.3). The exact time scales of relaxations are slightly different among ordering and disordering relaxations due to the difference in temperature step, followed by slightly different relaxation amplitude. Nevertheless, comparison of all Arrhenius plots makes it clear that ordering and disordering processes present similar mechanism of atomic ordering evolution, all plots show slowing down within wide temperature domain near T_t .

4.2.6 Jumps statistics

Detailed analysis of jump statistics during the "order-order" relaxations in FePt shows that among all possible jumps, the ones performed by Fe-atoms along Fe monoatomic planes were the most frequent (fig. 4.2.4a)). Quite similar behavior could observed in antisite diffusion (fig. 4.2.4b)), where Pt-antisites more often moved along Fe-sublattice than Fe-antisites did on Pt-sublattice. Those facts indicate that during the relaxation, the vacancy acts for most of the time on Fe monoatomic planes, which makes Fe-atom and Pt-antisite migration along Fe planes more probable than Pt-atom and Fe-antisite migration along Pt sublattice. It is consistent with defect energies calculations (tab. 4.1) where vacancy creation on Fe-sublattice requires less energy than on Pt-sublattice.

The creation and annihilation of antisites is in general much more frequent than antisite diffusion which can be seen in fig. 4.2.4 a). It is remarkable that during the relaxation Fe-antisites are more often created and annihilated than Pt-antisites. The configurational energy plays an important part in this case. Pt-antisites require more energy to be created (tab. 4.1), and thus are effectively created less frequently.

The equilibrium state is sustained by dynamic balance between creation and annihilation of antisites where effective number of created and eliminated antisites P_{dis} (eq. 4.2.5) (fig.4.2.4b)) fluctuates around 0. However, before equilibrium is achieved, there is a clear imbalance between antisites creation and annihilation ($P_{dis}(t)$), which is perfectly consistent with the shape of the LRO relaxation ⁷.

 $[\]overline{{}^{7}\text{Note that }\eta\left(t\right) \sim N_{Fe}^{Pt}\left(t\right) \sim \sum_{0}^{t_{i}=t} \left(P\left(t_{i},\Delta t\right)_{Fe}^{Fe \rightarrow Pt} - P\left(t_{i},\Delta t\right)_{Fe}^{Pt \rightarrow Fe}\right) = \int_{t} P_{dis}dt,$ having in mind that $\eta\left(t\right) \sim \exp\left(t\right) \sim \frac{d}{dt} \exp\left(t\right)$ it is correct to say that $\eta\left(t\right) \sim P_{dis}$



(a)



(b)

Figure 4.2.4: Jumps probabilities during simulated relaxation from 0 K to 1100K.(a) P(t) - time dependence of all possible jumps. (b) Effective disordering jumps with antisite diffusion.

4.3 "Order-order" kinetics in $L1_0$ thin layers

The results presented in this chapter were partially published in refs. [74, 70].

4.3.1 Samples construction

Four sample shapes (fig. 4.3.1) and two variants of L_{10} superstructure orientation were taken into account. Thin layers limited by free surfaces were modeled from the original bulk sample by removing periodic boundary conditions in the [001] direction, whereas the periodic boundary conditions were retained in [100] and [010] directions. While the number of atomic layers in [001]-direction was reduced, the [100]- and [010]-sizes of the sample were increased, so that the total number of atoms and the vacancy concentration was conserved (fig. 4.3.1).

The samples were initially perfectly ordered in a- or c- $L1_0$ superstructure variant. The simulation algorithm was exactly the same as the one used in the case of bulk samples.



Figure 4.3.1: Thin layer sample shapes: (a) 40x40x40 [unit cells]; (b) 80x40x20 [unit cells]; (c) 80x80x10 [unit cells]; (d) 160x80x5.

4.3.2 Monitored parameters

The monitored parameters were defined in such a way that possible evolution of particular L1₀ variant domains may be analyzed. The LRO parameter η_{α} corresponding to particular superstructure orientation α (a-, b-, or c-variant) was defined as follows:

$$\eta_{\alpha} = 1 - 2 \frac{N_{Pt_{\alpha}}^{Fe}}{N_{Pt_{\alpha}}} \tag{4.3.1}$$

where $N_{Pt_{\alpha}}^{Fe}$ is the number of antisites occupying Pt-sublattice sites in α -variant superstructure.

The analysis of possible effects related exclusively to the surface was enabled by means of a specific surface(-processes) related LRO parameter η^{surf} , however, before the definition of the parameter, let us clarify the assumptions that are behind it:

1. In the layered sample there are two processes responsible for antisites generation: the surface-originated one and the bulk-like. The number of antisites generated by both processes can be denoted as:

$$N_{Pt}^{Fe^{tot}} = N_{Pt}^{Fe^{surf}} + N_{Pt}^{Fe^{bulk}}$$
(4.3.2)

where: $N_{Pt}^{Fe^{surf}}$ is a number of Fe antisites generated by surface-induced processes, $N_{Pt}^{Fe^{bulk}}$ is a number of Fe antisites generated exclusively in the

bulk-like process and $N_{Pt}^{Fe^{tot}}$ is a total number of Fe antisites generated by both the surface-originated and the bulk-like processes. All the above numbers of antisites refer to the whole sample. Using equation 4.3.3 the number of antisites generated by the surface-originated processes can be denoted as:

$$N_{Pt}^{Fe^{surf}} = N_{Pt}^{Fe^{tot}} - N_{Pt}^{Fe^{bulk}}$$
(4.3.3)

2. Based on the numbers of antisites by particular processes, related LRO parameters can be defined as:

$$\eta^{tot} = 1 - 2 \frac{N_{Pt}^{Fe^{tot}}}{N_{Pt}}$$
(4.3.4)

$$\eta^{surf} = 1 - 2 \frac{N_{Pt}^{Fe^{surf}}}{N_{Pt}}$$
(4.3.5)

$$\eta^{bulk} = 1 - 2 \frac{N_{Pt}^{Fe^{bulk}}}{N_{Pt}}$$
(4.3.6)

where N_{Pt} is the number of Pt-sublattice sites in the sample.

3. The bulk-like process is homogeneous in the whole volume of the sample, thus η^{bulk} parameter can be estimated by the total order parameter calculated in the bulk region of the layered sample (4.3.2) with an assumption that surface-induced processes do not affect this region:

$$\eta^{bulk} = \left(1 - 2\frac{N_{Pt}^{Fe^{bulk}}}{N_{Pt}}\right) \simeq \left(1 - 2\frac{N_{Pt_{bulk}}^{Fe_{bulk}^{tot}}}{N_{Pt_{bulk}}}\right) = \eta_{bulk}^{tot}$$
(4.3.7)

where: $N_{Pt_{bulk}}^{Fe_{bulk}^{tot}}$ is the total number of Fe antisites in the bulk region, $N_{Pt_{bulk}}$ is a number of Pt sites in the bulk region.

Consequently, the surface (-processes) related LRO parameter η^{surf} can be defined as:

$$\eta^{surf} = 1 - 2 \frac{N_{Pt}^{Fe^{surf}}}{N_{Pt}} =$$

$$1 - 2 \frac{N_{Pt}^{Fe^{tot}} - N_{Pt}^{Fe^{bulk}}}{N_{Pt}} =$$

$$\left(1 - 2 \frac{N_{Pt}^{Fe^{tot}}}{N_{Pt}}\right) - \left(\left(1 - 2 \frac{N_{Pt}^{Fe^{bulk}}}{N_{Pt}}\right) - 1\right) =$$

$$\eta^{tot} - (\eta^{bulk} - 1) \simeq$$

$$\eta^{tot} - (\eta^{bulk} - 1)$$

$$(4.3.8)$$

In this way, by monitoring LRO evolution in the whole layered sample $\eta^{tot}(t)$ and in the bulk of the layer $\eta^{tot}_{bulk}(t)$ separately, it was possible to extract the evolution of LRO caused purely by the surface-originated processes $\eta^{surf}(t)$.

In this work, the bulk region (fig. 4.3.2) of the layered sample was experimentally chosen as 40x40x20 unit cells (for cubic samples built of 40x40x40 unit



Figure 4.3.2: Schematics of the thin layer sample with its defined bulk and surface volumes.

cells), 10 unit cells away from each surface. The distance of 10 unit cells from both surfaces appeared sufficient to isolate the bulk volume from surface-induced effects.

4.3.3 "Order-order" kinetics in $L1_0$ a-variant thin layers

For each one of the mentioned sample shapes (fig. 4.3.1) a series of isothermal relaxations was simulated at temperatures T_{eq} below the order-disorder transition. In each case, the initial layer configuration corresponded to perfectly ordered L1₀ a-variant superstructure. The main features of the obtained "order-order" relaxations were the same as those in the bulk samples; the antisites were generated (almost) uniformly all over the layer volume. However, a substantial influence of the surface to volume ratio (represented by a fraction of atoms located at the surface: $s = N_{surf}/N_{tot}$) on particular relaxation parameters was observed, as illustrated in figure 4.3.3. The increase of the surface among samples caused slowing down of a relaxation and decrease of the equilibrium long range order $\eta_{a \ eq}$ at particular T_{eq} .



Figure 4.3.3: LRO relaxations obtained at 1200K for various shapes of a-variant thin layers.

The observed result is caused by the fact that the Fe vacancy formation energy is lower at the surface (see tab. 4.1), thus it is more probable for the vacancy to reside and act at the surface⁸. This means, in turn, a lower effective vacancy concentration inside the sample, followed by slower antisites creation.

Considering antisite formation energy averaged over both sublattices, it appears that at the surface it is lower than in the bulk (tab. 4.1). Due to that, more antisites are created (at the same temperature) in samples with bigger surface area. This fact explains observed decrease of η_{eq} in thinner samples (fig. 4.3.3), and complies with experimental observations of reduced L1₀ superstructure stability caused by decreased size in FePt nano-crystals [13, 18].

4.3.4 "Order-order" kinetics in $L1_0$ c-variant thin layers

A detailed analysis of the ordering processes occurring in c-variant layers was performed by simulating the cubic samples built of 40x40x40 unit cells with PBC removed in [001] direction. The MC simulations revealed four processes, characterized by particular relaxation times:

- 1. Homogeneous disordering (relaxation time: τ) (subsec.4.3.4.1)
- 2. Nucleation of a- and b-variant $L1_0$ domains within the surface layer of $L1_0$ unit cells (relaxation time: τ_1)(subsec. 4.3.4.2)
- 3. Growth of the nucleated a- and b-variant $L1_0$ domains inward the layers (relaxation time: τ_2)(subsec.4.3.4.2).
- 4. Relaxation of the microstructure of a- and b-variant L1₀ domains (relaxation time: τ_3)(subsec.4.3.4.3)
- 5. Percolation of the a- or b-variant superstructure domain nucleated at the surface through the layer (subsec.4.3.4.4). Effect observed in sufficiently thin layers.

Temp.	LRO					SRO		E_{Conf}
[K]	η_c^{bulk}			η_c^{surf}	η_c^{surf} C_I		C_{PtPt}	
	τ	η^{bulk}_{ceq}	$ au_1$	$ au_2$	η_{ceq}^{surf}	τ_{Fe-Fe}	τ_{Pt-Pt}	$ au_3$
1000	$5.42 \cdot 10^{6}$	0.994	$2.80 \cdot 10^{7}$	$1.13 \cdot 10^{9}$	0.899	too slo	w proc.	$2.80 \cdot 10^{9}$
1200	$2.53 \cdot 10^6$	0.980	$9.92 \cdot 10^{6}$	$1.12 \cdot 10^{9}$	0.881	$1.7 \cdot 10^{9}$	$5.8 \cdot 10^{8}$	$9.93 \cdot 10^8$
1400	$2.09 \cdot 10^{6}$	0.871	$8.04 \cdot 10^{6}$	$1.24 \cdot 10^{9}$	0.834	$4.2 \cdot 10^{8}$	$2.0 \cdot 10^{8}$	$3.42 \cdot 10^{8}$

Table 4.3: Parameters of the η_c^{bulk} , η_c^{surf} , and E_{Conf} relaxations simulated in the FePt layer (values of relaxations times given in [MC steps]).

4.3.4.1 Homogeneous disordering

The process was extracted from the entire atomic order evolution by monitoring the MC time dependence of c-variant LRO parameter based on the sample interior (see subsec. 4.3.2). It showed exactly the same time scale as that observed

⁸It applies to the entire process of vacancy-mediated disordering due to the fact that in general vacancy prefers to occupy Fe-sublattice.

in the bulk samples - i.e. with 3-dimensional periodic boundary conditions imposed upon the simulated supercell (fig. 4.3.4).



Figure 4.3.4: MC time dependence of simulated η (eq. 4.2.1) for the bulk samples and η_c^{bulk} (eq. 4.3.7) for the layered FePt samples at particular temperatures.

The $\eta_c^{bulk}(t)$ curves fitted the single exponential decay function (eq. 4.2.6). The resulting values of the relaxation times and the equilibrium values of the LRO parameters at particular temperatures are displayed in table 4.3.

4.3.4.2 Nucleation and growth of L1₀ a- and b-variant domains

The simulated $\eta_c^{surf}(t)$ (eq.4.3.8) curves are shown in figure 4.3.5. The wellvisible complex time-scale structure of the curves has been elucidated by Laplace transforms (subsec. A.1), clearly revealing the parallel operation of two relaxation processes (fig. 4.3.5b)). The curves fitted, therefore, weighted sums of two exponential decays (eq. 4.2.7). The results, displayed in table 4.3, indicate that although being of the same order of magnitude, the rates of the homogeneous disordering (τ) and of the fast component of relaxation (τ_1) definitely differ from one another.



Figure 4.3.5: (a) MC time dependence of η_c^{surf} simulated at various temperatures; (b) Laplace transform of $\eta_c^{surf}(t)$ simulated at 1400 K.

In order to interpret the above result, the evolution of the sample atomic configuration was directly imaged (4.3.6) in a (010) cross section and in the Femonoatomic (00-1) free surface. After the number of MC steps corresponding to τ_1 time scale, the mosaic of a- and b-L1₀ variant domains covered the entire (00-1) surface (fig. 4.3.6b,c) indicating the completion of the domain nucleation and suggesting that the fast component of $\eta_c^{surf}(t)$ should be assigned to the L1₀ a- and b-variant domain nucleation.

Among the two remaining processes observed in the system: (i) $L1_0$ a- and b-variant domain growth inward the layer and (ii) relaxation of the $L1_0$ a- and b-variant microstructure, only the former process may affect the value of $\eta_c^{surf}(t)$. Therefore, the slow component of $\eta_c^{surf}(t)$ should be assigned to the kinetics of that process.

The analysis of MC time evolution of $\eta_{\alpha}^{surf}(t)$ parameters (subsec.4.3.2) for particular variants of L1₀ superstructure, following from a single simulation run (4.3.7)(i.e. without averaging over independent simulation runs) shows the fluctuating "saturation" levels of the parameters which reflect the irregular fluctuating movement of the re-orientation front i.e. the L1₀ c-variant-a(b)-variant APB, directly visible in [010]-cross-section view in fig.4.3.6(e) and fig.4.3.6(f). This specific fluctuation-like character of the process is the reason why the analysis of curves averaged over independent simulation runs (and, therefore, showing no fluctuations of the "saturation" level) yield the temperature-independent rate of the slow relaxation component (τ_2) (tab. 4.4).



Figure 4.3.6: MC-time evolution of initially Fe-monoatomic free surface of the FePt layer at 1200 K, the first and the third row contain the view of the initially Fe-covered surface ([00-1] view direction), the second and the forth row contain the [010] cross-section view; dark gray dots represent Fe atoms, light gray dots represent Pt atoms.



Figure 4.3.7: Particular LRO parameters evolutions following from a single simulation at 1200 K (without averaging over independent simulation runs)

4.3.4.3 Relaxation of the microstructure of L1₀ a- and b-variant domains

The process was analyzed by monitoring the MC-time dependence of the system configurational energy E_{conf} (eq. 3.1.1), C_{FeFe} and C_{PtPt} SRO parameters (eq. 4.2.3). In order to compare results obtained in layered samples with the bulk results, the parameters were calculated for the entire sample, without extracting the bulk or surface effects. The results are presented in fig. 4.3.8.

Both $E_{conf}(t)$ and C(t) isotherms⁹ show an initial, fast increase followed by a slow, decreasing relaxations. A comparison of the $E_{conf}(t)$ and C(t) curves simulated in the bulk and in the layered samples (fig. 4.3.8a, c) shows similar shape in terms of the initial sharp increase. It indicates that the initial increase is due to homogeneous disordering (generation of antisites). In layered samples, however, the E_{conf} (fig. 4.3.8a) and C_{FeFe} (fig. 4.3.8b) increase up to higher level than in the bulk, which seems to reflect nucleation of the L1₀ a- and b-variant domains. Thus, we assume that the initial increase in E_{conf} and C parameters in the layered samples is caused by both: (i) homogeneous disordering and (ii) L1₀ a- and b-variant surface domains nucleation. Since the mentioned processes have been well-recognized so far (subsec.4.3.4.1 and 4.3.4.2), let us now focus on the subsequent slow decreasing relaxation observed¹⁰ in the MC-time evolution of E_{conf} and C parameters.

The slow decrease of the configurational energy E_{conf} cannot be caused by domain growth process, since it virtually does not affect the energy at all. According to the heuristic calculations provided above (subsec. 4.1.2) the growth of the a- variant domain, from the surface inward the sample, increases the distance between the surface and the a-/c-variant interface, however, does not affect the configurational energy (eq. 4.1.28).

⁹Please note that $E_{conf}(t)$ is a linear combination of numbers of atomic pairs and pair potentials: $E_{conf}(t) \sim C_{FeFe}V_{FeFe}^{I} + C_{PtPt}V_{PtPt}^{I}$. It means that parameters $E_{conf}(t)$ and C are dependent and their behavior reflects qualitatively the same processes. However, correlation parameters C provide us with more detailed information about particular atomistic processes, especially in layered samples where (due to surfaces asymmetry) $C_{PtPt} \neq C_{FeFe}$.

 $^{^{10}}$ Observed only in L1₀ c-variant layers, and not in bulk or a-variant layers.

Consequently, the only possible process that can alter values of the mentioned parameters is relaxation of a microstructure of the L1₀ a- and b-variant domains. After rapid nucleation of a- and b- variant domains, the system tends to minimize configurational energy stored in APBs within the re-oriented volume of the FePt layer. Existence of APBs increases the number of NN Fe-Fe and Pt-Pt pairs in the system, and in this way, increases values of C correlation parameters and configurational energy. Thus, a decay of E_{conf} and C parameters (fig. 4.3.8b,d) clearly reflects the relaxation of the microstructure, and allows the estimation of relaxation time (τ_3 tab. 4.3) of the process.



Figure 4.3.8: Simulated $E_{conf}(t)$ and C(t) isothermal relaxations in FePt cvariant layers. (a) System energy evolution at the beginning of relaxation at 1200 K and at 1400K. (b) Complete energy relaxation at 1400 K in layered samples. (c) Evolution of the SRO C parameters at the beginning of relaxation at 1400K in a bulk and in a layer. (d) Complete C relaxations with inserts showing zoomed decreasing parts (C_{FeFe} -gray, C_{PtPt} -black). The curves in figs. (a) and (b) are compared with the corresponding ones simulated for bulk FePt.

The APB relaxation is associated with the evolution AP domain microstructure, which was directly observed in the atomic configuration evolution (fig. 4.3.6 b,c,d and e). After fast nucleation (fig. 4.3.6 b), the number of AP domains at the surface decreases (fig. 4.3.6 c,d), resulting in one surface a- or b-variant domain at the end of the process (fig. 4.3.6 e).

4.3.4.4 Percolation of the L1₀ a- and b-variant domains

As it was shown in subsec. 4.1 it is energetically favorable for the layered FePt system limited by (001) surfaces to create homogeneous a- or b-variant $L1_0$ superstructure. The energy gain comes from the surface which in a- or b-variant has lower energy than in c-variant.

Now, let us consider a situation where, after $L1_0$ a-variant nucleation at one surface of the sample, the growing domain, reaches the counterpart surface. Then, additional energy gain appears due to the removal of the a(b)-variant - c-variant APB and conversion of the second c-variant surface into the a(b)variant. However, only when the sample is sufficiently thin, the reorientation front, or in fact, fluctuations of this area, may reach the counterpart surface of the layer (see average reorientation depth in tab. 4.4).

The process may be well-illustrated by the time evolution of SRO parameters in the sample composed of 160x80x5 (fig. 4.3.1(d)) unit cells (the same volume as in 40x40x40 u.c. samples). It can be observed in figure 4.3.9, that the process of reorientation starts with an abrupt increase in C_{FeFe} correlation parameters which corresponds to the creation of the Fe-rich APB. Afterwards, at low temperatures, a plateau is observed in C_{FeFe} evolution, which corresponds to a nearly constant size of the APB, nevertheless, the a(b)-variant surface domain still grows. When the growing domain reaches the second surface and the APB disappears, the C_{FeFe} plateau decays.

In simulations carried out at higher temperatures (1200K, 1400K), after an initial decrease in the evolution of the C_{PtPt} parameter, a maximum and subsequent decay is observed. The maximum is associated with a dynamic reorientation of the second surface initially covered with Pt atoms. The second (initially Pt covered) surface transformation from c-variant to a-variant L1₀ superstructure cause Pt atoms to migrate from the surface into the second (counting from the surface) monoatomic layer where Pt atoms gain more Pt neighbors for the moment of transformation. Afterwards, all C correlations stabilize due to the microstructure relaxation (subsec. 4.3.4.3).

4.3.4.5 Equilibrium c- to a(b)-variant reorientation depth

The equilibrium value of η_c^{surf} may be rescaled into an average depth of the L1₀ c-variant \rightarrow a(b)-variant re-orientation. First of all, it should be recalled that η_c^{surf} does not account for homogeneous disordering, thus the value of the parameter is solely dependent on the surface-related effects. Moreover, η_c^{surf} in the c-variant thin layers is based on the original superstructure, and its value at the beginning of the simulation is $\eta_c^{surf}(0)=1$. During the simulation, when the a- and b- variant domains are nucleated at the surface, and subsequently during the a- and b-variant domains growth, the volume of the original c-variant superstructure domain shrinks, and this process is represented by the decrease of η_c^{surf} . Knowing that the L1₀ c-variant \rightarrow a(b)-variant re-orientation proceeds



Figure 4.3.9: (a): $C_{FeFe}(t)$ and (b): $C_{PtPt}(t)$ isotherms in c-variant L1₀-ordered FePt layer: 160x80x5 unit cells, simulated at marked temperatures.

Temperature [K]	Estimated re-oriented surface domain depth [nm]
1400	2,48
1200	1,80
1000	1,52

Table 4.4: Estimated depth of the $L1_0$ c-variant $\rightarrow a(b)$ -variant re-orientation in the FePt layer.

as a domain growth (subsec.4.3.4.4) we can assume that the average depth of the c-variant superstructure domain can be represented by d_c parameter:

$$d_c = \eta_c^{surf} \cdot h \tag{4.3.9}$$

where h is the total height of a sample. When the d_c parameter accounts for the non-transformed part of the sample, the parameter $d_{a,b}$:

$$d_{a,b} = h - d_c = (1 - \eta_c^{surf}) \cdot h \tag{4.3.10}$$

describes the average depth of the newly-nucleated a- and b- variant domains. In this way, the value of η_c^{surf} can be rescaled into the average depth of the a(b)-variant surface domain. The results of the estimated equilibrium depth of the reoriented surface domain for particular temperatures are presented in table 4.4.

4.3.4.6 Pt surface stabilizing effect

The analytic calculations (subsec. 4.1.2) as well as the MC results (subsec. 4.3.4.2) carried for Ising-type model c-variant $L1_0$ FePt thin layers shows that the process of the $L1_0$ c-variant $\rightarrow a(b)$ -variant reorientation starts at the surface covered by Fe monoatomic layer. However, the question arises: does the Pt monoatomic surface layer completely prevents reorientation? To check this

issue a non-stoichiometric, $108 \times 108 \times 5.5$ unit cells¹¹ big samples were generated with either Fe-atoms or Pt-atoms on both sides of the thin layer. The results of simulations carried out in the non-stoichiometric samples are presented in figure 4.3.10. The result clearly indicates that Pt monoatomic layer completely prevents the sample from the reorientation process. It is especially interesting finding that on the Pt surface, despite the fact that quite a few antisites can be noticed, there is no sign of reorientation process (fig. 4.3.10 (b)).



Figure 4.3.10: Results of MC simulations in non stoichiometric FePt layered samples: (a) a comparison of $\eta_c(t)$ simulated for samples with finishing Fe- or Pt-monolayers on both the surfaces; (b) a fragment of [001] projection of the simulated sample with Pt-monolayers finishing after 10⁹ MC steps, dark gray points denote Pt atoms, light gray points denote Fe atoms.

 $^{^{11}}$ Volume of 108x108x5.5=64,152 u.c. is nearly the same volume as in stoichiometric samples where 40x40x40=64000, thus the results are fully comparable.

Chapter 5

Atomic ordering kinetics in ABOP-based FePt model

The analysis of ordering kinetics in ABOP-based model was done, as far as it was possible, in a similar way as for Ising-type model (cha.4) to allow comparison of the obtained results. Nevertheless, basic differences between the models, especially relative complexity of the ABOP energy formulas, made it impossible to conduct exactly the same study.

It was impossible to provide identical heuristic analytic analysis as in the study based on the two-body FePt interactions (sec.4.1) thus, a basic energy analysis was performed by means of molecular statics (sec.5.1).

In order to enable proper use of distance-dependent ABOP interactions, the MC procedures had to be improved. Instead of simple MC, Monte Carlo / Static Relaxation (MC/SR) simulations were performed. Three approaches had been developed for MC/SR simulations. The first one, was the vacancy mediated quasi-kinetic (QKMC) algorithm utilizing only an energy change between subsequent atomic configurations (subsec. 2.1.2). The second approach involved fully kinetic MC algorithm (KMC) with calculation of energy barriers for migrating atoms. The third based on non-kinetic direct exchange algorithm, was designed to probe the equilibrium state of the simulated samples. The results of the three approaches, being substantially different, are presented in the separate sections (sec.: 5.2, 5.3 and 5.4).

5.0.5 Energetics of the ABOP-based model of FePt

At this point, it is important to mention a basic difference which lies in the energetics of the two considered models: Ising-type with pair-interactions and the ABOP-based one. In the Ising-type model the pair-interactions were developed based on the formation (mixing) energy of the Fe_xPt_{4-x} intermetallics with regard to various compositions and superstructures, and adjusted to obtain proper order-disorder transition temperature. It implies that the energetics of this particular Ising-type model does not contain information about the cohesive energy of pure elements and the intermetallic compound. The opposite situation applies to the ABOP-based model, whose interatomic potentials have been developed with regard to mechanical and energetical properties including cohe-

sive energy of pure metals and the formation energies of intermetallics. Thus, the configurational energy in the ABOP-based model can be related to cohesive energy:

$$E_{coh} = E_{conf}/N \tag{5.0.1}$$

where N is the number of atoms in the considered sample. Such a presentation of configurational energy allows an analysis independent on the sample size and straightforward comparison with other results including the experimental ones.

5.1 Preliminary study of FePt ABOP system

The preliminary study of ABOP-based FePt L1₀ ordered system was performed on samples built of 10x10x10 unit cells, 4000 atoms. In order to analyze samples arranged in c-variant L1₀ superstructure with symmetric Fe or Pt surfaces, simulated supercells were built of 10x10x10,5 unit cells and 4200 atoms. After the atoms were placed in the sample, in a certain variant of perfectly ordered L1₀ superstructure, the lattice constants¹ were optimized to obtain minimum of potential energy. In this way, the system evolved into the tetragonally distorted structure (tab. 3.4). This study was extended upon the cases where direction of the tetragonal distortion is perpendicular to the *c*-direction of the superstructure. Such configurations may appear in the system when a small domain with particular superstructure orientation is surrounded by the volume with superstructure variant of the perpendicular orientation².

After the lattice optimization, the relaxation of each atomic position was performed via Molecular Statics (MS, details in subsec. 2.2.2). The system energy was considered only after full relaxation.

The study of APB energetics was done with samples consisting of 8000 atoms (20x10x10 unit cells), two cubes of 4000, each with a defined $L1_0$ superstructure variant.

5.1.1 Tetragonal distortion in FePt ABOP-based bulk

The calculation was performed in the sample with c-variant superstructure and optimized lattice constants (fig.5.1.1(a)), and for the sample with c-variant superstructure but with lattice constants set as for optimized a-variant superstructure (fig.5.1.1(b)). Depending on direction of tetragonal distortion with respect to the direction of a superstructure orientation the configurational energy (presented as cohesive energy, subsec. 5.0.5) differs:

- $E_{coh} = -5,345$ eV for c-type tetragonalization: a = b > c (fig.5.1.1(a))
- $E_{coh} = -5,337$ eV for a-type tetragonalization: b = c > a (fig.5.1.1(b))

The relative difference between the energy among the samples was only around 0.15%, however, it clearly illustrates the fact that the relation between superstructure orientation and tetragonal distortion may affect the ordering.

¹The optimization of lattice constants is performed through relaxation of the total size of the simulated sample with proportionally transformed coordinates of atoms, see subsec. A.3.

 $^{^2 \}rm For}$ example small domain of a-variant $\rm L1_0$ at the surface of a sample with c-variant $\rm L1_0$ superstructure.



Figure 5.1.1: Two tetragonal distortion types in c-variant FePt superstructure corresponding to lattice parameters: (a) c-type tetragonalization: a = b > c (b) a-type tetragonalization: b = c > a

5.1.2 Surface energies

The analysis of surface stability was performed similarly to the one carried out for the Ising-type model (subsec.4.1.1). (001) surfaces were generated in the sample by opening boundary conditions in [001] direction and maintaining periodic boundary conditions in the remaining directions. The analyzed FePt samples had either c-variant or a-variant $L1_0$ superstructure. For each of the analyzed variants of $L1_0$ superstructure, three tetragonal distortion types were set: a-, b- or c-type tetragonalization (similarly as in previous subsec. 5.1.1). The non-stoichiometric samples (with c-variant ordering) limited by both surfaces covered with either Fe or Pt atoms were additionally taken into account to determine how the surface energy depends on the type of atoms covering the surface. Additional calculations were performed for completely disordered samples based on disordered and optimized bulk configuration. In all analyzed cases atomic positions were fully relaxed. The results are presented in table 5.1 where:

$$\Delta E_{surf_{\alpha}} = (E_{surf_{\alpha}} - E_{bulk})/N_{surf} \tag{5.1.1}$$

is the surface formation energy calculated as a difference between $E_{surf_{\alpha}}$ - the configurational energy of the layered sample α -variant L1₀ superstructure and E_{bulk} - the configurational energy in the bulk sample with exactly the same size and composition. The energy difference is normalized by number of surface atoms (N_{surf}). Note that the energy difference between the bulk and the layered sample is linearly dependent on the surface size i.e. number of atoms building the surface. $\Delta E_{surf_{\alpha}}$ was calculated for diverse compositions of surfaces and types of tetragonalization.

The energy gain due to transformation of a layered $L1_0$ c-variant superstructure sample into a-variant can be expressed by parameter ΔE_{a-c} denoted as follows (similar to eq.4.1.1) :

$$\Delta E_{a-c} = N_{surf} \left[\Delta E_{surf_a}^{(Case No\,1)} - \Delta E_{surf_c}^{(Case No\,7)} \right] = N_{surf} \left(-0, 202 \right) [\text{eV}]$$
(5.1.2)

The results indicate that the a(b)-variant surface is definitely more energetically favorable than c-variant. It complies with the result obtained for the

Case	L1 ₀	Atoms at	Tetragonali-	$\Delta E_{surf_{\alpha}}[eV]$
No.	variant (α)	the surface	zation type	(eq.5.1.1)
1	a	Fe and Pt	a	0,790
2	a	Fe and Pt	b	0,795
3	a or b	Fe and Pt	с	0,834
4	С	top Fe, bot. Pt	a or b	0,922
5	с	Fe	a or b	0,563
6	с	Pt	a or b	$1,\!190$
7	с	top Fe, bot. Pt	с	0,992
8	с	Fe	с	$0,\!629$
9	с	Pt	с	1,259

Table 5.1: 001 surface creation energies calculated for FePt $L1_0$ with use of ABOP model.

two-body potentials model. Influence of the direction of tetragonalization is not negligible, however, qualitatively it does not change the energy relations.

5.1.3 Antiphase domain boundary energies

The energy of APBs were calculated by setting up interface bulk samples with two different variants of superstructure (fig.5.1.2) and a variety of tetragonalizations. The antiphase boundary energy ΔE_{APB}^{i-j} was calculated according to the formula³:

$$\Delta E_{APB}^{i-j} = (E_{tot}^{i-j} - E_{tot}^{i-i}/2 - E_{tot}^{j-j}/2)/(2N_{int})$$
(5.1.3)

where E_{tot}^{i-j} is the total configurational energy of a i-variant and j-variant interface sample (*i* and *j* refer to a-,b- or c-variant superstructure or a disordered FCC structure denoted by 'd' which is disordered sample, i - i or j - j means bulk sample without APB), and N_{int} is the number of atoms located at the surface of the interface (on one side only). Results of the calculations are presented in table 5.2. The disordered sample was prepared by a few millions of MC steps at a very high temperature. Due to huge amount of time necessary for the calculations involving disordered samples, only one sample of each type was analyzed, without averaging over several independently disordered samples.

The main conclusion stemming from the results is that APBs parallel to monoatomic planes in one of the interfacing domains (fig.5.1.2(c),(e)) are far more energy requiring than those where the monoatomic planes in both interfacing domains are perpendicular to the APB (fig.5.1.2(d)).

As arises from the calculations, the sum of the energies stored in the a-variant surface and the a-/c-variant interface is higher than the c-variant surface energy and, therefore, too big to create a-variant surface domain on c-variant bulk. This fact may prevent the superstructure reorientation observed in the Isingtype model.

³The subtraction of $E_{tot}^{i-i}/2$ and $E_{tot}^{j-j}/2$ energies from E_{tot}^{i-j} gives energy stored solely in the interface region, whereas division by $2N_{int}$ gives natural normalization per one atom in the interface. Such an approach allows straightforward comparison of data with surface creation calculations (tab.5.1).



(c) a-c variants APB (d) b-c variants APB (e) b-a variants APB

Interface	Tetrago-	$\Delta E_{AP}^{i-j}[\text{eV}] \text{ (eq. 5.1.3)}$
variant (i - j)	nalization	per one int. atom
a - b	a	0,0895
a - c	a	0,0895
a - d	a	$0, 1^*$
b - c	a	0,0114
b - d	a	0,05*
c - d	a	0,05*
a - b	с	0,0950
a - c	с	0,1033
a - d	с	$0, 1^*$
b - c	с	0,0261
b - d	с	0,05*
c - d	с	0,05*

Figure 5.1.2: An example of particular APBs in $L1_0$ FePt.

Table 5.2: Antiphase domain boundary creation energies calculated for FePt $L1_0$ with use of ABOP model. * indicates a qualitative result with a significant statistic uncertainty due to a small size of the sample and low statistics (one sample).

5.1.4 Defect formation energies

A set of point defects was analyzed in a variety of configurations in a similar way as for the two-body interactions model (4.1). However, the values of defect formation energies were obtained by MS simulations, not by analytic calculations. The calculation of a point defect formation energy was performed according to the formula $4.1.30^4$. In the calculations carried out in the layered samples, configurations with the tetragonal distortion set as in either c- or a-variant of the relaxed L1₀ superstructure were analyzed (similarly as in previous subsections 5.1.1, 5.1.2 and 5.1.3).

There are quite a few remarkable differences in defect formation energies when comparing ABOP results (table 5.3) with two-body interactions model results (table 4.1), which seems to imply different atomic ordering processes in

⁴In the vacancy formation energy calculations, the cohesive energy of the subtracted atom was also taken into account because of the reasons stated in subsec.5.0.5.

Atom	Occupied	Surface	Tetrago-	ΔE_{def}
type	$\operatorname{sublattice}$	variant	nalization	[eV]
Pt	Fe	bulk	с	-0,751
Fe	Pt	bulk	с	1,988
V	Fe	bulk	с	1,024
V	Pt	bulk	с	2,286
Pt	Fe	a	a	-0,767
Fe	Pt	a	a	1,704
V	Fe	a	a	1,132
V	Pt	a	a	0,324
Pt	Fe	a	с	-0,825
Fe	Pt	а	с	1,698
V	Fe	а	с	1.01
V	Pt	a	с	0,311
Pt	Fe	с	a	-1,619
Fe	Pt	с	a	1,284
V	Fe	с	a	1,17
V	Pt	с	a	-0.199
Pt	Fe	с	с	-1,690
Fe	Pt	с	с	1,228
V	Fe	с	с	1,208
V	Pt	с	с	-0,375

Table 5.3: Defect creation energies in FePt $L1_0$ with ABOP interaction model.

the two models.

In all the (ABOP) cases Pt antisite formation energies are always negative, which means that creation of such defects is energetically favorable. However, when adding up formation energies of both types of antisites, the result is positive, which means that the system shows the general tendency for ordering.

The analysis of the antisite formation energies in the c-variant surface indicates that the surface, theoretically, would tend to disorder (generation of a pair of antisites exhibits negative formation energy: $\Delta E_{Pt}^{Fe} + \Delta E_{Fe}^{Pt} < 0$). Nevertheless, comparison of antisite formation energies in c-variant Pt-sublattice at the surface and Fe-sublattice in the bulk leads to prediction that the system at the Fe surface has a reduced order-disorder transition temperature (but keeps the superstructure). The configuration of the Pt monoatomic layer, however, more stable in terms of antisite formation energies than Fe surface, seems also less stable than the bulk.

The formation energies of Fe surface vacancies are higher that those for Pt surface vacancies, the same as in the Ising-type model. What is interesting is the fact that for $L1_0$ c-variant layers, the Fe surface vacancy formation energy is slightly higher than for Fe sublattice in the bulk, however, still lower than the Pt vacancy formation energy in the bulk. While comparing bulk Pt and surface Pt vacancy formation energies, it becomes clear that the surface (especially c-variant) is energetically attractive for vacancies. Both above observations regarding vacancy formation energy indicate that there might be a preference

to segregate vacancies at the surfaces of layered samples.

5.2 QKMC/SR simulations

The first approach to "order-order" relaxations in ordered $L1_0$ FePt modeled with ABOP was an application of the quasi-kinetic (subsec. 2.1.2.4) Glauber algorithm (subsec. 2.1.2.2) combined with lattice optimization (sec. A.3) and atomic positions relaxations (subsec.2.2.2).

5.2.1 Samples

Simulations based on complex many-body potentials require a few orders of magnitude more computer time than simple two-body based models, to obtain results in a reasonable time. Thus, samples were limited to several thousands of atoms. Typically, samples consisted of 4000 atoms, 10x10x10 unit cells. Thin layers were generated by removing periodic boundary conditions in [001] direction. The detailed analysis of the ordering kinetics in thin-layers involved samples ordered in both c-variant and a(b)-variant $L1_0$ superstructure. Each simulation started with a perfectly ordered superstructure and one vacancy introduced at a random site.

5.2.2 MC/SR algorithm convergence and optimization

As it was briefly mentioned in section regarding methods (sec.2.3), the MC/SR iteration consists of a number of MC steps followed by static relaxation which involves lattice optimization and/or Molecular Statics relaxation. In this approach, thermal vibrations and lattice expansion were not taken into account, however, the temperature is considered effectively in the jump probability formula (eq.2.1.10). In real intermetallics, a relaxation of atomic positions occurs in parallel to any change in the atomic configuration, although the time scales of atomic migrations are around 100 times slower than atomic relaxations. Due to a very high computational cost of SR calculations, it was decided to apply it in an effective way, after a certain number of MC steps. The interval between SR was then estimated by a set of convergence tests.

5.2.2.1 Lattice optimization

Regarding simulations in the bulk, MS relaxations do not bring any significant change in system parameters, because, even in highly disordered superstructure, the forces acting on single atoms remain compensated⁵ and atoms are very close to their equilibrium positions. Thus, initially the convergence of the algorithm consisting a number of MC steps (from 10^2 to 10^6) followed by the lattice optimization has been studied. Several samples with initially perfect superstructure and one vacancy, as described above, were simulated at 1200 K, each with a different time interval between lattice optimization routines. The resulting LRO relaxations were compared (fig.5.2.1). All obtained $\eta(t)$ curves (fig.5.2.1a) —

⁵There is no surface which makes surroundings of some atoms asymmetric. Every atom has a complete symmetric set of neighbors (except neighboring vacancy) thus the forces acting on the particular atom are compensated.



Figure 5.2.1: Convergence of relaxations in ABOP-based FePt bulk samples at 1200K with regard to lattice relaxations. a) $\eta(t)$ evolution, b) c/a(t) evolution.

however, with a significant amount of a statistical noise — show similar shapes and saturation levels. The tests show that intervals up to 200000 MC steps between the lattice optimizations do not bring about any error that could affect atomic disordering kinetics. However, to fulfill the assumption that lattice dynamics continuously follow the atomic configuration evolution, the interval between lattice relaxation should be at least an order of magnitude smaller than "order-order" relaxation time scale which, in this case, is around 10^6 MC steps. Thus the maximum interval between lattice relaxation was roughly estimated as 10^5 in the shortest relaxations. In the case of slow processes, the interval between lattice optimizations might be appropriately longer than 10^5 MC steps.

In the case of lattice optimization algorithm (subsec.A.3), the stop criterion was set arbitrary as the minimum value of lattice constant adjustment $\delta l < 10^{-6}$ nm, which proved to be accurate enough and sufficiently fast to obtain (up to 100 iterations of the optimization algorithm).

5.2.2.2 Molecular Statics

In a real system with surface, the atomic surroundings are not symmetric due to broken periodicity, and cause noticeable atom displacements followed by configurational energy relaxations. Thus Molecular Statics (MS) have a significant meaning in surface simulations, allowing surface relaxations in a simulated system. In the case of MS relaxations, first we have analyzed a minimization stop criterion, based on total energy parameter (including kinetic energy). Minimization procedure was observed on initially perfectly ordered samples with one vacancy introduced, and periodic boundary conditions removed in [001] direction. The sample was initially relaxed by 10000 MS steps allowing full surface relaxation.

The observation of MS relaxation convergence was carried out after several consecutive series of 10000 MC steps, which were causing minute but noticeable changes in atomic configuration (fig.5.2.2). The obtained $E_{conf}(t)$ curves show that the full relaxation required at least 1000 MS steps, however, around 95% of the relaxation saturation can be reached within 500 MS steps (fig.5.2.2(a)).

Taking into account that MS relaxations have a cumulative⁶ effect, it seems reasonable to set the maximum number of MS steps as 500, reducing computational time significantly.

Due to a great amount of time necessary to obtain full relaxation (MC/SR algorithm) in the layered L1₀-ordered FePt system, it was impossible to precisely check the influence of the time interval length between MS relaxations on the ordering kinetics (as it was mentioned above in the bulk MS relaxations are not important). The observed E_{conf} decays in the performed MS relaxations appear scattered (which is normal for MC simulations) with amplitudes around several eV (fig. 5.2.2 (b)). It seems that the number of MC steps between the relaxations has no particular influence on the E_{conf} relaxation amplitudes⁷. Thus, the interval of 10000 MC steps between MS relaxations, the same number as for the lattice optimizations, seems a reasonable choice.

5.2.3 Monitored parameters

In general, the same parameters as for the two-body potential model 4.2.2 were monitored during the simulations, with the most important Bragg-Williams LRO parameter η . The following parameters, modified and newly introduced, were monitored:

- LRO η parameter calculated for the entire sample (see eq. 4.2.1).
- LRO η^{bulk} parameter calculated for the internal (bulk, fig. 5.2.3) part of the sample without the surfaces.
- **LRO** η^{surf} parameter calculated for the **surface** area (fig. 5.2.3).
- Configurational energy understood as **cohesive energy**⁸ (eq. 5.0.1).
- **Tetragonality** c/a ratio which is a quotient of c lattice constant between monoatomic planes divided by a in-plane lattice constant (which is actually an average of two lattice constants within monoatomic planes). Such a parameter gives a direct measure of tetragonal distortion in the simulated sample.
- Normalized vacancy distance from the surface:

$$V_Z^{normal} = 1 - |Z_V - (L_Z/2)| / (L_Z/2)$$
(5.2.1)

where Z_V is z coordinate of the considered vacancy, L_Z is the sample size in z direction. $V_Z^{normal} = 0$ when the vacancy is located at the surface, $0 < V_Z^{normal} < 1$ when the vacancy is in the bulk of layer.

⁶Cumulative effect of consecutive MS relaxations stems from the fact that atoms whose local atomic configurations were not changed during MC steps are already very close to their equilibrium positions, and each next MS relaxation brings them only slightly closer to their minimum of potential energy.

 $^{^7\}mathrm{It}$ seems that the major part of observed E_{conf} decrease in MS relaxations is due to displacement of atoms that surrounding vacancy.

 $^{^8}$ For a detailed explanation why to use in ABOP-based model E_{coh} instead of simple E_{conf} see subsec. 5.0.5.



(a)



(b)

Figure 5.2.2: Evolution of configurational energy ($\Delta E_{conf}(t) = E_{conf}(t) - E_{conf}(0)$) during MS relaxation in ABOP-based FePt layered samples: (a) detailed shape of the MS relaxation after first 10⁵ MC steps continued up to 2000 MS iterations; (b) a complete set of series of consecutive MS relaxations, each one corresponding to particular interval of MC steps in between: \Box - 1000 MC steps, \bigcirc - 2500 MC steps, \triangle - 5000 MC steps, \bigtriangledown - 10000 MC steps, \diamondsuit - 20000 MC steps.



Figure 5.2.3: Scheme of the thin layer sample with its defined bulk and surface volumes.

5.2.4 Order-disorder transition

Order-disorder transition was simulated for ABOP-based model samples. The calculations were performed by means of Glauber algorithm with vacancy mechanism. Subsequent lattice constants relaxation allowed for decrease (and finally complete decay) of tetragonal distortion which followed the decrease of a degree of LRO. The results were averaged over 8 independent simulation runs. The temperature dependence of the parameters of η , c/a and E_{coh} are presented in figure 5.2.4. The order-disorder transition was observed at T_t =1265 K. It showed a clearly discontinuous character, typical for FCC-based compounds [22]. The drop-off of LRO parameter from the level of around 0.84 to 0 was accompanied by serious slowing down in ordering processes, making it difficult to saturate the relaxations simulated at temperatures close to T_t . A direct observation of LRO evolution clearly showed which relaxations were saturated and which were not (fig.5.2.5). Discontinuous character of order-disorder transition showed up also in the evolution of the tetragonality parameter c/a and the configurational energy E_{coh} (fig. 5.2.4)

The above results seem to be quite important in terms of parametrization of simulated ordering kinetics. From the thermodynamical point of view, internal energy (in this particular model referred by E_{coh} cohesive energy) is the most important parameter that gives the evidence of a phase transition. The definitely discontinuous temperature dependence of E_{coh} clearly indicates the discontinuous phase transition. On the contrary, the decay of η and even c/amay also result from the creation of anti-phase domains which individually show yet a still high degree of LRO. Only tight correlation between the discontinuity of $\eta(T)$, (c/a)(T) and $E_{coh}(T)$ at the same temperature, proves adequacy of η parameter to parametrize degree of atomic long range order in the simulated "order-order" relaxations.

In the case of order-disorder transition the results presented here are substantially different from those obtained by ABOP authors. Muller et al. claim to obtain T_t 1595 K which is very close to the experimental value [1]. However, when comparing figure 5.2.4 with appropriate figure 2 in reference [17] it seems that their relaxations were not saturated (see fig. 5.2.5).

5.2.5 "Order-order" kinetics in $L1_0$ bulk

A series of $L1_0$ "order-order" relaxations in FePt bulk samples were simulated at temperatures between 1000 K and 1300 K. The results were averaged over



Figure 5.2.4: Temperature dependencies in simulated ABOP-based FePt $L1_0$ a) LRO and tetragonality b) configurational (cohesive) energy.

32 independent simulations yielding curves still showing quite a high level of statistical noise. The results are, however, sufficiently accurate to allow the estimation of the relaxation time τ_b of $\eta(t)$ and η_{eq} equilibrium LRO level (fig. 5.2.5(a)). Analysis of $\eta(t)$ curves revealed that all the LRO relaxations showed clearly one time scale (fig. 5.2.5(a)). The processes of disordering of ABOP-based FePt L1₀ bulk samples were exactly the same as in bulk FePt L1₀ modeled with two-body interatomic potentials. Arrhenius plot (fig. 5.2.6) of the fitted relaxation times τ shows a significant slowing down near transition temperature T_t 5.2.6. The relaxation parameters are presented in table 5.4.


Figure 5.2.5: a) Example of fully saturated $\eta(t)$ relaxation in simulated FePt L1₀ bulk sample at 1200K. b) Example of not saturated $\eta(t)$ relaxation in simulated FePt L1₀ bulk sample at 1265K (near T_t). Both results averaged over 32 independent simulations.



Figure 5.2.6: Arrhenius plot of the relaxation times fitted to $\eta(t)$ in L1₀-ordered FePt.

Temp. [K]	1000	1050	1100	1150	1200	1250	1300
η_{eq}	0.9874	0.9823	0.9750	0.9647	0.9472	0.9156	0.0
τ_b [MC steps]	59400	54100	50200	43200	49600	64000	-
$(c/a)_{eq}$	0.9640	0.9643	0.9647	0.9652	0.9662	0.9678	1

Table 5.4: "Order-order" relaxation parameters in simulated ABOP-based FePt bulk system.

5.2.6 "Order-order" kinetics in $L1_0$ layers

Samples with (001) surfaces initially perfectly $L1_0$ -ordered in a- or c-variant were simulated by means of MC/SR algorithm. It is important to remember that one vacancy was introduced to the system by removing one randomly chosen atom. The lattice parameters were initially set as equal to those in bulk samples, however, the following MS relaxations allowed to change lattice parameters in [001] direction due to surface (MS) relaxations. After several tests with full MC/SR algorithm, it appeared useful to fix lattice constants in [100] (*a*) and [010] (*b*) directions because the limited sample size in 001 direction (only 4 nm thick layer) was causing additional evolution of tetragonal distortion ⁹. Although it is an interesting physical effect¹⁰, the author's interest was focused on ordering processes in a "thick" system where *a* and *b* lattice constants are defined by a bigger bulk volume, and not by an artificial condition¹¹ of a very limited thickness of layer.



Figure 5.2.7: ABOP-based FePt model results: (a) LRO evolution (1200K): solid line - LRO in the entire layer (bulk + surfaces), dashed line - LRO in bulk of the layer (without 2 monoatomic layers from each surface) and (b) vacancy distance d from a free surface at 1000K and

 $^{{}^{9}}c/a=0.973$ in fully relaxed and optimized c-variant layer.

¹⁰The effects on crystal structure caused by limited thickness of layer (ultra-thin metal films) are themselves a subject of research [75, 76].

¹¹Caused by simulation computational demands.

The kinetics of disordering in ABOP $L1_0$ ordered FePt layered samples can be described as composed of the following processes:

- 1. The **rapid homogeneous bulk-like disordering** a relatively fast relaxation of LRO observed at the beginning of the "order-order" relaxation in the layered systems (fig.5.2.7(a)). The process seems to be a result of two basic mechanisms operating in parallel and showing particular relaxation times:
 - (a) Homogeneous disordering process exactly the same process as observed in the bulk samples (fig.5.2.5), relaxation time τ_b .
 - (b) Vacancy migration towards the surface (fig.5.2.7(b)) relaxation time τ_v alters the rates of the homogeneous disordering and surface-induced processes (subsec.5.2.6.1).

The two mechanisms result in the initial fast η relaxation showing shorter time scale (τ_f) and smaller amplitude (η_1) than the pure bulk disordering process (subsec.5.2.6.2).

- 2. Surface-induced disordering due to lower defect formation energies at the surface (tab. 5.3), the LRO relaxation in the surface area exhibits its distinct features with a different time scale and relaxation amplitude (subsec.5.2.6.3).
- 3. Slow homogeneous disordering an extremely slow relaxation controlled by a remanent (very low) effective vacancy concentration in the bulk of the layered samples (subsec.5.2.6.4).

Due to the fact that surface-induced disordering (2) as well as slow homogeneous disordering (3) were extremely slow processes 12 , it was impossible to quantitatively evaluate them.

5.2.6.1 Vacancy migration towards the surface

The evolution of the LRO in the ABOP-based $L1_0$ FePt layered system appeared quite complex. The difference observed between the LRO evolution in the surface area and in the bulk of the samples is remarkable (figs.:5.2.8, 5.2.9, 5.2.11). The obvious reason for this difference is non-uniform effective vacancy concentration which alters the ordering kinetics.

In order to understand the vacancy migration process, a series of relatively short (up to 1e7 MC steps) "order-order" relaxations were performed, with monitored evolution of V_Z^{normal} parameter. Despite the fact that the results were averaged over 32 samples the statistic noise was still significant (estimated around $\delta \tau_v \simeq 15\%$). Nevertheless, mean lifetime of a vacancy in the bulk τ_v (before it reaches the surface) have been estimated by fitting single exponential to the simulation results (tab.5.5).

 $^{^{12}}$ 3·10⁸MC steps, which were around one month of simulations, was not enough to saturate the simulated $\eta(t)$ isotherms.







(b)



(c)

Figure 5.2.8: LRO evolution monitored in monoatomic layers (parallel to the surfaces) of the (QKMC) simulated ABOP-based $L1_0$ c-variant FePt layered samples: (a) T=1000 K, (b) T=1100 K, (c) T=1200 K.







(b)



(c)

Figure 5.2.9: LRO evolution monitored in one-atom-thick layers (parallel to the surfaces) of the (QKMC) simulated ABOP-based $L1_0$ a-variant FePt layered samples: (a) T=1000 K, (b) T=1100 K, (c) T=1200 K.

Temp.	$\tau_v [\text{MC steps}]$					
[K]	c-variant	a-variant				
1000	$5.29 \cdot 10^{4}$	$5.85 \cdot 10^{3}$				
1100	$3.86\cdot 10^4$	$5.20 \cdot 10^{3}$				
1200	$3.06 \cdot 10^4$	$3.90 \cdot 10^{3}$				
1300*	$2.06 \cdot 10^{4}$	$3.80 \cdot 10^{3}$				

Table 5.5: Values of τ_v - mean lifetime of a vacancy in the bulk of particular thin layered samples. Results obtained with use of ABOP and MC/SR algorithm, averaged over 32 simulations.*- the sample was undergoing order-disorder transition.

A difference between the values of τ_v in the layers $L1_0$ ordered in c- and avariant is remarkable. The fact that τ_v is by an order of magnitude shorter in $L1_0$ a-variant than in $L1_0$ c-variant samples, clearly indicates that it is much easier for the vacancy to migrate along monoatomic planes than across them (the same as in the Ising-type model).

The effective normalized vacancy concentration in the bulk of the layered sample $c_v^{bulk}(t)$ can be described by a single exponential decay based on the V_Z^{normal} parameter:

$$c_{v}^{bulk}(t) = c_{v \ eq}^{bulk} + \left(c_{v \ 0}^{bulk} - c_{v \ eq}^{bulk}\right) * \exp\left(\frac{-t}{\tau_{v}}\right)$$
(5.2.2)

where: $c_{v\,0}^{bulk}$ is the initial value of the effective concentration, $c_{v\,eq}^{bulk}$ is the equilibrium value of the effective vacancy concentration, and τ_v is the relaxation time of the vacancy migration process obtained from $V_Z^{normal}(t)$ evolution (eq. 5.2.1). It is assumed that $c_{v\,eq}^{bulk} > 0$ because the $\eta^{bulk}(t)$ continuously (very slowly) evolves even after the vacancy migrated to the surface¹³.

5.2.6.2 Rapid homogeneous bulk-like disordering

Rapid homogeneous bulk-like disordering is a process that occurs at the very beginning of relaxation, when vacancy acts within the bulk of layered sample. The vacancy surface segregation effectively limits the rate of this process, thus the relaxation time τ_f , as well as the semi-stable level of the degree of LRO η_1^{bulk} is different than in the bulk system.

The parameters of the initial "order-order" relaxations were estimated through a series of relatively short (up to 1e7 MC steps) simulation runs (fig. 5.2.10). The results were averaged over 32 independent simulation runs.

5.2.6.3 Surface-induced disordering

When the vacancy reaches the surface, the process of surface-induced disordering is initiated. It seems that the two features of the simulated system favor such a behavior: (i) a relatively low vacancy formation energy at the surface and (ii) antisite formation energy which is significantly lower at the surface than in the bulk (tab.5.3). Due to the first feature, vacancy stays at the surface, and, as an

 $^{^{13}}$ It means that the effective vacancy concentration cannot be equal 0 because the antisites are generated solely via vacancy migration.

Temp.		a-variant	c-variant		
[K]	η_1^{bulk}	τ_f [MC steps]	η_1^{bulk}	τ_f [MC steps]	
1000	0.996	$5.61\cdot 10^3$	0.989	$1.02 \cdot 10^{5}$	
1100	0.993	$5.18 \cdot 10^{3}$	0.977	$5.56 \cdot 10^{5}$	
1200	0.994	$2.48 \cdot 10^{3}$	0.970	$4.87 \cdot 10^{5}$	

Table 5.6: The parameters of the initial "order-order" relaxations (bulk-like disordering), η_1^{bulk} - the semi-stable state at the end of the initial relaxation, τ_f - time constant of the initial relaxation.



Figure 5.2.10: The initial part (rapid bulk-like disordering) of the $\eta(t)$ isotherm simulated in the ABOP-based FePt L1₀ c-variant layered system in 1200K.

agent of disordering enables any change in the atomic configuration. The fact that stems from the second feature is the higher antisite concentration near the surface. A direct observation of the atomic configuration clearly illustrates and proves the above statement (fig.5.2.11).

Regarding possible nucleation of $L1_0$ a- and b-variant domains, only very weak traces of this process can be noticed - surface antisites tend to emerge in small aligned clusters (fig.5.2.11a). Moreover, the surface-induced disordering, contrary to the reorientation in the Ising-type system, seems to be limited only to a single monoatomic layer at the surfaces in the case of $L1_0$ a-variant layers, and to two atomic layers of the surface in the case of $L1_0$ c-variant samples (fig.5.2.8 and 5.2.9)



Figure 5.2.11: ABOP-based FePt model results, a) (001)-surface and b) (010)cross-section view of the simulated sample after 10^8 MC steps at 1200K.

5.2.6.4 Slow homogeneous disordering

Contrary to Ising-type model results (subsec. 4.3.4), a significant influence of the surface on homogeneous disordering appeared in the ABOP-based model. Because of the vacancy segregation to the surface, the effective vacancy concentration in the bulk of layered sample is significantly reduced, and as a result, the bulk-like disordering is severely slowed down. It was never possible to observe its saturation. Nevertheless, even without quantitative analysis, it is clear (see fig.5.2.9 and 5.2.8) that slow homogeneous disordering in the bulk of the layered samples is at least 10^4 times slower than in the bulk samples.

Since the surface disordering observed in a series of temperatures is limited to the near surface area it can be assumed that the samples are not undergoing the order-disorder transition at these temperatures. Thus, despite the fact that the equilibrium saturation of the relaxations was not observed, it can be assumed that the relaxations will eventually saturate in the sufficiently long simulation time (several mounts of simulations would be necessary).

5.3 KMC/SR simulations

The KMC/SR algorithm is an upgrade of a quasi-kinetic MC/SR one, where migration barriers during atomic jumps are taken into account. Calculation of a single barrier requires several minutes of CPU real time. Thus, straightforward calculations of migration barriers during MC simulation are unrealistic. To

Migration parameters:		Window parameters:			Results:			
Atom	Orig. sub.	Target sub.	No Fe	No Pt	r [nm]	$\Delta E[\text{eV}]$	$E^+[eV]$	$E_{norm}^+[eV]$
Fe	Fe	Fe	0	4	0.2278	0.000	3.530	3.530
\mathbf{Fe}	\mathbf{Fe}	${\rm Fe}$	1	3	0.2278	0.000	2.983	2.983
${\rm Fe}$	\mathbf{Fe}	${\rm Fe}$	2	2	0.2278	0.000	2.192	2.192
\mathbf{Fe}	\mathbf{Fe}	${\rm Fe}$	3	1	0.2278	0.000	1.857	1.857
\mathbf{Fe}	\mathbf{Fe}	${\rm Fe}$	4	0	0.2278	0.000	1.373	1.373
${\rm Fe}$	\mathbf{Fe}	\mathbf{Pt}	2	2	0.2278	0.810	2.697	2.292
\mathbf{Pt}	${\rm Fe}$	${ m Fe}$	0	4	0.2278	0.000	3.350	3.350
${\rm Fe}$	\mathbf{Pt}	\mathbf{Pt}	4	0	0.2278	0.000	1.194	1.194
\mathbf{Pt}	\mathbf{Pt}	${ m Fe}$	2	2	0.2278	0.320	3.091	2.931
\mathbf{Pt}	\mathbf{Pt}	\mathbf{Pt}	4	0	0.2278	0.000	2.455	2.455
\mathbf{Pt}	\mathbf{Pt}	\mathbf{Pt}	3	1	0.2278	0.000	2.810	2.809
\mathbf{Pt}	Pt	\mathbf{Pt}	2	2	0.2278	0.000	3.028	3.028
\mathbf{Pt}	\mathbf{Pt}	\mathbf{Pt}	1	3	0.2278	0.000	3.416	3.416
Pt	Pt	\mathbf{Pt}	0	4	0.2278	0.000	3.720	3.720

Table 5.7: Example results of migration energy barrier evaluation in FePt ABOP bulk sample with optimized lattice constants.

avoid this particular problem, a simple analytic formula was developed which allowed fast and reasonably accurate calculation of atomic migration barriers (subsec. 2.4).

5.3.1 Evaluation of migration barriers

In KMC/SR simulations, migration barriers were estimated using simple analytic interpolation (subsec. 2.4). However, to obtain parameters for the formula, several energy barriers had to be calculated. Each barrier was calculated in the cubic sample consisting of 4000 sites. In the set of simulations, the atomic configuration as well as lattice constants were arranged to yield all basic possibilities in terms of atomic composition around the migrating atom, including surfaces.

The migration was simulated by a number of molecular statics simulations followed by a vary small shift (0.07Å) of the migrating atom towards the vacancy. During the MS simulation the atom was partially immobilized, it could not move in the direction of the forced migration, whereas, it could move in the plane perpendicular to the migration direction. Additionally, to stabilize the sample position, the base of the sample - a plane of 200 atoms was completely frozen. After each shift of the migrating atom, full MS relaxation was performed. About 40 steps were performed to evaluate a single saddle point during the migration. Example atomic migrations are presented in figure 5.3.1, and selected values of the saddle points are presented in table 5.7.

Obtained values were used to fit A and B parameters (eq. 2.4.3) (fig. 5.3.2a) and to calculate¹⁴ values of C and D parameters (eq. 2.4.4) (fig. 5.3.2b), according to the scheme presented in subsection 2.4. Results of the above procedure are presented in table 5.8, thus the interpolation of migration barriers was enabled.

¹⁴Migrations in the second from the surface layer $(N_n = 34)$ and in the bulk $(N_n = 36)$ were simulated resulting in only two points to calculate the values of C and D parameters (fig. 5.3.2).



Figure 5.3.1: Example of profiles of configurational energy $\Delta E_{conf}(d)$ during atomic migration to the NN vacancy. a) in-plane Fe-atom migration, b) inplane Pt atom migration c) comparison of Fe-atom in-plane migration and Fe antisite creation, d) comparison of Pt-atom in-plane migration and Pt antisite creation.



Figure 5.3.2: Example of plots of normalized migration barriers E_{norm}^+ for Fe atom migrating through the "window" composed of 4 Pt atoms. (a) a function of the "window" size with the fitted $E_{norm}^+ = Ar + B$ function; (b) a function of a number of neighbors around the pair of sites between which the atom migrates.

Atom	No Fe	No Pt	А	В	С	D
Fe	4	0	-2.269	6.491	0.0957	-2.440
Fe	3	1	-2.259	7.026	0.0891	-2.207
${\rm Fe}$	2	2	-5.137	13.976	0.0623	-1.242
Fe	1	3	-6.241	17.210	-0.00694	1.250
Fe	0	4	-8.452	22.812	-0.0208	1.750
Pt	4	0	-6.183	16.636	0.174	-5.273
Pt	3	1	-7.926	20.948	0.166	-4.959
Pt	2	2	-8.296	29.951	0.105	-2.793
Pt	1	3	-10.530	27.459	0.140	-4.040
Pt	0	4	-10.457	27.410	0.132	-3.758
Fe	2	0	-2.932	8.406	0	1
Fe	1	1	0.741	-0.499	0	1
Fe	0	2	-1.330	3.916	0	1
Pt	2	0	-5.912	15.063	0	1
Pt	1	1	-5.046	12.927	0	1
Pt	0	2	-4.495	11.489	0	1

Table 5.8: A complete set of parameters for migration energy barriers interpolation (sub.2.4) for ABOP FePt $L1_0$ thin layers simulations.



Figure 5.3.3: Comparison of η evolution in ABOP-based FePt bulk samples simulated at 1100 K with kinetic Glauber, Residence Time and Quasi-Kinetic Glauber.

5.3.2 Order-order relaxations by KMC/SR

A set of "order-order" relaxation simulations was performed using KMC/SR algorithm. There were two kinetic approaches used in this case, namely: kinetic Glauber algorithm with uniform probability of choosing NN atom as a candidate to jump into the vacancy, and residence time algorithm where an event probability is dependent on transition energy. The comparison of the showed that RT is much more efficient. However, the KMC/SR even with use of RT algorithm was still over 100 times slower than MC/SR. The comparison of $\eta(t)$ evolution in FePt bulk samples simulated with kinetic Glauber, residence time, and quasi-kinetic Glauber are presented in figure 5.3.3.

It appeared clear that with currently available computational resources it is not feasible to simulate full LRO relaxation in considered system using ABOP-based KMC/SR algorithms. There are several reasons why both kinetic algorithms appeared ineffective.

In the case of kinetic Glauber algorithm, the values of the migration energy barriers are so high that a probability of a jump execution is very small, causing mostly ineffective MC steps.

Whereas in kinetic Residence Time algorithm, relations between migration energy barriers for various possible jumps from one site play a crucial part. The energy barriers for atomic migration between sublattices are much lower than for the migration along sublattices. Thus atoms tend to perform sequences of forward and backward jumps resulting in extremely slow evolution of the atomic configuration. The kinetic Residence Time algorithm, however, is more effective than Kinetic Glauber.

5.4 Direct exchange MC/SR simulations

Since neither KMC nor QKMC algorithms were sufficiently efficient to generate the equilibrium configurations in the examined FePt $L1_0$ ordered thin layers, additional test involving direct exchange algorithm (subsec. 2.1.2) was performed. Before analyzing the details of the results, it is important to note that the algorithm simulates a non-physical process of exchanging randomly chosen atom pairs, thus, the interpretation of the obtained results should not go beyond discussion of equilibrium configuration.

5.4.1 FePt L1₀ equilibrium by direct exchange MC/SR

A set of simulations was performed using direct exchange MC/SR algorithm in the layered a- and c- $L1_0$ variant FePt samples (10x10x10 unit cells with (001)-surfaces). The relaxations were carried out from a perfectly $L1_0$ ordered configuration to an equilibrium one at the temperatures: 1000, 1100 and 1200 K, similar as in the previous ABOP-based simulations (sec.5.2). The applied algorithm consisted of a random selection of two atoms, and an attempt to exchange their lattice positions according to Glauber probability.



Figure 5.4.1: ABOP-based FePt model results obtained by means of the direct exchange algorithm, initially a-variant $L1_0$ ordered thin layers: a) (001) surface and b) (010)-cross-section view of the simulated sample after $5 \cdot 10^7$ MC steps at 1200K.

The simulated isothermal LRO evolution shows a definite preference for a(b)-variant $L1_0$ ordering. In samples initially arranged in the a-variant $L1_0$ superstructure, we observe partial disordering through generation of APDs rather than generation of separated single antisites (Fig.5.4.1). However, in the samples initially arranged in the c-variant $L1_0$ superstructure, the entire sample is undergoing a transformation from c- to a- and b- variants of $L1_0$ superstructure. The process starts at the surfaces (Fig. 5.4.2), and proceeds inwards the sample.

This result shows that when the kinetic barriers that appear in the vacancymediated atomic ordering processes are bypassed, the ABOP modeled FePt layers initially c-variant $L1_0$ ordered samples will tend to obtain a(b)-variant of the $L1_0$ superstructure orientation, which present the lowest (among considered variants) surface formation energy. This result is in a full agreement with the Ising-type model simulations, yet implemented with the vacancy mechanism of atomic migrations.



Figure 5.4.2: ABOP-based FePt model results obtained by means of the direct exchange algorithm, initially c-variant $L1_0$ ordered thin layers: a) (001) surface and b) (010)-cross-section view of the simulated sample after $5 * 10^7$ MC steps at 1200K c) LRO evolution monitored in monoatomic layers (parallel to the surfaces) of the sample at 1000 K.

Chapter 6

Summary and discussion

6.1 Ising-type model results - discussion

MC simulations based on Ising-type rigid lattice model were carried out to study atomic ordering kinetics in bulk and thin layers of $L1_0$ FePt. The method itself was derived from the successful study of Ni₃Al L1₂ system [71] where its adequacy had been proved. "Order-order" relaxations simulated in bulk samples showed clearly a single exponential (single time scale) process of homogeneous antisite defect generation/annihilation (ordering/disordering), which is in congruence with Phase Field Method (PFM) predictions of other authors [77].

Atomistic MC simulations of "order-order" phenomena in Ising-type FePt layered samples showed a strong effect of free (001) surfaces on the process. The possible influence of the free surface on the ordering in the 3D Ising model was already predicted [78, 79], however, only within the magnetic spin polarization formalism.

In the case of MC simulations in Ising-type L1₀ FePt thin films, the most important result is an indication of the definite preference for a- and b- variants of L_{10} -superstructure imposed by (001) Fe-surface and of the stabilization effect of (001) Pt-surface on the c-variant. The transformation of $L1_0$ c-variant into a- and b-variant domains at Fe-surface [69, 70] was observed for the first time. Relatively similar MC simulations in L1₀ FePt dimensionally limited systems (nano-layers and nano-particles) were carried out by a few authors, however none of them observed surface-induced superstructure reorientation. Yang et al.[19] have used Tight Biding Ising Model (TBIM) with artificial surface potentials set a priori, which resulted in a predefined Pt surface segregation. Similar results were obtained by Muller et al. [80] within an Ising model with an additional surface energy term. Chepulskii et al. [81] have used advanced mixing pair potentials based on Ab-Initio and CEM, but did not study (001) surface influence on the ordering (only spherical nanoparticles were considered). It is important to note that all the mentioned authors were studying equilibrium state only, without implementing the vacancy mechanism for atomic interchanges.

The mechanism of superstructure c- to a(b)- $L1_0$ variant reorientation was analyzed in detail. The observations, especially regarding microstructure relaxation, are perfectly in compliance with PFM results [77], where, except for homogeneous ordering process, the APB domain relaxation was observed as a separate process with its own unique time scale. The fact that triple junctions of APBs, well-known from Transmission Electron Microscopy (TEM) imagining [77], were observed in the presented results (fig. 4.3.6c, [00-1] view) is noteworthy.

There are several physical effects that have been neglected in the presented Ising-type MC simulations, which might have a significant influence on the atomic ordering. The following issues seem especially important: strain caused by a substrate, tetragonal distortion and surface relaxations. The latter two effects were addressed when working with ABOP potentials (cha.5).

6.2 ABOP-based model results - discussion

MC/SR simulations based on ABOP were applied to study atomic ordering kinetics in $L1_0$ FePt bulk and thin layers. The method was an extension of the MC simulation based on a rigid Ising-type lattice by introducing additional static relaxations between series of MC iterations. The algorithm was carefully tested and optimized for the ABOP-based $L1_0$ -ordered FePt system (subsec. 5.2.2). In view of a substantial difference in efficiency between QKMC and KMC algorithms (see subsec.), QKMC algorithm was used in the study.

In the case of bulk samples, as it was expected, "order-order" relaxations showed single-time-scale process of homogeneous antisite defect generation/annihilation (disordering/ordering). This result is, again, in agreement with Phase Field Method (PFM) calculations [77].

The presented results of atomistic MC/SR simulations of "order-order" phenomena in FePt layered samples showed a strong effect of free (001) surfaces on the process. Strong attraction of vacancies by surfaces was a remarkable feature of the layered system. It was observed in both a- and c- $L1_0$ superstructure variant layers. The results are in agreement with those of Muller et al. [17] obtained in Ising-type model based on ABOP. The surface attraction of vacancies resulted in effective vacancy concentration being higher at the surface of the layer than in the bulk of the layer. Consequently, complex "order-order" kinetics was observed in the layered samples including surface-induced disordering. It is significant that nucleation of a- and b-variant $L1_0$ domains on the Fe surface of $L1_0$ c-variant layers was not observed.

The results obtained in ABOP-based MC/SR simulations are in qualitative agreement with the ones obtained by Muller et al. [17] in off-lattice ABOP MC simulations and ABOP-based Ising-type model. The main feature of the ordering processes in layered systems seems to be the surface-induced disordering.

The study of substrate effects, being a complex issue itself, goes far beyond the scope of this dissertation, thus it has not been addressed.

6.3 Ising-type and ABOP model results - comparative discussion

Two different simulation approaches were applied to examine ordering phenomena in FePt bulk and [001] oriented layers. Both models, i.e. Ising-type and ABOP proved that the free surface induces metastability of the c-variant $L1_0$ atomic configuration. However, the results yielded by particular quasi-kinetic



Figure 6.3.1: Scheme of [001] layer with: a) pure c-variant superstructure; b) initial stage of $L1_0$ c-variant -> a(b)-variant transformation in a FePt layer, c) a pure a-variant superstructure. Atoms residing on two NN crystallographic planes are represented by small and big circles.

models applied (subsec.) differ in detailed features of the surface-induced processes.

MC simulations implemented with Ising-type model resulted in heterogeneous nucleation of the $L1_0$ a- and b-variant domains on the Fe surface. By contrast, simulations involving ABOP scheme yielded only surface-induced disordering with no clear nucleation of a- or b-variant domains.

In all considered models the configurational energy E_c of a (001)-oriented layer ordered homogeneously in L1₀ c-variant is higher that the energy E_a of the same layer ordered homogeneously in L1₀ a- (or b-)variant (fig. 6.3.1). Only the Ising-type model, however, E_c is still higher than the configurational energy $E_{c\&a}$ of the layer containing the L1₀ c-variant a-variant APB (fig. 6.3.1 b)) ($E_c > E_{c\&a} > E_a$). The corresponding relation between ABOP configurational energies is: $E_{c\&a} > E_c > E_a$, and as a result, only surface-induced disordering occurs.

It is very important to note that the c-variant \rightarrow a-variant reorientation *does* result from ABOP-based model simulations provided they are implemented with non-kinetic direct exchange algorithm. This fact emphasizes the important role of the kinetic processes in the analyzed systems, as the superstructure reorientation process was not observed in the quasi-kinetic simulations of the ABOP-based model with vacancy mechanism implemented.

6.4 Discussion of the results in view of other literature data

6.4.1 FePt layers by ab-initio calculations

The first general analysis of electronic structure of Fe-Pt alloys was published in 1991 by M. Podgórny [82]. Quite important contribution to the analysis of atomic ordering in Fe-Pt and Fe-Pd bulk alloys was done by Mohri, Chen et al. [46, 47, 83]. Their ab-initio calculations were the basis for the development of CEM and PFM models[77]. The CEM calculations were used to obtain FePt pair-interactions applied in this work in Ising-type MC simulations (cha.4).

Completely different approach to ab-initio calculations was presented by Dannenberg et al. [84] and Olsza [85] who straightforwardly compared the configurational energies of FePt layers ordered in various superstructures (in particular, in diverse $L1_0$ variants). All the results together with this dissertation are consistent in the conclusion that (001)-oriented layers ordered in $L1_0$ a- or b-variant are definitely the most stable. However, Dannenberg et al. show that the most energetically favorable surface is the (111)-oriented one built of Pt atoms, which corresponds to $L1_1$ superstructure. This result is very important, however, due to the fact that in this thesis the study was narrowed to $L1_0$ superstructures it could not have been verified.

6.4.2 Conversion electron Mössbauer spectroscopy (CEMS) results

Only two years after the first communication on our MC results [69], a related experimental work was published [86]. The Conversion Electron Mössbauer Spectroscopy (CEMS) experiment results published in this work can be straightforwardly compared with the MC simulations ones.

It was found that the FePt multilayer, initially ordered in the $L1_0$ c-variant, showed the presence of domains of $L1_0$ a(b)-variant superstructure and of a disordered phase after annealing (at 773 K, 848 K or 898 K). The experiment gives straightforward evidence for the c- to a(b)- $L1_0$ - variant superstructure reorientation, as well as for the surface-induced disordering.

6.4.3 Other experimental results

Plenty of publications on experimental analysis of FePt chemical ordering were published, however, only in few of them, authors present results concerning surface ordering phenomena in $L1_0$ FePt monocrystals. The fact that the results are somewhat ambiguous is intriguing.

Several publications concerning experimental analysis of $L1_0$ textures on the surface of ordered FePt thin layers were published by Kim et al. [87, 88] and recently by Reddy et al [89]. They analyze in detail the influence of the layer thickness and strain on equilibrium ordering in polycrystalline samples. At some points they claim to observe the preference for c-variant $L1_0$ superstructure orientation at the (001)-surface, however, the results report ordering in samples as deposited, or annealed at temperatures around 400K. In view of the experimental studies [86, 90, 91] as well as of the Ising-type MC and ABOP-based QKMC simulations presented in this work, these temperatures seem to be too low to obtain effective atomic order relaxation.

The Ising-type model result regarding the decrease of FePt $L1_0$ superstructure stability by the limited size of the studied sample (subsec.4.3.3) seems to be well confirmed by works of Takahashi, Miyazaki et al. [13, 92, 18]. Miyazaki et al. in their research take into account possible superstructure reorientation presented in this work.

6.5 Conclusions

General conclusion that stems from the presented study is the fact that the (001)-surface in the FePt L1₀-ordered intermetallic definitely destabilizes the c-variant L1₀ superstructure and promotes a- or b-variant L1₀ superstructure.

Two mechanisms of the related surface-induced transformations of atomic configuration were analyzed in detail:

- Reorientation of the c-variant $L1_0$ superstructure into the a(b)-variant one - initiated at the Fe surface by spontaneous nucleation and growth of aand b- $L1_0$ variant domains followed by the a- and b- variant domains microstructure relaxation.
- Surface-induced disordering occurring in (001)-oriented FePt layers ordered in any $L1_0$ variant.

In view of experimental results [86], it seems that both aforementioned mechanisms can operate in parallel, altering the FePt superstructure and effectively limiting the minimum size for the ordered nano-layers or nano-crystals.

Appendix A

Miscellaneous algorithms

A.1 Evolutionary algorithm for Laplace transform

A Laplace transform is an operation performed on a function that makes its explanation in a space of exponential functions. In this work Laplace transform was used to analyze time-dependent processes. It allows determination of complex exponent-like structure of a subjected to the transform function. By means of Laplace transform the complex, multi-exponential structure of the the "order-order" relaxation can be revealed.

The original integral definition of Laplace transform has the following form:

$$F(\tau) = L\{f(t)\} = \int_0^\infty e^{-t\tau} f(t)dt$$
 (A.1.1)

where $F(\tau)$ is a value of transform¹ for a given τ - exponent time constant, and f(t) is the original function dependent on time. To make it feasible for numerical computation it must be formulated as a finite sum over finite elements:

$$F(\tau) = L\{f(t)\} = \sum_{j=0}^{M} e^{-t_j \tau} f(t_j)$$
 (A.1.2)

where t_j are discrete points at which values of the f function are known. An inversed Laplace transform would have the following form:

$$f(t) = L^{-1} \{ F(\tau) \} = \sum_{i=0}^{N} F(\tau_i) e^{-t\tau_i} = \sum_{i=0}^{N} A_i e^{-t\tau_i}$$
(A.1.3)

In general the applied Laplace transform procedure was based on the process of fitting the sum of exponents (eq. A.1.3) to the f function. The square error ϵ of the difference between the function and the inversed transform was minimized by variation over A_i parameters:

$$\epsilon = \sum_{j=0}^{N} \left(f(t_j) - \sum_{i=0}^{M} A_i e^{-t_j \tau_i} \right)^2$$
(A.1.4)

¹The value of an Laplace transform $F(\tau)$ at a certain time constant point τ can be understood as a contribution of an exponent with a given time constant to the original function f(t) (see eq. A.1.3).

The choice of exponents space sampling (τ_i series) is crucial in terms of computational efficiency. To cover necessary range of time constants (from 10^1 to 10^{10}) and to keep a reasonable number of τ_i points the following formula was used for sampling:

$$\tau_i = b^{i+i0} \tag{A.1.5}$$

where b was constant between 1.01 and 1.2 and i0 was around 100. Such parametrization produced number of 10^2 magnitude of points, which was completely sufficient to determine potential complex exponent-like structure of analyzed functions.

Nevertheless, the number of above 100 independent variables is big enough to cause the failure of any classical minimization procedure, hence an **evolutionary algorithm** was applied to determine a minimum of ϵ function.

The evolutionary algorithm is an expansion of genetic algorithm (based on the idea of natural selection)[93], and belongs to a general class of Monte Carlo methods. The procedure can be drawn as the following recipe:

- 1. Samples generation N random sets (series of A_i parameters) is generated: {A¹,..,A^j,..A^N}, where each A^j = {A_i} and all A^j-sets are based on the same { τ_i }
- 2. Error estimation for each A^j -set error ϵ^j is calculated
- 3. Best fitted multiplication a number <N of A^j-sets with the lowest ϵ error is chosen, and randomly multiplied to produce total number of N A^j-sets
- 4. Mutation (genes modification) randomly (with probability P_{mut}) chosen elements of A^{j} -sets are modified according to the formula:

$$A'_{i} = A_{i} + F_{mut}(1 - 2u)((1 - F_{dep}) + F_{dep} \cdot A_{i})$$
(A.1.6)

where u is a random number between 0 and 1, F_{mut} is a mutation amplitude factor and F_{dep} is a mutation dependence factor.

- 5. Crossing (genes exchange in population) for each A^{j} -set an another random one is chosen A^{k} , and between those two, some A_{i} elements are exchanged according to crossing probability P_{cross}
- 6. Factors modification a number of performed steps is calculated with respect to possible change in total fitting error $\epsilon_{tot} = \sum^{N} \epsilon_{i}$, if the total fitting error was not improved significantly over a certain number of steps, mutation factor P_{mut} and possibly other factors and probabilities are decreased by a small value.
- 7. Iteration if the number of steps without improvement is large enough the whole procedure is over, if not - go to point 2.

The described procedure, in order to be efficient, requires a very fine adjustment of all parameters. Moreover, it is important to supply it with a high-quality data. The method is very sensitive, statistical noise at the beginning of relaxation easily shown can be by Laplace transform as an additional short-time exponential contribution. Nevertheless, according to the author's experience, the method is far more reliable than analysis performed by fitting set of exponential functions with variable time constants.

A.2 Bulk modulus calculation

In this study bulk modulus calculations were carried out. The results were used as a physical property of a simulated system to verify the application of ABOP potentials. The bulk modulus K measures resistance of a substance to uniform compression, usually measured in GPa². It is defined as the increase in pressure needed to achieve a given relative decrease in volume. The bulk modulus K can be formally defined by the equation:

$$K = -V\frac{\partial p}{\partial V} \tag{A.2.1}$$

where p is pressure, V is volume, and $\partial p/\partial V$ denotes partial derivative of pressure with respect to volume. The inverse of the bulk modulus gives a substance's compressibility. Taking into account thermodynamic relation for pressure p:

$$p = -\left(\frac{\partial F}{\partial V}\right)_T \tag{A.2.2}$$

where F is the free energy of the system, the bulk modulus may be formulated as:

$$K = V \left(\frac{\partial^2 F}{\partial V^2}\right)_T \tag{A.2.3}$$

with respect to the fact that volume change is made at constant temperature. It becomes straightforward to apply this formulation into the MD system when the following assumptions are imposed:

- Infinitesimal small change is exchanged with the finite volume rescaling
- Free energy at 0K can be replaced with the system potential energy
- Potential energy responds harmonically to a small change of the volume around the minimum value

$$E_p = \frac{K}{2V_{eq}}V^2 + aV + b \tag{A.2.4}$$

• There is no external pressure: p = 0

With the above assumption, to calculate K bulk modulus there are necessary at least three points (V, E_p) . A natural choice would be: potential energy at equilibrium state $E_p^{eq} = E_p(V_{eq})$ and two energies obtained from the sample with slightly changed volume $E_p^+ = E_p(V_{eq} + \Delta V)$, and $E_p^- = E_p(V_{eq} - \Delta V)$.

$$K = \frac{\left(2E_p^{eq} + E_p^+ + E_p^-\right)}{8\Delta V}$$
(A.2.5)

Effectively, instead of real value of volume, uniform rescale factors were used, then the formulation had the following form:

$$K = \frac{2}{9V_{eq}} \cdot \frac{\left(E_p^- - E_p^{eq}\right) \left(\gamma^+\right)^3 - \left(E_p^+ - E_p^{eq}\right) \left(\gamma^-\right)^3}{\left(\gamma^+\right)^3 \left(\gamma^-\right)^2 - \left(\gamma^-\right)^3 \left(\gamma^+\right)^2}$$
(A.2.6)

 $^{^{2}}$ It is important to remember the units at which the calculations are performed, in some publications are mixed and unclear causing significantly time-consuming queries. The relationship between internal simulation units and those commonly used in publications would be: 1[eV/] = 1.6023[GPa].

where γ^+ and γ^- are the uniform volume rescaling factors:

$$\gamma^{+} = \sqrt[3]{\frac{V + \Delta V}{V}} \tag{A.2.7}$$

$$\gamma^{-} = \sqrt[3]{\frac{V - \Delta V}{V}} \tag{A.2.8}$$

A.3 Lattice (optimization) relaxation - pressure control algorithm

When simulating the system with variable anisotropic sample geometry, like FePt $L1_0$ with decreasing tetragonal distortion in normal pressure conditions, one should apply a method to adopt system volume, i.e. simulated sample shape, to its changing condition. The studied system should be considered rather as NPT than NVT ensemble as used in standard in MC based on the rigid lattice.

Application of such conditions was performed in hybrid Monte Carlo / Static Relaxation (MC/SR) simulations. The static relaxations involved a rescale of the volume (separately x, y, and z dimension) of the sample to obtain minimum of potential energy. Such relaxation resembles a condition of complete lack of external pressure. Regarding the fact that we are interested in results comparable with experiments obtained at atmospheric pressure, this assumption is completely safe and does not bring a significant error. In the case of solid-state metallic systems, like the ones studied here, the value of atmospheric pressure (10^5 Pa) is negligibly small when compared with the value of bulk modulus parameter $(217 \cdot 10^9 \text{ Pa} \text{ for simulated FePt}).$

The algorithm used for the relaxation is an adaptation of the simplex method [94], where minimization is performed over sample sizes in all directions separately (x, y and z). It refers to a rescale operation performed on all vectors of positions in the simulated system $\mathbf{r}' = (\mathbf{r}_x \cdot \gamma_x, \mathbf{r}_y \cdot \gamma_y, \mathbf{r}_z \cdot \gamma_z)$, where γ_i are rescaling factors along x, y and z coordinates. Rescaling factor for x coordinate would be $\gamma_x = (l_x + \Delta l_x)/l_x$ where l_x is a size of the sample in x direction and Δl_x is a considered change of l_x value.

Alphard

Alphard is the environment for atomistic simulations, designed with special features useful for atomic ordering studies. The main part of Alphard's source code was elaborated by the author of this thesis and addressed to deal with the issues investigated. However, it was developed with an intention to make it as general and flexible as possible. The program is object-oriented, written in C++. Software engineering standards were applied to make the code developer friendly and easy to expand. Alphard's source code is open in terms of General Public License (GPL) and available at **sourceforge.net/projects/alphard**. It is virtually hardware-independent, extensively tested on a variety of Linux operating systems.

On the basis of Alphard several master's theses were completed. Alphard, as an open source project, is hereby announced and welcomes anybody willing to use it or join the developers' team.

Oświadczenie

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Kraków, dnia 28 maja 2010

(podpis doktoranta)

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