Characterization and design of advanced stratified materials using X-ray spectroscopy

(X 線 分光法と用いた先進多層材料のキャラクタリゼーション及び設計)

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PREFACE
Since their discovery, x-rays have played a significant role in our lives: they make the unseen in our bodies visible; they enhance our security in air travel; they make possible nondestructive testing of a wide variety of materials. And through x-ray diffraction, reflection and spectroscopy they make it possible to probe the order of matter at the atomic level.

The aim of this thesis is to present several examples of the x-ray based techniques application. It starts from the x-ray fluorescence and absorption spectra interpretation, which allows the exploration of the electronic structure of crystalline (Part I). Such a way of the x-ray spectroscopy data treatment can be rightfully considered as a traditional.

Modern growth techniques allow materials to be designed and fabricated at the atomic or molecular level. One of the most interesting classes of materials is the multilayer. X-ray reflectivity turns out to be a powerful tool to get the information on the thickness, density, interface roughness, layers ordering and other properties. Part II is devoted to novel characterization technique, which is based on the measurement of energy distribution of the reflected beam intensity. To apply it, the “Multilayer Reflectivity” database was developed.

The high source brightness of the so-called third generation of the synchrotron radiation facility stimulated a large amount of researches on the microbeam formation. Microbeam diffraction, microbeam fluorescence spectroscopy and others small beam using techniques became of great interesting. More recently planar x-ray waveguides were used successfully for the microbeam formation followed by the microdiffraction measurements. The theory, which is developed for the total x-ray reflection in the stratified media, can be used not only for the multilayers characterization, but for developing of the new materials with the desirable properties too. In Part III it is used for the waveguide parameters revision to obtain the guided beam of highest intensity. An optimization procedure is based on the novel numerical technique, the so-called genetic algorithms. These algorithms copy the process of the natural system evolution while optimum searching in the population of the string-encoded trial solutions.
Appendices contain the short theoretical description of the x-ray propagation in the stratified media for the incident beam glancing angles, lying below the total x-ray reflection critical angle (Appendix A), mathematical backgrounds of genetic algorithms (Appendix B) and description of the types, tables and procedures, which are used in the “Multilayer Reflectivity” database.
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I would like to thank all the personnel, who take part in the preparation of the samples and help to carry out the experiments. I wish to express the individual thanks to S. Harada (Master course student at the Kyoto University) for the reflectivity measurements, to Dr. H. Takenaka (NTT-AT) for multilayer samples preparation, to N.A. Skorikov (Doctor course student at the Institute of Metal Physics, Urals Division of the Russian Academy of Sciences) for DOS and band structure calculations.

I wish to thank my family and my friends, who supported me.
Publications list

Publications related to the present thesis:

※ P.Karimov, J.Kawai, E.Z. Kurmaev: Planar x-ray waveguides optimization for the incident beam energy below 10 keV, prepared for submitting
※ P.F. Karimov, E.Z. Kurmaev, A. Moewes, V.I. Okulov, M. Neumann, K. Endo: Local electronic structure of Fe impurity atoms in HgSe semiconductor, prepared for submitting
Other publications:


INTRODUCTION
Chapter 1. Introduction

X-rays were discovered by W.C. Röntgen in 1895. Since that time they have become established as an invaluable probe of the structure of matter. The range of the problems where x-rays have proved to be decisive includes at one limit of complexity simple compounds, through to more complex examples, such as DNA, proteins and even the functional units of living organism. An interaction of x-rays with matter is classified into:

- conversion to heat,
- photoelectrical effect,
- fluorescence,
- electron production,
- absorption,
- no interaction.

The discovery of x-ray diffraction in crystals by Max von Laue, Walther Friedrich and Paul Knipping, followed by William Bragg's interpretation of the diffraction spots as proof of the wave nature of x rays, provided the foundation for the x-ray crystallography. X-ray crystallography turned out to be essential in revealing the atomic structure of solids, their functional and physical properties. It was found that the intensity distribution in the diffraction patterns reveal how electrons were distributed within the atom and give more information about how the atoms in a solid vibrated about their equilibrium positions. In more complex crystals the unit cells of which is built of molecules, the spot intensities in diffraction patterns are modulated in a way that directly revealed the atomic structure of the molecule — a discovery that revolutionized chemistry and molecular biology. Diffraction patterns from the liquid state of matter indicated the correlations in the positions of the atoms in the liquid which formed the basis of the physics of liquids.
Early in the history of x-rays, Compton scattering revealed the energy and momentum distributions of electrons as well as vividly illustrating Heisenberg's uncertainty principle. But the real birth of x-ray spectroscopy came with the discovery that Bragg scattering could be used to select x-rays of a particular wavelength. Using this technique, Moseley found that the discrete lines superimposed on the continuous spectrum varied systematically with the anode material's atomic number, making possible the completion of the periodic table before all the elements had been chemically separated. X-ray spectroscopy made it possible to determine nondestructively the chemical composition of samples by looking at the x-ray fluorescent spectra when the atoms in the sample were excited by x-rays or in other way. Now one can determine the chemical composition of the sample with less than a few tens of nanometers resolution.

The attenuation of x-ray beam through the sample due to absorption follows an exponential decay with a characteristic linear attenuation length $1/\mu$, where $\mu$ is the absorption coefficient, related to absorption cross-section. The absorption cross-section has a distinct dependence on photon energy and varies with the atomic number of absorber. It is this variation, and consequently the contrast, between different elements that make x-rays useful for the tomography imaging.

Modern growth techniques allow materials to be designed and fabricated at the atomic or molecular level. Many technologically important materials are now produced in this way. One of the most interesting classes of materials is the multilayer. This is a system grown by depositing one material on top of another in a repetitive sequence. Materials, that are used to fabricate the multilayers, range from metallic or semi-conducting elements, through to complex molecules. But what is common to all of these systems is that there is a need to characterize the resulting structures. X-ray reflectivity turns out to be a powerful tool for this task since the penetration depth is very small and x-rays probe the surface area mainly. Consequently, the total x-ray reflection is used for many kinds of surface analysis methods, such as total reflection x-ray fluorescence analysis, grazing incidence diffraction, total reflection x-ray absorption spectroscopy and others.
The high source brightness of the so-called third generation of the synchrotron radiation facility stimulated a large amount of researches on the microbeam formation. Microbeam diffraction, microbeam fluorescence spectroscopy and others small beam using techniques became of great interesting. More recently planar waveguides, which are the simplest representatives of the multilayer class of materials, were used successfully for the microbeam formation followed by the microdiffraction measurements. It turns out, that the theory, which was developed for the total x-ray reflection in the stratified media, can be used not only for the multilayers characterization, but for developing planar waveguides with desirable properties too.

This thesis starts from the x-ray fluorescence and absorption spectra interpretation, which allows the exploration of the electronic structure of crystalline (Part I). Such a way of the x-ray spectroscopy data treatment can be rightfully considered as a traditional one. Two examples are considered. One is a determination of the energy position of impurity Fe 3d-states and a determination of the Fe$^{3+}$ ions percentage in Hg$_{1-x}$Fe$_x$Se diluted magnetic semiconductor, which is traditionally considered as a Fe mixed valence system (Chapter 2). Chapter 3 describes how the resonant inelastic x-ray scattering spectra can be used for the calculated band structure verification.

These techniques can be applied to the stratified media too. One of the characterization methods is based on the characteristic x-ray fluorescence dependence on the incident beam glancing angle, which allows to extract the information about the composition, and density of each of the layers and about the ordering of the layers. Such measurements require the complicated experimental setup and are not suitable for the small laboratories. Consequently, the more simple techniques, based on the reflected beam intensity measurement, become of great interest. These techniques can be divided into two groups. One group is based on the angular distribution of the reflected beam intensity measurement, another one is based on the reflected beam intensity dependence on the incident photon energy.

There are several ways to perform the experimental data treatment. One of them is based on the experimental data fitting with the calculated one. Such an approach requires the x-ray reflectivity
coefficient to be calculated many times. In the Part II the database is described, which was developed for x-ray reflectivity coefficient calculation (Chapter 4). This database was used for the estimation of the real layer thickness in the layered structures using the experimental data. In addition it helped to verify the usefulness of the used experimental scheme (Chapter 5).

The theory of the total x-ray reflection in stratified media can be used not only for multilayer characterization. It can be used in developing of the novel layered materials with prescribed properties. Part III shows, how it can be used for the planar x-ray waveguide parameters revision. The purpose was to find such the parameters of waveguide which provide the strongest electric field enhancement in the core layer (Chapter 6). Numerical procedure was based on the novel optimization technique, the so-called genetic algorithms. These algorithms are the artificial realisation of the natural system evolution. A population of the artificial creatures (string encoded trial solutions) evolves in computer in accordance with the rule of the survival of fittest.

Examples, which are considered in this thesis, are only the small part in the ocean of the experimental x-ray techniques. Nevertheless, they show clearly that x-rays are still the powerful tool for the materials exploration. And these techniques can be used not only for the characterization, but for design too.
Part I. X-RAY EMISSION AND ABSORPTION IN MATERIALS CHARACTERISATION
Chapter 2. Local electronic structure and valence state of Fe impurity atoms in HgSe semiconductor

Soft x-ray fluorescence measurements were used to determine the energy position of impurity Fe 3d-states in Hg$_{1-x}$Fe$_x$Se diluted magnetic semiconductor. It is found that for iron concentration ranging from $5 \times 10^{19}$ to $1 \times 10^{21}$ cm$^{-3}$ ($x=0.05$) Fe$^{3+}$ states are concentrated mainly at $\sim 3$ eV below the top of the valence band and are mixed with Hg 5d-states.

2.1 Introduction

HgSe-based diluted magnetic semiconductors (DMS) belong to the large family of II-VI semiconductors in which some of the cations are replaced by 3d magnetic ions. The substitution of the cation leads to the crystalline, chemical and magnetic disorder and these mixed ternary alloys have attracted a considerable attention due to a wide range of novel magneto-optical properties such as giant Faraday rotation, large negative magneto-resistance or large g factor [1-3]. In comparison to the substitutional Mn$^{2+}$ which possesses only spin momenta ($S=5/2$, $L=0$) the Fe$^{2+}$ is a more general case, since it possesses both spin and orbital momenta ($S=2$, $L=2$) [4-5]. Hg$_{1-x}$Fe$_x$Se is usually considered as a mixed valence system of Fe$^{2+}$ and Fe$^{3+}$ where the overall magnetization is caused simultaneously by the Brillouin paramagnetism of Fe$^{3+}$, the Van Vleck paramagnetism of Fe$^{2+}$ and the diamagnetic de Haas-van Alphen effect of free electrons [6]. Based on the measurements it is concluded that Fe$^{2+}$ (3d$^6$) level is a resonant donor state in zero-gap semiconductor HgSe located in the conduction band. It is expected that for low iron concentration all these states are ionized and present in Fe$^{3+}$ (3d$^5$) state. While the iron concentration is increasing, the amount of Fe$^{3+}$ ions is increasing until its critical value will be reached. After that, the further increasing of the iron concentration leads to the increase of the amount of Fe$^{2+}$ ions. It is believed that when the concentration of Fe atoms is
more than a critical value $n_c=4.5\times10^{18} \text{ cm}^{-3}$, only a very small quantity of Fe$^{3+}$ exists in the system [7].

The calculation of electronic structure of Hg$_{1-x}$Fe$_x$Se made by the CPA (coherent potential approximation) method has shown that Fe 3d-states spread over the valence band in region of 0 - 5 eV [8]. These results were confirmed by indirect way using the measurements of ultraviolet photoemission spectra (UPS) at antiresonance (E=54 eV) and resonance (E=57 eV) regime, i.e. under resonant Fe 3p $\rightarrow$ 3d excitation [8]. The difference spectrum (ΔEDC) attributed to Fe 3d-contribution has shown the wide maximum around 3 eV with a weak shoulder at 0.5 eV. In this chapter a direct study of Fe 3d-partial density of states distribution in Hg$_{1-x}$Fe$_x$Se system is performed with help of x-ray fluorescence measurements.

2.2 Experimental

Using tunable synchrotron radiation from Beamline 8.0.1 of the Advanced Light Source at Lawrence Berkeley National Laboratory, the non-resonant Fe L$_{2,3}$ (3d4s $\rightarrow$ 2p transition) x-ray emission spectra (XES) was measured. The excitation energy for Fe L$_{2,3}$ emission was 733 eV, which is well above the iron L-edge. The Fe L$_{2,3}$ XES measurements were recorded with an energy resolution of about 0.7 eV using an excitation bandwidth of 0.4 eV. The spectra were calibrated using reference samples of Fe metal. All XES spectra presented in this paper were measured at a room temperature. The XPS measurements were carried out with a PHI 5600 ci multitechnique spectrometer using monocromatized Al Kα radiation ($E_{xre} = 1486.6$ eV). The estimated energy resolution consists of 0.35 eV and the base pressure in the vacuum chamber during measurements was about $5 \times 10^{-9}$ Torr. The crystals used in the present study were bulk alloys grown by modified Bridgman method. The samples of Hg$_{1-x}$Fe$_x$Se with Fe-content from $1\times10^{19} \text{ cm}^{-3}$ (x=0.0005) to $1\times10^{21} \text{ cm}^{-3}$ (x=0.05) were uniform in composition. X-ray diffraction measurements did not show any segregation of Fe-ions.
2.3 Results and discussion

Fe L_{2,3} XES of Hg_{1-x}Fe_xSe for different concentrations of Fe are presented in Figure 1. These spectra are strongly overlapped with the second order of Se L_3 and Se L_2 XES located at 685.5 and 709.6 eV, respectively [9]. Se L_{2,3} XES probe occupied 3d-states which are filled and not affected by the chemical bonding. Therefore one can suppose that Se L_{2,3} XES contribution should be the same for all spectra given in Figure 1. Since the Fe contribution in spectrum of the specimen with lowest Fe concentration (1 \cdot 10^{19} \text{ cm}^{-3}) is negligible we can estimate the contribution of Se for this spectrum and extract it from the other spectra. Using such procedure the contributions of Fe L_{2,3} XES for Fe content of 5 \cdot 10^{19} and 1 \cdot 10^{21} \text{ cm}^{-3} were determined (see Figure 1).

Due to the dipole selection rules and the element specific excitation the Fe L_{2,3} emission spectra probe the local Fe 3d density of states (DOS). Therefore Fe L_{2,3} XES can be directly compared with UPS of the host material (HgSe) and location of Fe 3d-impurity states with respect to the top of the valence band can be determined. Figure 2 shows the results of such comparison. From the XPS data for Hg_{1-x}Fe_xSe a binding energy of the Fe 2p_{3/2} level was found approximately at 710 eV and using this value Fe L_3 XES was converted to the binding energy scale. It is found that impurity Fe 3d-states are mainly concentrated at \sim 3 eV below the top of the valence band (maximum A) and very close to the difference photoemission spectrum (ΔEDC) measured for Hg_{0.88}Fe_{0.12}Se in Ref. [8].

Angle-resolved photoemission experiments of Hg_{1-x}Fe_xSe showed also the contribution of Fe-derived states in the binding energy region from the top of the valence band by 6 eV below with the maximum at \sim 3 eV [10]. The low intensity subbands (B and C) of the Fe L_3 XES located at 7.6 and 9.6 eV are found to be very close in energy to the main peaks of the UPS of HgSe which can be attributed to Fe 3d-Hg 5d hybridization.
Figure 1. Iron and selenium L\textsubscript{2,3} XES of Hg\textsubscript{1-x}Fe\textsubscript{x}Se. Dashed line is a sum of Fe L and Se L\textsubscript{3} emission contributions shown by solid and dotted line, respectively.
Figure 2 Comparison of Fe L₃ XES of Hg₀.₉₅Fe₀.₀₅Se with difference of resonance and non-resonance UPS of Hg₀.₈₈Fe₀.₁₂Se and UPS of host HgSe.
Fe L\textsubscript{2,3} XES can be used for estimation of oxidation state of Fe-ions in HgSe. As seen from the Table 1, \(I(\text{L}_2)/I(\text{L}_3)\) is rather small for pure metal (0.15) and deviates from the value 0.5 expected from the \(j=3/2\) and \(j=1/2\) occupancy ratio due to the Coster-Kronig (C-K) process \(L_2L_3M_{4,5}\) [11]. It is known that \(I(\text{L}_2)/I(\text{L}_3)\) intensity ratio is increasing on going from pure 3d-metals to their oxides because the nonradiative \(L_2L_3M_{4,5}\) C-K transition probability is expected to be lower for oxides [12]. Fe L\textsubscript{2,3} XES measured for Fe-concentration of \(5\cdot10^{19}\) and \(1\cdot10^{21}\) cm\textsuperscript{-3} only can be used for the estimation of oxidation state of Fe impurity atoms in Hg\textsubscript{1-x}Fe\textsubscript{x}Se because spectrum measured for Fe:1\cdot10^{19} cm\textsuperscript{-3} has a very low intensity (Figure 1). The comparison of Fe L\textsubscript{2,3} XES of HgFe:Se (5\cdot10^{19} and 1\cdot10^{21} cm\textsuperscript{-3}) with spectra of reference samples of FeO (Fe\textsuperscript{2+}) and Fe\textsubscript{2}O\textsubscript{3} (Fe\textsuperscript{3+}) shows (Figure 3) that the intensity ratio \(I(L_2/L_3)\) of Fe-impurity atoms in HgSe (0.33-0.34) is close to that of Fe\textsubscript{2}O\textsubscript{3} (0.31) and quite different with respect to that of FeO (0.45) (see Table 1). This means that Fe-ions in HgSe are mainly trivalent for both concentrations: 5\cdot10^{19} cm\textsuperscript{-3} and 1\cdot10^{21} cm\textsuperscript{-3}.

As it was mentioned, the \(I(L_2)/I(L_3)\) intensity ratio is affected by C-K process, which effect is not cleared still. From another hand, x-ray emission probes the near surface area of the sample. Consequently, it is strongly affected by the condition of the sample surface, its cleanness and degree of oxidation. To check the speculations above, the X-ray absorption spectra (XAS) were analyzed.

### Table 1. \(I(L_2)/I(L_3)\) intensity ratio for Fe-impurity atoms in HgSe:Fe and reference samples.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Fe</th>
<th>FeO</th>
<th>Fe\textsubscript{2}O\textsubscript{3}</th>
<th>HgSe:Fe (5\cdot10^{19} cm\textsuperscript{-3})</th>
<th>HgSe:Fe (1\cdot10^{21} cm\textsuperscript{-3})</th>
</tr>
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<tbody>
<tr>
<td>(I(L_2)/I(L_3))</td>
<td>0.15</td>
<td>0.45</td>
<td>0.31</td>
<td>0.34</td>
<td>0.33</td>
</tr>
</tbody>
</table>
Figure 3. Fe L$_{2,3}$ XES spectra comparison for pure metal, oxides and HgSe:Fe.
Fe 2p XAS of Hg$_{1-x}$Fe$_x$Se for several concentrations of Fe are presented in Figure 4. These spectra are normalized with respect to the same intensity of peak $a$. For comparison the XAS data for Fe$_2$O$_3$, where iron is Fe$^{3+}$, and for ZnSe:Fe 3.8·10$^{20}$, where iron is Fe$^{2+}$, are presented in the same figure. As one can see, Fe$^{3+}$ states are characterized by strong peak $b$ and relatively weak peak $a$. In contrast, Fe$^{2+}$ states are characterized by strong peak $a$ while peak $b$ is relatively weak.

Since HgSe:Fe is considered as mixed valence system, where Fe$^{2+}$ and Fe$^{3+}$ both coexist, we can estimate the contribution of each kind of ions into the spectra. For that purpose, we decompose each of the spectra into the sum of Fe$^{2+}$ and Fe$^{3+}$ contributions, using reference spectra. The results of the treatment are presented in Figure 5 and Figure 6. As one can see, the concentration of the Fe$^{3+}$ ions really decreases with the increasing of Fe concentration in the system. This conclusion is in a good agreement with the theory. Another conclusion, which can be done, based on the Figure 6, contradicts to the theoretical model. Namely, when the iron concentration in the sample is higher than the critical value (4.5x10$^{18}$ cm$^{-3}$), the sample should contain Fe$^{2+}$ ions and a very small amount of Fe$^{3+}$ ions. Nevertheless, the experimental data treatment shows that for Fe concentration 5x10$^{19}$ cm$^{-3}$, which is 10 times higher than the critical one, the Fe$^{3+}$ ions amount is more than 25 percents. For the Fe concentration 5x10$^{18}$ cm$^{-3}$, which is close to the critical one, the Fe$^{3+}$ percentage is more than 50 percents (see the insert in Fig.6).

### 2.4 Conclusions

In conclusion, the Fe 3d contribution to the valence band of the Hg$_{1-x}$Fe$_x$Se has been analyzed by means of soft x-ray fluorescence measurements. We can conclude that Fe 3d-states are located in the binding energy region between 1 and 6 eV below the Fermi level with the maximum at 3 eV. It is found that Fe 3d-states located at the bottom of the valence band are mixed with Hg 5d-states. Based on the experimental data we can conclude, that while the Fe concentration in HgSe:Fe is increasing, the amount of the Fe$^{3+}$ ions is decreasing as the theory predicts. From another hand, for the Fe concentration 5x10$^{19}$ cm$^{-3}$, which is 10 times higher than the critical value, the Fe$^{3+}$ ion percentage is more than 25 percent. It is too big to call it “a very small amount”.
Figure 4. Fe 2p XAS for HgSe:Fe samples, ZnSe:Fe $3.8 \times 10^{20}$ (Fe$^{2+}$) and Fe$_2$O$_3$ (Fe$^{3+}$).
Figure 5. The estimation of Fe$^{2+}$ and Fe$^{3+}$ contributions into absorption spectra. Circles are the experimental data, solid line is a fitted curve.
Figure 6. Fe$^{3+}$ ions percentage depending on the Fe atoms concentration in HgSe:Fe. Solid squares correspond to the experimental data; dot line is an approximating curve. The insert shows the same data for the range of small concentrations of impurity.
References in Chapter 2

Chapter 3. Resonant inelastic soft x-ray scattering and electronic structure of LiBC

The electronic structure of LiBC has been studied using soft x-ray fluorescence measurements. Resonance inelastic x-ray scattering (RIXS) spectra were measured with the excitation energy tuned to the boron and carbon K-edges. RIXS spectra show dispersive features, which were assigned to the calculated energy bands using the site-selective quantitative band mapping method based on the concept of k-momentum conservation. It is concluded that though electronic structure calculations are in general agreement with experimental spectra, carbon and boron K-emission bands show different structure which can not allow the usage of the rigid band model for prediction of superconductivity in off-stoichiometric LiBC.

3.1 Introduction

The discovery of superconductivity ($T_c=39$ K) in MgB$_2$ [1] has stimulated a strong interest in related layered compounds. The crystal structure of MgB$_2$ is similar to intercalated graphite [2], with carbon atoms replaced with boron. LiBC has a comparable crystal structure to MgB$_2$, with boron and carbon atoms alternately occupying the sites within the hexagonal sheets. By replacing Mg$^{2+}$ with Li$^+$ the charge remains neutral in this material. The unit cell along the hexagonal axis doubles because of the interchange of boron and carbon positions in neighboring planes [3]. Stoichiometric LiBC is a large gap semiconductor [3]. Due to the role of hole-doping in MgB$_2$ [4], the focus has recently shifted to the possibility of achieving such doping for LiBC. Band structure calculations of supercells of Li$_x$BC (doubled within the layers) for $x=1.0$; 0.75; 0.5 [6] show that the Fermi level moves into the valence band with decreasing $x$ and the behavior in the region of the gap and Fermi level is not far from rigid band. These rather idealized model calculations for ordered non-stoichiometric compounds predict that introducing off-stoichiometric Li could give rise to a finite density of states at the Fermi level and make the system metallic [5-8]. As a result, the Li deficient compound has been suggested to be superconducting with $T_c$ as high as 100 K [6] or 65 K [7] (for a Li stoichiometry of 0.5).
Following these theoretical predictions, several attempts to synthesize Li deficient Li_{x}BC were undertaken to look for superconductivity in this system [9-10]. So far, no diamagnetic signal or zero resistance, corresponding to a superconducting transition, has been observed in Li deficient LiBC at low temperatures.

To understand why predictions of high-\( T_{c} \) superconductivity, based on band structure calculations, are failed the calculated energy bands of LiBC must be checked by comparison with experimental spectra. The electronic structure calculations of Li-deficient LiBC are compared with those of stoichiometric compound. Therefore at first we need to check the validity of band structure calculations of stoichiometric LiBC. For analysis of changes in the electronic structure in non-stoichiometric compound the rigid band model is used. Therefore the next open question is a correctness of this model for simulation of off-stoichiometry in LiBC. The answers on these questions can be obtained through the experimental RIXS study of LiBC. The obtained results are compared with linear muffin-tin orbitals (LMTO) band structure calculations.

3.2 Experimental and Calculation Details

In the synthesis of LiBC, crushed Li metal chunks (99.9%), amorphous boron powder (99.9%), and graphite (99.9%) were mixed in inside a He glovebox. The mixture was sealed in Ta cells and inductively heated in a BN crucible surrounded by a graphite susceptor to 940 - 1020 °C for 10 - 14 hours. The resulting LiBC powder was pressed into pellets at 3000 atm and annealed. The samples were structurally characterized using high-resolution powder x-ray diffractometry with Cu K\( \alpha \)-radiation.

Measurements of stoichiometric LiBC were performed at the soft x-ray fluorescence endstation located at Beamline 8.0 of the Advanced Light Source at the Lawrence Berkeley National Laboratory. The emitted radiation is partially collected in a Rowland circle type spectrometer with spherical gratings and recorded by an area sensitive multi-channel detector. This
combination provides an instrumental resolution of about 0.4 eV at the C and B Kα emission energies. The x-ray absorption spectra were measured in partial fluorescence and total electron yield (PFY and TEY) mode. The resolving power E/ΔE for the absorption spectra was 5000. Additional spectral broadening occurs due to the core hole lifetime. For boron and carbon K-edge spectra, the core level width is approximately 0.2 to 0.3 eV. All absorption and emission spectra are normalized to the number of photons falling on the sample, monitored by a gold mesh in front of the sample.

The available band structure calculations for LiBC [5, 6] are limited because they consist of only the total density of states and the E(k)-curves are calculated for an energy range insufficient for understanding the RIXS spectra. This was the motivation for our calculation of total and partial DOS and E(k) dispersion curves for LiBC for the extended energy region of −15 to +20 eV. We calculated the electronic structure of LiBC using a self-consistent linearized muffin-tin orbital (LMTO) method (TBLMTO-47 computer code [11]). The von Barth - Hedin parametrization is used for the exchange correlation potential within the local density approximation. Brillouin zone (BZ) k-point integrations were made using the tetrahedron method on a grid of 549 k-points in the irreducible part of the BZ. The crystal structure of LiBC was modeled by the space group P63/mmc, D46h, No. 194, and the lattice parameters were a = 2.752 Å, c = 7.058 Å = 2 × 3.529 Å with coordinates of the atoms Li (2a) (0 0 0), B (2c) (1/3 2/3 1/4) and C (2d) (1/3 2/3 3/4) [3].

The B and C atoms form a planar heterographite layer with a B-C distance of 1.589 Å and the Li atoms fill the interlayer regions. The unit cell along the hexagonal axis is doubled due to the interchange of boron and carbon positions in neighbouring planes [3].

### 3.3 Results and Discussion

The measurements of non-resonant (excited far from threshold) carbon and boron Kα x-ray emission spectra (XES) and C 1s and B 1s x-ray absorption spectra (XAS) of LiBC are presented in Figure 1(a) and (b), respectively. Taking into account the dipole selection rules, these element
specific spectra probe the local occupied and unoccupied states of p-symmetry. When displayed together on the same energy scale, the XAS and XES spectra provide an experimental probe of the partial DOS. Figure 1(c) displays the calculated total density of states of LiBC. We adjust the energy axis of the DOS calculations to correspond to the experimental data for comparison.

By aligning the \(a\)-features, located at the high-emission energy of the carbon and boron K-emission bands in Figures 1(a) and (b), with the \(A\)-feature in the total DOS displayed in Figure 1(c), it is concluded that the XES data does correspond to the valence band in the calculated total DOS. Considering that the C 2p and B 2p occupied states are strongly mixed at the top of the valence band, feature \(A\) is a direct result of the boron and carbon occupied states.

The results of our band structure calculation of stoichiometric LiBC are in agreement with previous calculations \([5,6]\). According to our calculations (Figure 2), carbon and boron 2p-states give the main contribution to the density of states at the Fermi level whereas Li provides very little contribution to the total DOS at this energy. The calculated DOS predicts insulating behavior with a band gap of about 2 eV which seems to be lower because LDA calculations underestimate band gap values. It is rather difficult to estimate band gap from the experimental spectra because of smearing effects due to the core hole life time and instrumental distortion but we can note that the main absorption features \(a'\) and \(b'\) of the B 1s TFY and C 1s TEY are close to the main features \(A'\) and \(B'\) in the calculated total DOS.

The comparison of the carbon and boron spectra (Figure 1) shows that the most intense emission features a, b and c of C K\(\alpha\) XES can be related to the results of band structure calculations by the main subbands A, B and C in the total DOS whereas b feature is not seen in B K\(\alpha\) XES. The \(a\) and \(c\) emission features in both spectra are formed as a result of strong hybridization of the C 2p and B 2p-states (Figure 2). The Li DOS does not effectively contribute to these features. On the other hand, calculations show almost identical distribution of C 2p and B 2p-states. Therefore, experimental spectra show that the distribution of C 2p and B 2p-states has an individual character and therefore a hole doping in LiBC system can not be simulated by rigid band approach.
Figure 1. Comparison of (a) boron, (b) carbon K-emission and absorption spectra (c) with calculated total density of states of LiBC.
Spectral feature $d$ located in the carbon K-emission band is close to the energy of the calculated subband $D$, which has mainly B 2s character (see Figure 2). Feature $e$ located in the boron XES spectrum is close to the calculated $E$ subband, which has mainly C 2s character (see Figure 2). The revealing of C 2s-states in B Kα XES and B 2s-states in C Kα XES is due to the C 2s-B 2p and B 2s-C 2p hybridization (Figure 2).

The C 2s and B 2s are not seen in C Kα XES and B Kα XES, respectively, because the 2s→1s transition is not allowed by the dipole selection rules. The $\sigma$ bands with C 2s-character are concentrated more heavily at the bottom of the bands because the on-site orbital s-energies are lower for carbon than for boron. This means that carbon is chemically different from boron in LiBC, which suggests that rigid band can not be simply applied to this system for simulation of hole-doping.

Resonant boron and carbon Kα XES of LiBC are displayed in Figure 3, where the excitation energies are given in the left corner of each spectrum. The spectra are strongly dispersive. The interpretation of RIXS spectra is based on the concept that x-ray absorption and emission events should be treated as a single inelastic scattering process with well defined crystal momentum conservation for the photoelectrons and the valence band hole [12]. It is supposed that when a core electron is promoted to the conduction band with a certain crystal momentum, which depends on the incident photon energy, an emission from the valence band at the same point in the Brillouin zone will be induced. Therefore, quantitative band mapping can be realized with help of RIXS data [13].

To perform the band mapping for LiBC the experimental data shown in Figure 3 and the procedure described in [14] were used. As one can see from Figure 1, the top of the valence band in band structure calculations is related to the x-ray photon energy scale (to boron emission energy of 186.1 eV and carbon emission energy of 283.0 eV) by alignment of peaks in calculated density of states with spectral features in XES curves.
Figure 2. Calculated total and partial DOS of LiBC.
Fig. 3: Resonant boron (a) and carbon (b) K-emission bands of LiBC.
The features of the boron and carbon K-emission bands selected for band mapping were determined with the assistance of the first and second derivatives calculation for the curves (Figure 5) and are shown in Figure 3 by the intersections with the dashed lines. Then the dotted horizontal lines (see Figure 4(a-b) and Figure 6), corresponding to the RIXS selected excitation energies at B K and C K-edges, are built up crossing the dispersion curves for unoccupied states. The intersection points determine the possible k-values that will induce the 1s → 2p transition. Using k-momentum conservation, the vertical lines from the intersection points are drawn down through the dispersion curves for the occupied states. Then the energy of selected spectral features is determined on XES curves and new horizontal lines are drawn through calculated dispersion curves for occupied states (Figures 6). Finally the intersection points of horizontal and vertical lines allows the experimental points with respect to the calculated occupied energy bands to be determined. If band structure calculation is correct, each experimental point will be situated near the calculated dispersion curve for at least one possible k-value. RIXS is especially efficient to use in insulators and polycrystalline materials (such as LiBC) that are difficult or impossible to study by angle-resolved ultraviolet photoemission (ARPES). A disadvantage of RIXS is the fact that k-selectivity is given rather indirectly, and depends on the dispersion of the unoccupied bands. Only at special points, such as band edges and high symmetry points, k can be determined unambiguously using inelastic scattering experiment.

By using this procedure the quantitative band mapping for boron and carbon sites of LiBC is realized in Figures 4 (a) and (b). The experimental points are generally found to be very close to the calculated energy bands in the region of occupied electronic states demonstrating a reasonable agreement between theory and experiment.
Fig. 4: Band mapping of LiBC using RIXS measured at carbon (a) and boron (b) K-edges; curves show the calculated band structures and symbols represent the experimental results for various excitation energies. Zero on the calculated energy scales correspond to carbon emission energy of 283.0 eV and boron emission energy of 186.1 eV.
Figure 5. Spectral features allocation for a) B Kα XES using b) first and c) second derivatives. Circles are the experimental data, solid line is a smoothed by FFT filter curve.
Figure 6. Example of the LiBC band mapping performing using B K\textsubscript{a} XES (excitation energy $E_{\text{exc}}=191.5$ eV).
3.4 Conclusion

To summarize, the comparison of experimental RIXS data with our density functional theory calculations shows that in spite of a general agreement between experimental and calculated energy bands of stoichiometric LiBC, carbon and boron electronic states do not completely hybridize, and retain some of their individual character. With this in mind, the lack of superconductivity in off-stoichiometric LiBC could be due to several different reasons:

(1) the lack of complete hybridization of the B and C states which is inconsistent with the calculations;

(2) preparational factors such as a B-C disorder [8] or a strong structural relaxation in the vicinity of the hole dopants [9] are known to be crucial for superconductivity and are not currently taken into account in the LDA model calculations of hole doped LiBC.
References in Chapter 3

Part II. TOTAL X-RAY REFLECTION IN LAYERED STRUCTURES
Chapter 4. MS-Access database “Multilayer Reflectivity”

This chapter contains a description of the database, which was developed for the multilayer reflectivity coefficient calculation. This database has been developed to simplify the process of the reflectivity coefficient calculation, since it requires the tabulated data. The goal was to make a simple and easy modifying program with user-friendly interface without any excessive functions. The database was used to verify the applicability of the novel experimental technique of the stratified media characterization.

4.1 Introduction

X-ray reflection from the layered structures is of particular importance in recent years. Modern growth techniques allow materials to be designed and fabricated at the atomic or molecular level. Many technologically important materials are now produced in this way. One of the most interesting and important class of materials is the multilayer or superlattice. This is a system grown by depositing one material on top of another in a repetitive sequence.

Materials, that are used to fabricate the multilayers, range from metallic or semi-conducting elements, through to complex molecules. In most cases a specific growth technique is used to produce the multilayer of interest. But what is common to all of these systems is that there is a need to characterize the resulting structures. X-ray reflectivity turns out to be a powerful tool for this task since it allows to get the information on the thickness, density, interface roughness, layers ordering and other properties.

There are several ways to perform the experimental data treatment. One of them is based on the experimental data fitting with the calculated one, for which the parameters are chosen according to the certain procedure (genetic algorithm based procedure, for example [1]). To simplify the calculation, the computational program was developed. Of course, there are several commercial
software products available for X-ray reflection analysis. This software covers a wide variety of
the problems, to satisfy as much users as possible. But the common for all the commercial
programs is that its source code is unavailable. Experimental techniques for surface and interface
analysis using X-rays are developed rapidly, but it is impossible to adjust the software until the
upgraded version will be issued. Another reason is that the same algorithm can be realized in the
several ways. Moreover, some simplifications or assumptions can be done (linear or spline
approximation, neglecting of the high-order terms, for example) and their presence and character
can not be clarified unless the source code is known. Consequently, it was decided to make an
own program for x-ray reflectivity calculation which could be easy modified depending on the
problem under consideration.

Since the data under operation are tabulated the program has been developed in the form of MS-
Access® database. MS-Access is contained in the Professional version of the Microsoft Office®.
The Visual Basic for Applications (VBA) built in the all products of MS-Office series is simple
for understanding and allows to construct the user-friendly interface.

Database contains:

- Atomic scattering factor data [2];
- Complex refractive index calculation utility;
- Multilayer X-ray reflection coefficient calculation utility;
- Material properties data.

Atomic scattering factor data are taken from the DABAX project’s homepage [3]. Data covers
the elements with atomic numbers from 1 to 92. There are more than 400 points in logarithmic
mesh from 30 to 30000 eV for each element.

For X-ray reflection coefficient calculation the atomic scattering factors data and materials data
(density and chemical composition) are used. It is possible to vary glancing angle at fixed energy
or energy value (or wavelength) at fixed glancing angle. Multilayers are restricted to be flat and
periodic with the ideal interfaces. Substrate is assumed to be infinite. Energy values are from 30
to 30000 eV. Results are presented in graphical form but it is possible to export it into MS-Excel® file.

4.2 Theory

The detailed description of the x-ray reflection at interface can be found in Appendix A. Here it will be presented briefly.

The X-ray reflection coefficient for multilayer may be obtained using Maxwell’s equations, namely the continuity requirement for the electric and magnetic fields components at each interface. Consider the plane wave of the form

\[ E(r, t) = E_0 e^{i(\omega t - k r)}, \]  

(1)

propagating with initial amplitude \( E_0 \). The effects of X-rays on material are characterized by complex refractive index \( n \). Usually, it is written in the form

\[ n = 1 - \delta - i\beta, \]  

(2)

where \( \delta \) and \( \beta \) are the optical constants related to the atomic scattering factor and electron density of the material. For X-rays with wavelength \( \lambda \) the optical constants can be expressed as [4]

\[ \delta = \frac{n^2}{4\pi} \sum_j N_j f_{1j}, \quad \beta = \frac{n^2}{4\pi} \sum_j N_j f_{2j}. \]  

(3)
Here \( r_0 = \frac{e^2}{4\pi \varepsilon_0 mc^2} = 2.81794 \times 10^{-13} \) cm is the classical electron radius, \( N_j \) - the number of the \( j \)-th element atoms per unit volume, \( f_{1j} \) and \( f_{2j} \) - the real and imaginary parts of the atomic scattering factor.

Denote the air (or vacuum) as the first layer and substrate as \( N \)-th layer. The thickness of the \( j \)-th layer will be \( d_j, j=2,3,\ldots,(N-1) \) (the thickness of the first layer is of no concern, the thickness of the substrate is assumed to be infinite). Incident radiation usually is decomposed into two geometries to simplify the analysis, one with incident electric field \( E \) parallel to the plane of incidence (p-polarization) and one with \( E \) perpendicular to that plane (s-polarization). Arbitrary incident wave can be represented in terms of these two polarizations so from here only s-polarized and p-polarized waves will be considered.

Continuity equations for interface between \((j-1)\)-th and \( j \)-th layers may be written in the form

\[
a_{j-1}E_{j-1} + a^{-1}_{j-1}E^R_{j-1} = a^{-1}_j E_j + a_j E^R_j
\]

\[
(a_{j-1}E_{j-1} - a^{-1}_{j-1}E^R_{j-1})n_{j-1} \cos \phi_{j-1} = (a^{-1}_j E_j + a_j E^R_j)n_j \cos \phi_j
\]

in case of s-polarization, and

\[
(a_{j-1}E_{j-1} + a^{-1}_{j-1}E^R_{j-1})\cos \phi_{j-1} = (a^{-1}_j E_j + a_j E^R_j)\cos \phi_j
\]

\[
(a_{j-1}E_{j-1} - a^{-1}_{j-1}E^R_{j-1})n_{j-1} = (a^{-1}_j E_j + a_j E^R_j)n_j
\]

in case of p-polarization, where

\[
a_j = \exp\left[-\frac{i\pi d_j}{\lambda} n_j \cos \phi_j\right].
\]

In these equations \( E_j \) is the vector amplitude of the electric field referred to the middle of the \( j \)-th layer and \( a_j \) is the amplitude factor for half depth of the \( j \)-th layer, \( n_j \) is the complex refractive
index \((j=2,3,...,N)\). \(E_1\) is referred to the interface between air and multilayer, similarly \(E_N\) is referred to the interface between multilayer and substrate, so \(a_1=1\) and \(a_N=1\) (in fact, \(a_N\) will be of no concern). The superscript \(R\) is used for reflected wave. The angle \(\phi_j\) of the wave propagation in the \(j\)-th layer may be found from Snell’s law

\[
\sin \phi_j = \frac{\sin \phi_j}{n_j},
\]

Now the recurrent formula for X-ray reflection coefficient may be obtained. Following the procedure described by Parratt, convenient variables are introduced as follows

\[
R_{j,j+1} = a_j^2 \frac{\tilde{E}_j^R}{\tilde{E}_j}, \quad F_{j-1,j} = \frac{f_{j-1} - f_j}{f_{j-1} + f_j},
\]

where

\[
\tilde{E}_j = \begin{cases} E_j, & \text{for s-polarization} \\ E_j n_j, & \text{for p-polarization} \end{cases},
\]

\[
f_j = \begin{cases} n_j \cos \phi_j, & \text{for s-polarization} \\ \frac{\cos \phi_j}{n_j}, & \text{for p-polarization} \end{cases}, \quad j=1,2,...,N.
\]

In these notations the eqns. (4), (5) may be rewritten as

\[
R_{j-1,j} = a_{j-1}^2 \frac{F_{j-1,j}}{1 + F_{j-1,j} R_{j,j+1}}, \quad j=2,3,...,N.
\]

The substrate is assumed to be infinite so there is no reflected wave in this layer and \(R_{N,N+1}=0\). Starting to solve eqns.(10) from the \(N\)-th layer upward to the first layer one can find \(R_{1,2}\). Recalling that
\[ R_{1,2} = a_1^2 \frac{E_i^R}{E_i} = \frac{E_i^R}{E_i}, \]  

(11)

the ratio of reflected to incident intensity (X-ray reflection coefficient) may be obtained

\[ \frac{I_R}{I_0} = \left| \frac{E_i^R}{E_i} \right|^2 = |R_{1,2}|^2. \]  

(12)

4.3 System requirements

The database was developed using MS-Access® 97 program of the Microsoft Corp. Consequently, the hardware and software should match the system requirements for the MS-Access operating:

- Personal or multimedia computer with a 486 or higher processor;
- Microsoft Windows® 95 operating system or Microsoft Windows NT® Workstation 3.51 Service Pack 5 or later (will not run on earlier versions);
- For Use on Windows 95. 12 megabytes (MB) of RAM required to run Microsoft Access; more memory may be required to run additional applications simultaneously;
- For Use on Windows NT Workstation. 16 MB of memory required to run applications individually; more memory may be required to run additional applications simultaneously;
- Office Professional required 73–191 MB of Hard-Disk Space; approximately 121 MB required for typical installation, depending on configuration (use the Office Upgrade Wizard during setup to maximize free disk space);
- VGA- or higher-resolution video adapter (Super VGA, 256-color recommended);
- Microsoft Mouse, Microsoft IntelliMouse®, or compatible pointing device.
Approximately 6 MB of free space are required for database itself (in addition, approximately 1.5 MB of free space is required to save the archived file). Of course, MS-Access is to be installed. File is available for downloading in zipped form. More details about MS-Access®, MS-VBA®, WinZip® can be found on the sites of their developers [5,6].

The database has been tested successfully with the MS-Access® 2000. The system requirements for the database launching under the MS-Access 2000 are as follows:

- **PC with a Pentium 75-megahertz (MHz) or higher processor**
- **Microsoft Windows 95 or later operating system, or Microsoft Windows NT Workstation operating system version 4.0 Service Pack 3 or later**
- **For Windows 95 or Windows 98: 16 MB of RAM for the operating system, plus an additional 8 MB of RAM for Access**
- **For Windows NT Workstation: 32 MB of RAM for the operating system, plus an additional 8 MB of RAM for Access**
- **161 MB of available hard-disk space (Number indicates typical installation; the hard-disk usage will vary depending on configuration. Choices made during custom installation may require more or less hard-disk space.)**
- **CD-ROM drive**
- **VGA- or higher-resolution monitor; Super VGA recommended**
- **Microsoft Mouse, Microsoft IntelliMouse®, or compatible pointing device**

Unfortunately, for some unknown for now reasons the database does not work properly with the Japanese version of MS-Access® 2003. The detailed analysis of the possible reasons of it will be performed in the future. There is no any information about the possibility to use the database with the MS-Access® XP.
4.4 Installation

Database does not require any specific installation procedure. The unzipped file is ready for usage with the MS-Access program.

4.5 Running the database

To open the database one should double click on the file name in the explorer window or select File – Open in the MS-Access menu. The database menu will be activated (Figure 1).

![Figure 1. “Multilayer Reflectivity” Database main menu.](image)
4.5.1 Scattering factors database

To view the scattering factors data one should click the “Scattering Factors Database” button. The data preface window will be opened (Figure 2). Clicking the “Go to the database” button, one will activate the main scattering factors database window (Figure 3). To return to the previous menu the “Cancel” button should be clicked. The scattering factors database window is organized as a periodic table. To obtain the information about the element of interests, one should just click the corresponding cell in the periodic table. For example, to get the data for Iron, one should click the “Fe” cell in the periodic table, then the information window will be opened (Figure 4). This window shows the information about atomic number of the element, atomic weight, density in normal state and scattering factors $f_1, f_2$ values for several energies.

Figure 2. Scattering Factors Database preface window
Figure 3. Atomic Scattering Factors database window

Figure 4. Atomic Scattering Factor information window for Iron.
4.5.2 Materials database

It is possible to input, keep and modify the information about the materials under consideration for further usage in calculations. To do it one should enter the materials manage utility by clicking the “Materials Database” button (Figure 1) in the main window. After that the materials manage window will be open (Figure 5).

All the materials can be grouped based on some criteria. To navigate between the groups “First”, “Previous”, “Next”, “Last” buttons are to be used. To close the window the “Close” button may be used. Each material is characterized by its name, chemical expression and density. Any changes and modifications can be done directly in the corresponding fields. To create a new group the “New” button is to be pressed, and then the new group name materials can be entered into the corresponding fields (Figure 6).

Figure 5. Materials manage utility window.
4.5.3 Refractive index calculation

To calculate the refractive index of the media of interest one should press the “Refractive Index Calculation” button (Figure 1). It will activate the refractive index calculation utility window (Figure 7). This utility is based on the Equations (3). Chemical expression and density can be inputted directly into the corresponded fields (Figure 8) or can be selected from the materials database. To take the data from the database one should press the “Select from Database” button, then the “Select Material” window will be activated (Figure 9). To select a particular material data one should find it using navigation buttons and scroll bar and then just click in the field with material name or chemical expression. Selected material chemical expression and density will appear in the corresponded fields (Figure 10). By clicking the “Select” button one will be returned to the previous window with the selected material data substituted into the corresponded fields (Figure 8).

![Figure 6. New materials group input window.](image-url)
By clicking the “Cancel” button one will be returned without any selections. Entering the energy value and clicking the “Calculate” button one will start the procedure of the calculation. Calculated values will be substituted into the corresponded fields (Figure 11).

“Close” button should be clicked to return into the main menu.

Figure 7. Refractive index calculation utility window.
Figure 8. Refractive index calculation utility window with filled out fields.

Figure 9. “Select Material” window.
Figure 10. “Select Material” window with selected material data

Figure 11. Calculated values of the optical constants.
4.5.4 Multilayer reflectivity coefficient calculation

To calculate the multilayer reflectivity coefficient one should press the “Multilayer Reflectivity Calculation” button. After that, the reflectivity coefficient calculation utility window will be activated (Figure 12). User should enter amount of the layers, forming the periodic group, and amount of the periods. Then, selecting the corresponding layer in the “Choose the Layer” list one should enter the layer width in angstrom, chemical composition and density. Again, as in refractive index calculation utility, materials data can be selected from the materials database (see paragraph 4.4.3). Also the chemical composition and density should be entered for the substrate.

Next, the tracing parameter should be selected. It can be glancing angle at fixed incident photon energy, or incident photon energy or wavelength at fixed grazing angle. Angles should in the range from 0 to 90 degrees, incident photon energy – from 30 to 30000 eV (consequently, wavelength – from 0.41 to 410 Å). To start the calculation one should click the “Scan” button. The results of the calculations will be presented in graphical form in new window (Figure 13). To print the graphic one should press “Print” button. To export data into MS-Excel file one should press “Export to MS-Excel” button and enter the file name in the “Export to…” dialog window (Figure 14).
Figure 12. Input data window of the Multilayer reflectivity coefficient calculation utility.
Figure 13. Calculated reflectivity coefficient window.

Figure 14. “Export to…” dialog window.
4.6 Results verification

The results, obtained with the “Multilayer Reflectivity” Database were compared with the data, which can be obtained at the homepage of the Center for X-Ray Optics (CXRO) at the Lawrence Berkeley National Laboratory [7]. Figure 15 shows the results of the optical constants calculation for Mo, compared with the CXRO data. Figure 16 shows the results of the x-ray reflectivity coefficient calculations for 30 Mo-C bi-layers on Si substrate. Mo layer thickness is 3 nm, C layer thickness is 2 nm. As one can see, the results, obtained with the database agree satisfactorily with the CXRO data.

4.7 Conclusions

In conclusion, the “Multilayer Reflectivity” database was developed to calculate the x-ray reflectivity coefficient for the periodic layered structures. This database is based on the tabulated values of the complex atomic scattering factors data by Henke et al. [2] and on the iterative procedure similar to the Parratt’s one [8]. The results, obtained with this database, are in a satisfactory agreement with the CXRO data.
Figure 15. Optical constants for Mo, calculated using “Multilayer Reflectivity” database, and obtained at the CXRO homepage.
Figure 16. X-ray reflectivity coefficient for the 30 Mo-C bi-layers a) at the incident beam photon energy 8 keV, b) at the glancing angle 0.94 degrees.
References in the Chapter 4


5. www.microsoft.com

6. www.winzip.com


Chapter 5. “Multilayer Reflectivity” database application for the determination of the layers thickness’ real values

Several experiments were performed to investigate the x-rays propagation in the layered media. Energy distribution of white x-ray beam, reflected from the multilayer samples, was recorded using silicon drift detector (SDD), which allows to make the measurements directly without any attenuators. “Multilayer Reflectivity” database, described in the previous chapter, was used to get the information about the thickness of the layers in the samples and to verify the applicability of such experimental scheme for the multilayer characterization. It is shown that, when the parameters of the layers differ significantly, it is possible to estimate the layer thicknesses without the angular distribution measurements, which require more precise setup.

5.1 Experimental setup

The experimental technique was similar to the proposed by Dhez [1] and Horiuchi [2] one. The energy spectra of the reflected x-rays were measured for the several values of the glancing angles of the incident white x-ray beam. White x-ray radiation of high intensity allows the measurements using the simple instruments and optics so the measurements can be done using common laboratory equipment. The main difference from the mentioned author’s scheme was that the SDD detector has been used instead of the silicon solid state detector (SSD). In case of the total x-ray reflection the direction of the reflected beam is quite close to the direction of the incident beam. Consequently, the SSD detector can be easily broken by the intense direct beam. The SDD detector is not so sensitive to the direct beam and the beam intensity can be measured without any attenuators.

The experimental setup is shown in Figure 1. X-ray tube with Mo target was used to generate the white x-ray radiation, which were collimated less than 0.5 mm diameter. A detector was mounted on the goniometer. For all the measurements the relation between the glancing angle $\theta$ and the measurement angle $\varphi$ was always $\varphi=2\theta$. Glancing angle was varied from 0.1 degree to 1 degree
with 0.1 degree increment. The duration of the measurement for each of the samples and detector positions was 300 sec.

### 5.2 Samples

Two kinds of samples were prepared by H. Takenaka (NTT-AT). One was a 30 pairs of the alternated Mo and B₄C layers on Si substrate ((Mo/B₄C)₃₀/Si), another one was a 6 alternated Ni and Mn layers sputtered on Au film which covered Si substrate ((Ni/Mn)₆/Au/Si). The parameters of the samples are as follows:

※ Sample #1: Mo - 3.1 nm, B₄C - 3.8 nm;
※ Sample #2: Ni – 9.7 nm, Mn – 9.7 nm, Au – 100 nm.

![Experimental setup](image-url)
5.3 Experimental results

Figures 2 and 3 shows the experimental measurements and the results calculated using the “Multilayer Reflectivity” database for the first sample, respectively. As one can see, the qualitative character of both sets of data is almost the same. The interference peaks are well distinguished in the experimental as well as in calculated data. Nevertheless, there is a shift in the peak position. This difference can be explained as follows. Due to the inferiority of the sample preparation process the actual layers thickness is higher, than declared. To check it, the calculations have been done for the same structure, in which the layer thicknesses were magnified by fixed factor (see Figure 4). As one can see, most appropriate results are for the factor value 1.2. Thus, the actual layer thicknesses can be estimated as 3.72 nm for the Mo layers and 4.56 nm for B₄C.

More accurate determination of the waveguide parameters can be done using the genetic algorithm based optimization procedure, for example [3], or any other optimization technique. The program code of the database can be easy modified for that purpose.

Figure 5 and 6 show the experimental and calculated results for the second sample. As one can see, it is impossible to detect the interference peak position in the experimental data. Consequently, it is difficult to extract the meaningful information about the second structure, using this dataset only.

The explanation of such a qualitative difference in the experimental data can be given as follows. The densities of the materials, which the first sample consist of, are very different (density of Mo in four times higher, than density of B₄C), while for the second sample they has quite close values. In addition, manganese and nickel atomic numbers differ slightly. Consequently, the experimental technique used is not appropriate for the analysis of the samples, the layers of which has quite the same properties.
Figure 2. X-ray reflectivity coefficient of (Mo/B₄C)₃₀/Si sample. Experimental data.
Figure 3. X-ray reflectivity coefficient of (Mo/B₄C)₃₀/Si sample. Calculated data.
Figure 4. Experimental data fitting using the layers thickness adjustment
Figure 5. X-ray reflectivity coefficient of (Ni/Mn)$_3$/Au/Si sample. Experimental data
Figure 6. X-ray reflectivity coefficient of (Ni/Mn)$_3$/Au/Si sample. Calculated data.
5.4 Conclusions

The energy spectra of reflected white X-ray beam were measured for the (Mo/B4C)30/Si and (Ni/Mn)3/Au/Si multilayers. Comparison with the calculated data shows that the real thickness of Mo and B4C layers is higher probably in 1.2 times than declared.

Experimental data for (Ni/Mn)3/Au/Si multilayer shows, that a used scheme of measurements is not appropriate for such kind of structures, since there were no any interference peaks observed. Probably, it is due to the layers have quite close properties. Consequently, some other measurements should be done to extract the information about the structure.
References in the Chapter 5

Part III. MODELLING OF THE PLANAR X-RAY WAVEGUIDES FOR THE MICROBEAM FORMATION
Chapter 6. Planar x-ray waveguides in the microbeam formation and the way of their optimization

An optimization procedure has been developed to optimize parameters of the planar waveguide with beryllium core for the microbeam formation. This procedure is based on the genetic algorithm that is a novel optimization technique, modeling the process of the natural system perfection under the survival of fittest rule. It is shown that a revision of the waveguide parameters should result in the waveguide improvement, since it is possible to find the structures with the highest degree of electric field excitation in core layer.

6.1 Introduction

The problem of the x-ray effective focusing and transmission on the large distance is still of great importance. Even the well-used policapillary optics has relatively small efficiency (4-15 % for Cu Kα, for example [1]). One of the possible directions of the progress in this area is a development of the planar waveguides, which are the layered structures.

The first attempt to fabricate and study waveguides for the hard X-ray range was performed by Spiller and Segmuller [2] in 70-s of the last century. They used BN films of 300 – 500 Å thickness sandwiched between Al2O3 cladding layers. They could detect a beam propagated almost 0.3 mm. They also showed that the waveguide mode formation can be revealed by the deep in the x-ray reflection curve.

After this publication, planar waveguides became of the great interest [3-6]. An ejection of the heavy atoms, the so-called markers, into the layers allowed to verify that at certain conditions the electric field enhancement may occur in these layers, which is accompanied by the peak in the angular distribution of the characteristic x-ray emission from the markers [3]. It was shown the
degree of the electric field enhancement in the core layer is affected by the covering layer parameters [4]. Electric field enhancement in the guiding layer results in the attenuation of the standing wave field above the surface of the layered structure. Consequently, standing wave field above the layered structure is also modulated. It means that if some atoms are placed on the surface of the waveguide, then additional modulation of the characteristic fluorescence is expected from these atoms. This effect resulted in the new method of the surface analysis, when the waveguide structure is used as sample holder.

The success in the x-ray guiding phenomenon investigation could open wide perspectives of practical application of the waveguides. The capability to achieve any beam dimension independently of the source size and relative simplicity of their production make these structures very attractive for small beam application, x-ray lasers, hard x-ray monochromators and others. New methods of the surface and interface analysis were developed, a lot of experimental data were obtained, but the absorption in the material core was too significant to achieve any perspective. Some authors selected the alternative way – they start to investigate the waveguides with vacuum “core” [7, 8].

The recent development of the so-called third generation x-ray synchrotron radiation facilities stimulated many studies on microbeam formation and waveguides with material core became once again of interests. The waveguides with Be and C core were investigated in details [9-14]. Authors were able to detect the guided beam at the exit of the waveguide and showed that this beam has the high degree of coherence. The guided beam was used successfully for microdiffraction measurements.

Unfortunately, the authors of these publications give no answer on the question, why the particular thickness of each of layers was chosen. In such a case it is reasonable to check are the used waveguides optimal or not. Consequently, a numerical procedure was developed to optimize the waveguide parameters. This procedure is based on the genetic algorithm concept [15, 16].
More recently genetic algorithms were used successfully for the multilayer parameters determination [17]. The program was used to obtain layer thicknesses and layer roughnesses for several multilayer structures. On simulated data, the exact solution was found in 61% of the experiments. In the other 39% of the experiments the errors were small. In the measured data fitting the errors were small compare with the currently used methods, which has indicated a good performance of the procedure, based on the genetic algorithm.

In the present Chapter, genetic algorithm is used to find the waveguide parameters, which provide the strongest electric field enhancement in the core layer. This should correspond to the most intensive beam at the exit of waveguide. The waveguides with Be core were under consideration.

### 6.2 Brief review of the optimization techniques

The theory of optimization studies how to describe and attain what is the best, once one knows how to measure and alter what is good or bad. It encompasses the quantitative study of optima and methods for finding them [18]. In another words, in optimization one tries to improve some function by altering its parameters in accordance with the some optimization algorithm. During the selection process one usually pays the main attention on the optimum value alone and whether the algorithm is capable to reach it, but not on the algorithm itself. There are some other points which should be considered too:

- the size and complexity of the algorithm;
- the complication for implementation and usage;
- its speed (does it takes seconds or several days to find the optimum);
- amount of additional information one should know about the process or function under optimization (does one need to know the derivatives or inverse function).

Some optimization techniques contain the parameters, which also should be optimized. For example, the back-propagation algorithm, which is used in feed-forward neural networks,
contains the so-called learning rate parameter. Increasing of the learning rate allows to decrease the time that it takes for the net to learn some task. From another hand, too big value of the learning parameter leads to an unstable net [19]. There is also one problem: Is the achieved solution local or global solution? Consequently, choosing and using the optimization algorithm is not a trivial task.

Optimization techniques are usually divided into three main categories [15]:

- calculus-based,
- enumerative,
- random.

Calculus-based techniques are divided into two groups of methods: direct and indirect. Direct search methods look for optima by moving in a direction related to the local gradient of function under optimization. Algorithms move in steepest permissible direction. A gradient can be calculated numerically or analytically from the objective function. This kind of methods is called hill-climbing. In the indirect search the local extremum is seeking by solving the set of usually nonlinear equations resulting from setting the gradient of the objective function equal to zero. Both methods have been studied heavily, improved and extended. The main problem is that calculus-based methods are local in scope and the optima they found is the best in the neighborhood of starting point. In addition, these methods strongly depend on the existence of the derivatives.

The enumerative methods are based on the simple idea: within a finite solution space the optima can be obtained by comparing the values of the object function at each point once at a time. This kind of simple algorithms is easy to use and compute but it requires excessive computation in problems involving a large number of variables.

Random search is based on the idea of selecting randomly the parameters that are being optimized and then the best set of parameters is saved. Guided random search methods are enumerative in nature. However, they use additional information to guide the search process. In
case of the big solution spaces the efficiency of these methods is close to the efficiency of enumerative schemes.

In principle, once the parameter, which should be optimized, has been decided, the optimum waveguides parameters can be found in manual try and error search. Actually, even if the optimization is for the internal electric field and is limited to the reasonable materials (low Z materials for the guiding layer and high Z materials for the cladding layers), the search can require excessive computation. For the optimization of more complicated parameters instead the optimization strategy is not so obvious and thus it should be left to intelligent computer code. That is why genetic algorithms were selected for x-ray waveguide optimization.

6.3 What the genetic algorithms are

Genetic algorithms are the search and optimization techniques which are based on the mechanics of fittest surviving, similar to the process of natural selection in natural systems. These algorithms differ from the traditional optimization methods. The main differences are as follows:

1. Genetic algorithms operate with string encoded elements of the solution space, but not with the parameters themselves. They can be applied when, and only when the elements of the solution space can be represented as finite length string under the some finite alphabet. There are many ways of encoding, but in this thesis the binary representation will be used mainly.

2. Genetic algorithms do search among the population of solution space points. Usually, in traditional methods the search is performed by moving from one point of space to another, using some transition rule to determine the next point. The week point of such a procedure is that in case of several peaks the solution may be not correct. Genetic algorithms operate with a large number of points (population of strings), climbing several peaks in parallel. Thus, the possibility to locate the incorrect peak is decreased.
3. Object function values only are used in genetic algorithms. Traditional search techniques usually require the knowledge of some additional information (derivatives or tabulated coefficients, for example). Genetic algorithms need no any additional information to perform an effective search for better and better structures.

4. There is the element of randomness in the genetic algorithms. Genetic algorithms use probabilistic transition rules to guide the search. But it does not mean that these algorithms are the simple random search. Genetic algorithms use the random choice as a tool to direct the search in the solution space toward the region of the possible perfection.

These four differences make genetic algorithms to be the most advanced optimization technique.

### 6.4 Basic genetic algorithm

The basic genetic algorithm which gives a good result is based on three operations: reproduction, crossover and mutation. The main object of genetic algorithms is a string, which represents the element of the solution space. In this thesis binary string will be used mainly.

In *reproduction* every individual is copied according to its objective function (fitness function) value. Since the purpose of the search is to find the suitable values of parameters, a cost function is required for evaluating the efficiency of the guiding system achieved by different strings. It means that the fittest string have more chance to contribute the next generation. Reproduction is the artificial realization of the survival of the fittest in the natural systems. In the biological system the adaptation of the individual is determined by its ability to survive in the aggressive environment and procreate the offspring. In the artificial system the objective function value determines will the string live or die. After all the strings have received their fitness values, the fittest are copied into the mating pool to produce the offspring.
After the reproduction the *crossover* operation is implemented between the strings in the mating pool. This operation is performed in two steps. First, the individuals in pool are mated randomly. Next, integer \( j \) is selected randomly from the range 1 to \((L_s-1)\), where \( L_s \) is the length of the binary string. New strings are created by swapping all characters between positions 1 and \((j+1)\). After that each newly generated string obtains its fitness value. The new fittest strings are moved from the mating pool into the population, replacing the weaker predecessor.

The last operation, *mutation*, usually plays a secondary role in genetic algorithms. Its main function is to recover the useful information, which may be lost during crossover. From another hand, it can destroy the vital information because it works without any control. The probability of mutation is very small, so some algorithms even do not use it. The operation of mutation is performed as follows. The several positions in the string are chosen randomly with uniform distribution and the characters values in these positions are replaced arbitrary. In case of string under binary alphabet, if the chosen character value was “0” it becomes “1”, if it was “1”, it becomes “0”. This operation is applied just after crossover, before the fitness values were assigned.

An illustrative description of the basic genetic operations is presented in Figure 1.

### 6.5 Genetic algorithm implementation

To apply genetic algorithm, one should determine first the rule of the trial solution-to-string converting, since genetic algorithms work with the population of the string encoded trial solutions only. Then the gain function should be selected, which will define the fitness measure. Only after that, the program code can be written. In the present thesis the Pascal based compiler was used for program writing.
Figure 1 Schematic illustration of the basic genetic operations
6.5.1 Waveguide-string-waveguide converting

In present thesis the waveguides which consist of three layers were considered only. Consequently, every such a waveguide can be coded as concatenation of the three substrings where each of the substrings contains the information about the certain layer. If the layers materials are pre-chosen than the only thing one should know about each layer is the layer thickness. Consequently, each of the substrings may represent the coded thickness of the corresponded layer. Actually, the thickness should be considered as a real number, but for the practical applications it is enough to restrict the consideration to the angstrom scale. Under such assumption, the layer thickness can be considered as integer. The integer number can be translated into string form by many ways. The simplest one is a direct translation as it is into the string under the decimal alphabet \{0,1,2,3,4,5,6,7,8,9\}. For example, the waveguide (100 Å - 500 Å - 650 Å) can be represented as ‘100500650’, ‘010005000650’ or ‘001000050000650’. Such a presentation is convenient for the demonstration purpose, but not for computing. All the calculations are binary oriented, so in this thesis the binary representation was used. The same waveguide may be represented as ‘0001100100011111010010001010’, for example. The substrings of 11 symbols length were used to keep the thickness of each of the layers. Consequently, the thickness of each of the layers was varied in the range from 1 Å to 2047 Å.

The problem of the optimal waveguide determination when the material of each layer is pre-selected is quite simple and can be solved within the one of the possible enumerative scheme realization. To make the problem not so trivial, the cladding layers materials variation has been taken into account. In such a case, the string, which represents the waveguide, should be modified somehow to keep the information about the material of each of the cladding layers. The easiest way is to numerate all the materials under consideration and keep the order number of the layer material in addition with the layer thickness. In the present thesis three or four additional symbols were added to the first and third substrings to keep the order number of the corresponding layer material. Three symbols allow the coding of the numbers from 0 to 7, four symbols allow to code the numbers from 0 to 15. Consequently, 8 or 16 possible materials for the
cladding layers were under consideration, depending on the problem. In fact, the source code can be easy modified to take into account much more materials.

### 6.5.2 Gain function

The gain function which defines the fitness of the string also can be chosen in several ways. The most obvious way is to choose the function that is the quantitative measure of waveguide efficiency. For example, in [1] the theoretical gain function was defined as the electric field intensity, integrated over the core layer thickness and normalized to the full width at half maximum of the exciting intensity distribution. In the present thesis the maximum of the electric field intensity in the core layer has been chosen as a measure of the waveguide efficiency. This is a reasonable choice, which facilitates the optimization, as the electric field intensity in the core layer can be calculated using a well-known iterative procedure [20].

### 6.5.3 Initialization of the population

At the beginning the strings, which the population consist of, are filled by ‘1’ and ‘0’ arbitrary. The built-in random number generator was used for this purpose. Since the built in generator is usually of the average quality, it was reinitialized for each of the strings.

```plaintext
procedure InitPopulation;
var i,j:integer;
   rl:double;
   s:string[GenLen];
begin
  for i:=1 to popcount do
    begin
      randomize;
      s:=zeroStr;
      for j:=1 to GenLen do
        begin
          rl:=random;
          if rl<0.5 then s[j]:=chr(48) else s[j]:=chr(49);
        end;
      population[i].gen:=s;
    end;
end;
```
In this procedure \texttt{population} is an array that contains \texttt{popcount} records. Each record represents a particular individual of the population and contains two fields: \texttt{gen} is the string of GenLen length, which is a string coding of the waveguide structure; \texttt{weight} is a value of the goal function for the corresponding waveguide, calculated by \texttt{CalcWeight} procedure. \texttt{chr(48)} and \texttt{chr(49)} are equal to ‘0’ and ‘1’, respectively.

After initialization the population is sorted. The fittest individuals, which have the highest value of the goal function, are moved in the beginning of array.

\begin{verbatim}
procedure SortPopulation;
var i,j:integer;
    wIndivid:individ;
begin
    for i:=popcount downto 2 do
        for j:=i-1 downto 1 do
            if population[j].weight<population[j+1].weight then
                begin
                    wIndivid:=population[j+1];
                    population[j+1]:=population[j];
                    population[j]:=wIndivid;
                end;
end;
\end{verbatim}

Here the simplest bubble sort method was used.

\subsection*{6.5.4 Reproduction, crossover, mutation}

There are many way to select the mating individuals. Usually the fittest are selected. Such an approach often results in the big amount of the identical offspring. To relieve the offspring, the mating pairs were selected randomly from all the individuals to produce \texttt{childcount} offspring. In principle, each of individuals can be selected several times for mating.

\begin{verbatim}
procedure nextGen;
\end{verbatim}
var i,j,k: integer;
dad,mom: integer;
mutation: double;
s: string[GenLen];

begin
  // reproduction and crossover
  for i:=1 to (childcount div 2) do
  begin
    randomize;
dad:=1+random(popcount);
mom:=1+random(popcount);
j:=1+random(GenLen-1);
    Children[2*i-1].gen:=concat(copy(population[dad].gen,1,j),
copy(population[mom].gen,j+1,GenLen-j));
    Children[2*i].gen:=concat(copy(population[mom].gen,1,j),copy(population[dad].gen,j+1,GenLen-j));
  end;

  // mutation
  randomize;
  for i:=1 to childcount do
  begin
    mutation:=random;
    if mutation<mutationProb then
    begin
      s:=children[i].gen;
k:=1+random(GenLen);
      if (s[k]='0')then s[k]:=char(49) else s[k]:=char(48);
      children[i].gen:=s;
    end;
    CalcWeight(children[i]);
  end;
end;

Operator of mutation was applied to the offspring with the probability mutationProb. The mechanism of mutation was very simple – one symbol at arbitrary position was reversed. After that, the goal function value was calculated for each of offspring using CalcWeight procedure. The offspring with the highest fitness measure were entered into the population, replacing the weaker predecessors, only if the individuals with the same string combination were not presented in the population.

procedure insertChild;
var i,j,k: integer;


```plaintext
i_thWeight: extended;
i_thGen: string[GenLen];
p,q: boolean;
begin
for i:=1 to childCount do
begin
  i_thWeight:=children[i].weight;
i_thGen:=children[i].gen;
j:=0;
q:=false;
repeat
  inc(j);
  q:=(population[j].gen=i_thGen);
until q or (j=popcount);
if (not q) then
begin
  j:=0;
  repeat
    inc(j);
p_eq:=(population[j].weight<=i_thWeight);
until p or (j=popcount);
if p then
begin
  for k:=(popcount-1) downto j do
    population[k+1]:=population[k];
population[j]:=children[i];
end;
end;
end;
end;
```

6.6. Mo-Be-Mo waveguides at the incident beam energy 13 keV

Recently, a series of works has been published on Mo-Be-Mo waveguides, which were used successfully for the microbeam formation (see, for example, [9,14]). These structures naturally have become a subject of investigation. In [14] the waveguides with the guiding layer width from 130 nm to 150 nm were used successfully for the microdiffraction purposes at the photon energy 13 keV. Since the authors gave the range of the guiding layer width only, it seems reasonable to check the efficiency of the waveguides, they used.
The waveguides were coded using the strings of 33 symbols length and binary representation, so each layer width was varied from 1 Å to 2047 Å. Actually, the affect of the bottom cladding layer width on the electric field distribution in the guiding layer is insignificant. Nevertheless, all three layers were taken into consideration. Optical constants for each of the layers were calculated using MS-Access “Multilayer Reflectivity” database [21] (see Table 1).

### Table 1
**Optical constants for Mo and Be at the incident photon energy 13 keV**

<table>
<thead>
<tr>
<th></th>
<th>Optical constants</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\delta)</td>
<td>(\beta)</td>
</tr>
<tr>
<td>Mo</td>
<td>1.07784542296617E-05</td>
<td>3.2504986358857E-07</td>
</tr>
<tr>
<td>Be</td>
<td>2.01794089935219E-06</td>
<td>2.7698588412513E-10</td>
</tr>
</tbody>
</table>

A population of 400 strings (individuals), generated at the beginning in arbitrary manner and evolved during the 200 generation, has been considered. To calculate the fitness measure, each string was re-converted into three integers, which give the width of the layers in angstrom. Then the electric field intensity in the guiding layer was calculated for the glancing angles ranging from 0 to 0.25 degrees using an iterative procedure [20, 21] and its maximum value was assigned to the fitness measure of the corresponding individual. Fifty pairs of “parents” were selected in the population in arbitrary manner and then exactly two “children” were generated from each pair using a crossover operation. To avoid the degeneracy of the population the operation of mutation was applied to each child. Then the fitness measure was calculated and children with the highest fitness measure were introduced into the population, displacing the more “week” predecessors.

The ‘leaders’ in the 200th generation for the several running of the procedure, which has been described above, are presented in the Table 2. As one can see, all of them have the same core layer thickness and almost the same top cladding layer thickness. Also, the wide variety of the
bottom cladding layer thickness proves our assumption about the weak effect of the bottom cladding layer thickness on the electric field intensity distribution. The bottom layer just should be thick enough. Figure 2 shows the reflectivity curve and electric field intensity distribution in the core layer of the one of the numerically found waveguides for the first four excited waveguide modes.

Table 2
Parameters of the best Mo-Be-Mo waveguide for the incident beam photon energy 13 keV

<table>
<thead>
<tr>
<th>Procedure Running</th>
<th>Layers Width, Å</th>
<th>Mo, top layer</th>
<th>Be</th>
<th>Mo, bottom layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>47</td>
<td>1273</td>
<td>1952</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>47</td>
<td>1273</td>
<td>2020</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>47</td>
<td>1273</td>
<td>1456</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>47</td>
<td>1273</td>
<td>636</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>50</td>
<td>1273</td>
<td>1506</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>49</td>
<td>1273</td>
<td>962</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>49</td>
<td>1273</td>
<td>641</td>
</tr>
</tbody>
</table>

Unfortunately, the direct comparison of the numerically found waveguides with the waveguides, which were used in [14], is not possible. As one can see, the best waveguide (based on the chosen gain function, of course) is very close to the bottom of the guiding layers range used in [14]. A comparison with two waveguides, which were studied in [9] between 8 and 30 keV photon energy is not possible too, as a calculated waveguides are thicker, and so the standing wavefield is expected to be stronger. To make a correct comparison, the search was restricted with the Mo-Be-Mo waveguides, for which the core layer thickness is less than 50 nm. Since the guiding layer is thinner, one might expect the smaller standing wavefields. Nevertheless, this waveguide looks more attractive for the microbeam formation applications (Figure 3).
Figure 2 X-ray reflectivity coefficient and core layer electric field intensity distribution for the first four excited waveguide modes in Mo (4.9 nm)-Be(127.3 nm)-Mo(64.1 nm) waveguide
Figure 3 Electric field intensity distribution in the guiding layer for the first four excited waveguide modes at 13 keV photon energy. The waveguides with Be layer of 74 nm and 110 nm reported in [1] in comparison with the numerically found one with Be layer of near 50 nm.
6.7. Waveguides with Be core at the incident beam photon energy 13 keV

The next step was to check, whether Mo is really the best material for the cladding layers or not. For this modelling, strings of 39 symbol length were used. Three additional symbols were added to the first and third substrings to keep the order number of material. Eight possible materials for the cladding layers were considered. The optical constants, calculated with the “Multilayer reflectivity” database are presented in Table 3.

Table 3
Optical constants for cladding layers materials at the incident photon energy 13 keV

<table>
<thead>
<tr>
<th>Optical constants</th>
<th>( \delta )</th>
<th>( \beta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo</td>
<td>1.07784542296617E-05</td>
<td>3.2504986358857E-07</td>
</tr>
<tr>
<td>Co</td>
<td>1.01056643430916E-05</td>
<td>6.35871495157983E-07</td>
</tr>
<tr>
<td>Cr</td>
<td>8.28024672965895E-06</td>
<td>3.79338623130692E-07</td>
</tr>
<tr>
<td>Ni</td>
<td>1.04799126372977E-05</td>
<td>7.37754698194605E-07</td>
</tr>
<tr>
<td>Cu</td>
<td>1.00395562512565E-05</td>
<td>7.80157051755148E-07</td>
</tr>
<tr>
<td>Zn</td>
<td>7.97561155614424E-06</td>
<td>6.82591465411247E-07</td>
</tr>
<tr>
<td>Pb</td>
<td>1.04458733949194E-05</td>
<td>5.8385186552316E-07</td>
</tr>
<tr>
<td>Ag</td>
<td>1.11663633445327E-05</td>
<td>4.63821520189366E-07</td>
</tr>
</tbody>
</table>

Again, a population of 400 individuals initialized at the beginning in an arbitrary manner was considered. Now it was evolved during 800th generations. Operator of mutation was applied to an arbitrary amount of the offspring. The results of the evolution for the several running are
presented in Table 4. As one can see, the waveguides with Mo cladding layers were the fittest structures during the artificial population evolution for all running of the procedure. These results allow to suppose that the Mo was the best material for the cladding layers among the other materials under consideration. The similar calculations were performed for 16 materials under consideration (4 additional symbols were added to the first and third substrings): Si, Ti, V, Cr, Co, Ni, Cu, Zn, Nb, Mo, Ru, Rh, Pd, Ag, Cd, Hf, Ta, W, Au, Pb, Pt. All the materials were selected by guess with no particular reasons. And again Mo was without a rival. Thus, Mo can be considered as a really best material for the cladding layers of the waveguide with Be core at least for the selected incident beam photon energy.

Table 4
Evolution of the cladding layers combination for the waveguide with Be core at the incident beam photon energy 13 keV

<table>
<thead>
<tr>
<th>Procedure Running</th>
<th>Best Waveguide</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>50-th generation</td>
</tr>
<tr>
<td>1</td>
<td>Zn-Be-Zn</td>
</tr>
<tr>
<td>2</td>
<td>Co-Be-Cu</td>
</tr>
<tr>
<td>3</td>
<td>Ag-Be-Ni</td>
</tr>
<tr>
<td>4</td>
<td>Cr-Be-Ag</td>
</tr>
<tr>
<td>5</td>
<td>Pb-Be-Zn</td>
</tr>
<tr>
<td>6</td>
<td>Ni-Be-Mo</td>
</tr>
<tr>
<td>7</td>
<td>Mo-Be-Cr</td>
</tr>
</tbody>
</table>
6.8 Waveguides with Be core at the incident beam photon energy 8 keV

The authors of [9, 14] were able to register the guided beam at the exit of the waveguide for the incident beam energies above 10 keV, but they had some difficulties when the incident beam energy was below 10 keV. These difficulties could be due to improper choice of the layer thickness and cladding layer material. Consequently, it was decided to find the optimal waveguide parameters for incident beam photon energy 8 keV.

Traditionally, the simplest waveguide is considered as a layer of the low-density material, sandwiched between the metal layers. This simple structure allows the x-ray standing wave field formation in the core layer. The periodicity of this standing wave depends on the incident angle, and each time that the standing wave period is an integer fraction of the core layer thickness, the intensity of electric field in the core layer increases in resonance manner. The enhancement may achieve tens or even hundreds of times compare with the incident beam. The resonantly excited electromagnetic field can travel along the core layer. The guided beam has in one dimension the size of the same order as the core layer thickness.

As in previous paragraph, the strings of 39 symbol length were used. Three substrings of 11 symbol length were used to save the binary representation of the each layer thickness. Two additional substrings of 3 symbol length were used to save the binary representation of the order number of each cladding layer material. Eight materials were selected for cladding layers by guess. The optical constants, calculated using the “Multilayer Reflectivity” database are presented in Table 5. The main argument to include C in the list of the possible materials was that the energy loss in the carbon layer should be not so high compared with the metal layer. Actually, we did not pin hopes on it, believing that Mo will be without a rival again.
Table 5
Optical constants for cladding layers materials at the incident photon energy 8 keV, calculated with the “Multilayer Reflectivity” database

<table>
<thead>
<tr>
<th>Material</th>
<th>Optical constants</th>
<th>Optical constants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\delta$</td>
<td>$\beta$</td>
</tr>
<tr>
<td>Mo</td>
<td>2.89678305619062E-05</td>
<td>1.98256297208295E-06</td>
</tr>
<tr>
<td>Al</td>
<td>8.58188092426036E-06</td>
<td>1.64783729710761E-07</td>
</tr>
<tr>
<td>Ag</td>
<td>2.97921325697338E-05</td>
<td>2.81442708182636E-06</td>
</tr>
<tr>
<td>Ni</td>
<td>2.51517946269442E-05</td>
<td>5.40870854252695E-07</td>
</tr>
<tr>
<td>Cr</td>
<td>2.13074358386407E-05</td>
<td>2.28172529604068E-06</td>
</tr>
<tr>
<td>Zn</td>
<td>2.01969204668059E-05</td>
<td>5.21397608915134E-07</td>
</tr>
<tr>
<td>Zr</td>
<td>1.84504035390906E-05</td>
<td>1.10338026787707E-06</td>
</tr>
<tr>
<td>C</td>
<td>7.15325146162463E-06</td>
<td>1.20739772405802E-08</td>
</tr>
</tbody>
</table>

A population of 400 strings generated at the beginning in an arbitrary manner and evolved during 800 generations has been considered. In each generation, 50 pairs of parent strings were selected arbitrary to generate 100 child strings using a crossover operation. To avoid the degeneracy of the population the operator of mutation has been applied to an arbitrary number of the child strings.

The results of several numerical procedure runnings are presented in Tables 6 and 7. As one can see, unintentionally introduced into the set of cladding layers materials C turns out to be the most suitable for this incident beam energy.

Figure 4 shows the electric field intensity distribution in the core layer of C-Be-C waveguide at incident beam energy 8 keV, compared with the electric field intensity distribution in the core layer of Mo-Be-Mo waveguide at incident beam energy 13 keV [9]. This comparison allows to conclude that the beam guided in C-Be-C waveguide at 8 keV should be well detected.
Table 6
Parameters of the best waveguide with Be core for the incident beam photon energy 8 keV

<table>
<thead>
<tr>
<th>Procedure Running</th>
<th>Material : Layers Width, Å</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>top layer</td>
<td>Be</td>
</tr>
<tr>
<td>1</td>
<td>C : 255</td>
<td>719</td>
</tr>
<tr>
<td>2</td>
<td>C : 317</td>
<td>508</td>
</tr>
<tr>
<td>3</td>
<td>C : 310</td>
<td>480</td>
</tr>
<tr>
<td>4</td>
<td>C : 251</td>
<td>784</td>
</tr>
<tr>
<td>5</td>
<td>C : 279</td>
<td>664</td>
</tr>
<tr>
<td>6</td>
<td>C : 311</td>
<td>540</td>
</tr>
<tr>
<td>7</td>
<td>C : 279</td>
<td>664</td>
</tr>
</tbody>
</table>

Table 7
Evolution of the cladding layers combination for the waveguide with Be core at the incident beam photon energy 8 keV

<table>
<thead>
<tr>
<th>Procedure Running</th>
<th>Best Waveguide</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>50-th generation</td>
<td>100-th generation</td>
</tr>
<tr>
<td>1</td>
<td>C-Be-Zn</td>
<td>C-Be-Zn</td>
</tr>
<tr>
<td>2</td>
<td>Ni-Be-Mo</td>
<td>C-Be-C</td>
</tr>
<tr>
<td>3</td>
<td>C-Be-Ni</td>
<td>C-Be-C</td>
</tr>
<tr>
<td>4</td>
<td>C-Be-Ni</td>
<td>C-Be-Ni</td>
</tr>
<tr>
<td>5</td>
<td>C-Be-Cr</td>
<td>C-Be-Ni</td>
</tr>
<tr>
<td>6</td>
<td>C-Be-C</td>
<td>C-Be-C</td>
</tr>
<tr>
<td>7</td>
<td>C-Be-Zn</td>
<td>C-Be-C</td>
</tr>
</tbody>
</table>
Figure 4. X-ray reflectivity coefficient of the C-Be-C waveguide at incident beam photon energy 8 keV and electric field intensity distribution in the core layer of the same waveguide for the first four excited waveguide modes in comparison with the electric field intensity distribution for the first four waveguide mode excited in the Mo-Be-Mo waveguide used in [9] at the 13 keV.
The obtained result looks very strange. Both carbon and beryllium usually are used for core layers due to the relatively small absorption. Consequently, they should be undistinguished for the x-ray radiation. But the calculations show that actually such speculations are incorrect and the waveguide compiled from the light materials could provide a strong electric field enhancement in the core layer. If the calculations are correct, the traditional approach to the waveguide as a light core, sandwiched between metal layers should be revised at least for the incident beam photon energies below 10 keV (for highest photon energies traditional approach gives the sufficient results).

To check the results and the assumption that the light cladding layers should provide the strongest electric field enhancement in the core layer, another series of calculations was performed. The optical constants for these calculations were obtained at the homepage of the Center for X-Ray Optics (CXRO) at the Lawrence Berkeley National Laboratory [22] (Table 8). The list of the cladding layer materials has been modified a little. In particular, the boron has been added in the list.

Table 8
Optical constants for cladding layers materials at the incident photon energy 8 keV, obtained at the CXRO homepage

<table>
<thead>
<tr>
<th>Material</th>
<th>$\delta$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>2.4759E-05</td>
<td>5.6196E-07</td>
</tr>
<tr>
<td>Ni</td>
<td>2.4732E-05</td>
<td>5.2149E-07</td>
</tr>
<tr>
<td>Zr</td>
<td>1.8426E-05</td>
<td>1.0656E-06</td>
</tr>
<tr>
<td>Zn</td>
<td>2.0143E-05</td>
<td>5.0328E-07</td>
</tr>
<tr>
<td>Mo</td>
<td>2.8984E-05</td>
<td>1.9144E-06</td>
</tr>
<tr>
<td>B</td>
<td>7.0343E-06</td>
<td>5.8004E-09</td>
</tr>
<tr>
<td>Al</td>
<td>8.5746E-06</td>
<td>1.5857E-07</td>
</tr>
<tr>
<td>C</td>
<td>7.1526E-06</td>
<td>1.1560E-08</td>
</tr>
</tbody>
</table>
Table 9
Parameters of the best waveguide with Be core for the incident beam photon energy 8 keV

<table>
<thead>
<tr>
<th>Procedure Running</th>
<th>Material : Layers Width, Å</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>top layer</td>
<td>Be</td>
<td>bottom layer</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>B : 402</td>
<td>372</td>
<td>B : 1603</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>B : 369</td>
<td>439</td>
<td>B : 1248</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>B : 319</td>
<td>560</td>
<td>B : 2044</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>B : 255</td>
<td>701</td>
<td>B : 2046</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>B : 342</td>
<td>415</td>
<td>B : 847</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>B : 319</td>
<td>525</td>
<td>B : 2047</td>
<td></td>
</tr>
</tbody>
</table>

Table 10
Evolution of the cladding layers combination for the waveguide with Be core at the incident beam photon energy 8 keV

<table>
<thead>
<tr>
<th>Procedure Running</th>
<th>Best Waveguide</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>50-th generation</td>
</tr>
<tr>
<td>1</td>
<td>B-Be-C</td>
</tr>
<tr>
<td>2</td>
<td>C-Be-B</td>
</tr>
<tr>
<td>3</td>
<td>C-Be-Zn</td>
</tr>
<tr>
<td>4</td>
<td>B-Be-C</td>
</tr>
<tr>
<td>5</td>
<td>C-Be-B</td>
</tr>
<tr>
<td>6</td>
<td>C-Be-Cu</td>
</tr>
</tbody>
</table>
Figure 5. X-ray reflectivity coefficient of the B-Be-B waveguide at incident beam photon energy 8 keV and electric field intensity distribution in the core layer of the same waveguide for the first four excited waveguide modes in comparison with the electric field intensity distribution for the first four waveguide mode excited in the Mo-Be-Mo waveguide used in [9] at the 13 keV.
Figure 6. Electric field intensity depth distribution in the B(40.2nm)-Be(37.2nm)-B(160.3nm) waveguide for the first excited waveguide mode at the incident beam photon energy 8 keV.
Again a population of 400 strings evolved during 800 generations has been considered. In each generation 50 pairs of parent strings were selected to generate 100 child strings using a crossover operation. The operator of mutation has been applied to an arbitrary number of the child strings.

The results of this series of calculations are presented in Tables 9 and 10. As one can see, the waveguides with the light cladding layers are the fittest in the population and structures with the B cladding layers provide the strongest electric field enhancement in the core layer. Also it should be pointed out that the core layer thickness of such a waveguides is small. The degree of electric field resonant enhancement is comparable with one for the Mo-Be-Mo waveguides at 13 keV (Figures 5, 6). All these factors make the waveguides with the light cladding layers very attractive for the microbeam applications at the incident beam photon energies below 10 keV.

### 6.9 Conclusions

The results of the numerical modeling allow to make the following conclusions:

1. Genetic algorithms can be used for the optimization of the waveguide parameters for various kinds of application. Within the frameworks of the present thesis the process of optimization was performed from microbeam formation point of view. The numerically found structures provide the strong electric field enhancement each time the waveguide mode is excited in the core layer.

2. Traditional approach to the simplest waveguide — the light material core layer, sandwiched between metal cladding layers — provides the satisfying results at the incident photon energy above 10 keV. The guided beam was well detected by several scientific groups so the only necessary thing to do is to choose the layer thicknesses properly. The most suitable material for the cladding layers of waveguide with Be core at the incident beam energy 13 keV is Mo.

3. For the incident photon energy below 10 keV, traditional approach provides the poor results. This can explain the difficulties with the experimental observation of the guided beam.
Numerical modeling shows that the most effective waveguide for the relatively small energy values should be compiled from the light materials. For example, the best results for the waveguide with Be core at the incident photon energy 8 keV can be achieved if boron is used for the cladding layers. In this case it is possible to provide the same order of the electric field intensity enhancement as for the incident energies above 10 keV and keep the core layer thickness small enough for the microbeam formation.
References in the Chapter 6


Conclusions

In this thesis it is shown how the x-ray techniques can be used for the material properties characterization and for design of advanced materials with desirable properties.

In Chapter 2 the x-ray fluorescence and absorption Fe L₂,3 spectra in Hg₁₋ₓFeₓSe diluted magnetic semiconductor were analyzed to determine the energy position of impurity Fe 3d states. We can conclude that Fe 3d-states are located in the binding energy region between 1 and 6 eV below the Fermi level with the maximum at 3 eV, which agrees good with the results of other researchers. It is found that Fe 3d-states located at the bottom of the valence band are mixed with Hg 5d-states. Based on the experimental data we can conclude that, while the Fe atoms concentration is increasing, the Fe³⁺ ions amount in HgSe:Fe is decreasing as the theory predicts. From another hand, the Fe³⁺ ions percentage which was obtained for the Fe concentrations above the critical value is too large to call it “a very small amount”.

In Chapter 3 the electronic structure of LiBC has been studied using soft x-ray fluorescence measurements. The comparison of experimental RIXS data with our density functional theory calculations shows that in spite of a general agreement between experimental and calculated energy bands of stoichiometric LiBC we found that carbon and boron electronic states have an individual character because of difference of their orbital s and p-energies. Therefore the rigid band model can not be used for prediction of electronic structure of off-stoichiometric LiBC.

In Chapter 4, the “Multilayer Reflectivity” database description is given. This database was developed to analyze the structure of layered materials. Its simplicity allows the fast modification of the program code for particular problem under consideration. The results of the calculations agree well with the known one. This database is used in Chapter 5 for the determination of the real thickness of layers in (Mo/B₄C)₃₀/Si and (Ni/Mn)₃/Au/Si multilayers for the particular scheme of measurements. It is shown that this scheme is not suitable for the multilayers, the layer materials of which has similar properties.
The same database was used in Chapter 6 for modelling of the planar x-ray waveguide with Be core, which can produce at its exit the microbeam of high intensity. It is shown that traditional approach to the waveguide as a structure in which the light core layer is sandwiched between the metal (or high Z) layers should be revised, since the highest electric field excitation is expected in the B/Be/B waveguides.
APPENDICES
Appendix A. X-ray reflection and refraction at interface

This appendix gives a brief description of the process of the electromagnetic wave propagation through the planar interface between two media and through the planar layered structures. In a homogeneous medium the x-ray beam behaves like a light beam and follows a straight path. If the beam hits the boundary surface of the second medium it will be deflected from the original direction. At certain conditions it can be even reflected back into the first medium.

Reflection and refraction at an interface

A plane electromagnetic wave

\[ E(t, r) = E_0 \exp[-i(\omega t - k \cdot r)], \]  

propagated with initial amplitude \( E_0 \) in the direction of wave vector \( k \) will be under consideration (Fig.1.1). The following rules are valid [1]:

- The incident, reflected and refracted beams are in the same plane, the so-called plane of incidence, which is normal to the boundary plane.
- The glancing angles of incident and reflected beams are equal (\( \alpha_i = \alpha'_r \)). Consequently, the incident angles of incident and reflected beams are equal too (\( \varphi_i = \varphi'_r \)).
- The glancing angels of the incident and refracted beams follow the Snell’s law:

\[ v_2 \cos \alpha_i = v_1 \cos \alpha_r, \]  

where \( v_1, v_2 \) are the phase velocities of the beam in media 1 and 2, respectively. Phase velocity is the velocity at which the planes of constant phase propagate within the medium. It depends on the wavelength \( \lambda \) and the medium itself. In vacuum it equals to the light velocity \( c \) and is independent on the wavelength \( \lambda \).
Figure 1.1 X-ray propagation through the interface depending on the glancing angle.
Dividing equation (1.2) by $c$ one can obtain

$$n_1 \cos \alpha_1 = n_2 \cos \alpha_2,$$

(1.3)

where $n_1$ and $n_2$ are the absolute refractive indices of medium 1 and 2, respectively ($n_{1,2} = c/v_{1,2}$).

If $n_2 > n_1$, the refracted beam in medium 2 will be deflected off the boundary. If $n_2 < n_1$, the refracted beam in the medium 2 will be deflected towards the boundary.

The refractive index $n$ usually is written in the complex form

$$n = 1 - \delta - i\beta,$$

(1.4)

where $i$ is the complex unit. In equation (1.4) $\delta$, called the decrement, defines the deviation of the real part of the refractive index from 1, and $\beta$ defines the beam attenuation.

For x-rays incident from vacuum ($n=1$) or air ($n \approx 1$) a refracted beam is usually deflected toward the boundary surface [1], (Fig. 1.1a). If the angle $\alpha_2$ becomes zero, the refracted beam will lie in the boundary plane. Consequently, where is a critical angle $\alpha_c$, for which refraction is just possible (Fig. 1.1b). This critical angle can be found from equation (1.3):

$$\cos \alpha_c = n_2,$$

(1.5)

where it is taken into account that $n_1 = 1$. For angles $\alpha_1 < \alpha_c$ no beam enters the second medium and boundary completely reflects the incident beam back to the first medium (Fig. 1.1c). This phenomenon is called the total reflection.

The critical angle of the total reflection can be easily calculated from equation (1.5). Since the critical angle $\alpha_c$ is small, the following approximation is valid:
Comparing equations (1.5-6) one can easily obtain

$$ \alpha_c \approx \sqrt{2\delta}.$$  \hspace{1cm} (1.7)

This model is incomplete since it does not include the effect of finite $\beta$. Since the losses are incurred, the total reflection is not achieved.

**Coefficient of x-ray reflection at an interface**

Figure 1.2 shows the geometry of the incident, reflected and refracted beams. Incident beam of any polarization can be described in terms of two orthogonal polarizations. It is common to decompose the incident radiation into two geometries. One with the incident electric field $\textbf{E}$ perpendicular to the plane of incidence (s-polarization) and another one with $\textbf{E}$ parallel to that plane (p-polarization). Any incident wave polarized or not, can be represented in terms of these two polarizations.

**s-polarization**

At the interface where incident, reflected and refracted beams meet, the fields must obey certain boundary conditions [2-6] in order to satisfy Maxwell’s equation. One of these conditions is a continuity of field components of $\textbf{E}$ and $\textbf{H}$ parallel to the interface. In case of s-polarization the electric field amplitudes at the interface must satisfy the condition

$$ \cos \alpha_c = 1 - \frac{\alpha_c^2}{2}. $$  \hspace{1cm} (1.6)
\[ E_\perp^0 + E_\perp^R = E_\perp^T. \]  

(1.8)

Continuity of the magnetic field at the interface requires

\[ H_\perp^0 \sin \alpha_0 - H_\perp^R \sin \alpha_0 = H_\perp^T \sin \alpha. \]  

(1.9)

Equations (1.8), (1.9) can be combined by recalling that amplitudes \( H \) and \( E \) are related by [7]

\[ H \sim nE. \]  

(1.10)

Equation (1.9) can be rewritten now as

\[ E_\perp^0 \sin \alpha_0 - E_\perp^R \sin \alpha_0 = nE_\perp^T \sin \alpha. \]  

(1.11)

Here it is taken into account that first medium is vacuum or air. Combining equations (1.8), (1.11), one obtains

\[ (E_\perp^0 - E_\perp^R) \sin \alpha_0 = n(E_\perp^0 + E_\perp^R) \sin \alpha. \]  

(1.12)

Consequently, the ratio of the field amplitudes is

\[ \frac{E_\perp^R}{E_\perp^0} = \frac{\sin \alpha_0 - n \sin \alpha}{\sin \alpha_0 + n \sin \alpha}. \]  

(1.13)

In equation (1.13) \( \alpha \) can be expressed in terms of \( \alpha_0 \) using Snell’s law and trigonometric relation as follows

\[ \sin \alpha = \sqrt{1 - \cos^2 \alpha} = \sqrt{1 - \frac{\cos^2 \alpha_0}{n^2}}. \]  

(1.14)
Figure 1.2 Interface geometry. Fields components for a) - p-polarization and b) – s-polarization.
Now equation (1.13) can be rewritten as

\[ \frac{E^R_\perp}{E^0_\perp} = \frac{\sin \alpha_0 - \sqrt{n^2 - \cos^2 \alpha_0}}{\sin \alpha_0 + \sqrt{n^2 - \cos^2 \alpha_0}}. \] (1.15)

The reflectivity \( R \) is defined as the ratio of the reflected beam intensity to the incident beam intensity and, consequently, is [7]

\[ R_s = \frac{\left| E^R_\perp \right|^2}{\left| E^0_\perp \right|^2} = \frac{\sin \alpha_0 - \sqrt{n^2 - \cos^2 \alpha_0}}{\sin \alpha_0 + \sqrt{n^2 - \cos^2 \alpha_0}}. \] (1.16)

The formula for the x-ray reflectivity in case of s-polarization is obtained.

**p-polarization**

The second decomposition of incident polarization is that in which the electric field vector lies in the plane of incidence and is referred as p-polarization. The boundary conditions should be written as follows

\[ H^0_\parallel + H^R_\parallel = H^T_\parallel. \] (1.17)

\[ E^0_\parallel \sin \alpha_0 - E^R_\parallel \sin \alpha_0 = E^T_\parallel \sin \alpha. \] (1.18)

Recalling (1.10) and combining (1.17), (1.18) one can obtain

\[ \left( E^0_\parallel - E^R_\parallel \right) \sin \alpha_0 = \left( E^0_\parallel + E^R_\parallel \right) \frac{\sin \alpha}{n}. \] (1.19)
which becomes

\[
\frac{E^R_{\parallel}}{E^0_{\parallel}} = \frac{n^2 \sin \alpha_0 - \sqrt{n^2 - \cos^2 \alpha_0}}{n^2 \sin \alpha_0 + \sqrt{n^2 - \cos^2 \alpha_0}}.
\]  \hspace{1cm} (1.20)

Finally, the reflectivity coefficient can be written for p-polarization as follows

\[
R_p = \frac{|E^R_{\parallel}|^2}{|E^0_{\parallel}|^2} = \frac{n^2 \sin \alpha_0 - \sqrt{n^2 - \cos^2 \alpha_0}^2}{n^2 \sin \alpha_0 + \sqrt{n^2 - \cos^2 \alpha_0}^2}.
\]  \hspace{1cm} (1.21)

In the region of the total x-ray reflection equations (1.16) and (1.21) give the same results for the lot of common materials [8].

Figure 1.3 shows example of the calculations using formulas (1.16, 1.21) for bulk silicon plate at incident beam photon energy 15 keV (Fig. 1.3a) and at glancing angle 0.1 degree (Fig. 1.3b).

**Multilayer x-ray reflectivity**

Using the theory described above now it is possible to obtain the formulas for the reflectivity coefficient of the simplest waveguide which consist of three layers with ideal interfaces, placed on same flat substrate (these formulas can be easy extended on the case of the arbitrary amount of layers). The substrate is assumed to be thick enough so the beam propagated it does not go through its bottom border. To calculate the reflectivity coefficient the recurrent procedure developed by Parratt [9] can be used.
Figure 1.3 X-ray reflectivity coefficient for bulk Si plate a) at incident beam energy 15 keV, b) at glancing angle 0.1 degree.
For $k$-th layer $d_k$ will denote the layer thickness, $n_k$ – complex refractive index ($k=1,2,\ldots, N$). The substrate (layer $N+1$) is assumed to be semi-infinite, and vacuum will be the layer 0 ($n=1$). As in previous paragraph, the boundary conditions should be valid at each interface.

\[ a_{j\rightarrow j-1} E_{\perp j-1} + a_{j\rightarrow j-1}^{-1} E_{\parallel j-1}^R = a_j^{-1} E_{\perp j} + a_j E_{\parallel j}^R, \]
\[
(a_{j\rightarrow j-1} E_{\perp j-1} - a_{j\rightarrow j-1}^{-1} E_{\parallel j-1}^R) n_{j-1} \sin \alpha_{j-1} = (a_j^{-1} E_{\perp j} + a_j E_{\parallel j}^R) n_j \sin \alpha_j,
\]

in case the incident beam is of s-polarization. And

\[ (a_{j\rightarrow j} E_{\perp j} + a_{j\rightarrow j}^{-1} E_{\parallel j}^R) n_j = (a_j^{-1} E_{\perp j} + a_j E_{\parallel j}^R) n_j, \]
\[
(a_{j\rightarrow j} E_{\perp j} - a_{j\rightarrow j}^{-1} E_{\parallel j}^R) \sin \alpha_{j-1} = (a_j^{-1} E_{\perp j} + a_j E_{\parallel j}^R) \sin \alpha_j,
\]

in case of p-polarization. Here amplitudes $E_j, E_j^R$ are taken at the half-thickness of the corresponding layer ($j=1,2,\ldots,N$). As a result, additional coefficients $a_j$ are included to account the beam attenuation at the layer half thickness path

\[ a_j = \exp\left[- \frac{\mu}{2} d_j \sin \alpha_j \right] (j = 1,2,\ldots,N), \]
\[ a_0 = a_{N+1} = 1, \]

Glancing angle $\alpha_j$ can be found from Snell’s law (1.14)

\[ \sin \alpha_j = \frac{\sqrt{n_j^2 - 1 + \sin^2 \alpha_0}}{n_j}. \]

To modify equations (1.22) the new variables are introduced as follows

\[ f \equiv n_j \sin \alpha_j, \ j=1,2,\ldots,N+1. \]

Thus, equations (1.22) can be rewritten as
\begin{align}
a_{j-1}E_{j,j-1} + a_j^{-1}E_j^R - a_j^{-1}E_{j-1}^R &= a_j^{-1}E_{j,j} + a_jE_j^R, \\
(a_{j-1}E_{j,j-1} - a_j^{-1}E_{j-1}^R)f_j = (a_j^{-1}E_{j,j} + a_jE_j^R)f_j, 
\end{align}

or

\begin{align}
(a_{j-1}E_{j,j-1} + a_j^{-1}E_{j-1}^R)(a_j^{-1}E_{j,j} - a_jE_j^R)f_j = (a_{j-1}E_{j,j-1} - a_j^{-1}E_{j-1}^R)(a_j^{-1}E_{j,j} + a_jE_j^R)f_j.
\end{align}

It follows from (1.28), that

\begin{align}
\left( a_j^4 + a_j^{-1} \frac{E_{j,j-1}^R}{E_{j-1}^R} \right) \left( 1 - a_j^3 \frac{E_{j,j}^R}{E_{j-1}^R} \right) f_j = \left( a_j^4 - a_j^{-1} \frac{E_{j,j-1}^R}{E_{j-1}^R} \right) \left( 1 + a_j^3 \frac{E_{j,j}^R}{E_{j-1}^R} \right) f_j.
\end{align}

Now, another additional variable may be introduced:

\begin{align}
R_{j,j+1} = a_j^2 \frac{E_{j,j}^R}{E_{j,j-1}^R}.
\end{align}

Equation (1.29) in new notations takes form

\begin{align}
(a_j^4 + R_{j=1,j}) \left( 1 - R_{j,j+1} \right) f_j = (a_j^4 - R_{j=1,j}) \left( 1 + R_{j,j+1} \right) f_j.
\end{align}

Solving (1.31) one can obtain

\begin{align}
R_{j-1,j} = a_j^4 \frac{(f_{j,j} - f_j) + (f_{j,j+1} + f_j)R_{j,j+1}}{(f_{j,j} + f_j) + (f_{j,j+1} - f_j)R_{j,j+1}},
\end{align}

or
\[ R_{j-1,j} = a_{j-1}^2 \frac{F_{j-1,j} + R_{j,j+1}}{1 + F_{j-1,j} R_{j,j+1}}, \]  

(1.33)

where

\[ F_{j-1,j} = \frac{(f_{j-1} - f_j)}{(f_{j-1} + f_j)}. \]  

(1.34)

Since the substrate is unlimited in depth, \( E_{N+1}^R = 0 \). Consequently, \( R_{N+1,N+2} = 0 \). Starting from this value, one can calculate \( R_{0,1} \) using equations (1.32), (1.33).

\[ R_{0,1} = a_0^2 \frac{E_{\perp 0}^R}{E_{\perp 0}^L} = \frac{E_{\perp 0}^R}{E_{\perp 0}^L}, \]

or

\[ R_S = |R_{0,1}|^2. \]  

(1.35)

Thus, the recurrent formula to calculate the reflectivity coefficient for s-polarized incident beam is obtained.

For the p-polarized beam all the speculations are carried out in the same manner. For this reason they are omitted in this thesis.

Now the final result can be presented:

\[ R_{N+1,N+2} = 0 \]  

(1.36)
$$R_{j+1,i} = a_{j+1}^4 \frac{F_{j-1,i} + R_{j+1,i}}{1 + F_{j-1,i}R_{j+1,i}}, \ (j=N+1,N,\ldots,1),$$

$$R = \left| R_{0,1} \right|^2,$$

where $F_{j+1,i}$ are calculated using (1.33), and

$$f_j = \begin{cases} n_j \sin \alpha_j, & \text{for } s \text{- polarization} \\ \frac{\sin \alpha_j}{n_j}, & \text{for } p \text{- polarization} \end{cases}, \ j=1,2,\ldots,N. \quad (1.37)$$

Figure 1.4 shows the results of the calculations according to equations (1.36) for the several Cr-C-Cr waveguides at incident beam energy 10 keV. As one can see, the character of reflection is strong depended on the layers thickness.

**Standing wave field formation**

As it has been mentioned, in case the beam incidents from vacuum on the lossy medium the total reflection is not achievable and part of radiation is propagated into the medium as the evanescent wave [9]. Nevertheless, for the small glancing angles the intensities of the incident and reflected beams are almost the same (consequently, the reflectivity coefficient is near 1). The interference of the incident beam and reflected beam leads to the standing wave field formation above the interface [10]. Planes of the maximum and minimum intensity of that wave are parallel to the interface and its period is equal

$$D = \frac{\lambda}{2 \sin \alpha}. \quad (1.38)$$
Figure 1.4 X-ray reflectivity coefficient calculated for several Cr-C-Cr waveguides at incident beam energy 10 keV.
The evanescent wave intensity decreases with the propagation depth. But at certain conditions its intensity in some layers may increase resonantly in ten and even hundred times compare with the intensity of the incident beam. In such a case the structure starts to work in the waveguiding mode [11]. This phenomenon can be revealed by the deep in the x-ray reflectivity curve, when the reflected beam intensity decrease significantly.

The total electric field at a point $r$ in the layer $j$ is the sum of the “down-directed” contribution $E_j^\downarrow$ and “up-directed” contribution $E_j^\uparrow$:

$$E = E_j^\downarrow + E_j^\uparrow, \quad (1.39)$$

where $E_j^\downarrow$, $E_j^\uparrow$ can be calculated using the iterative procedure, which was described previously (see for details [8], for example). Figure 1.5 shows the the x-ray reflectivity coefficient for calculated for the Mo(5 nm)-Be(50 nm)-Mo(50 nm) waveguide at incident beam photon energy 15 keV. Four arbitrary values for the beam incidence angle were selected to calculate the electric field intensity depth profile (figure 1.5). As one can see, the deep points of the reflectivity curve are corresponded to the electric field excitation in the core layer. Period of the excited in the core layer standing wave can be calculated using equation (1.38) and its minimum value is:

$$D_{\text{min}} \sim \frac{\lambda}{2n_2\sqrt{\delta_3 - \delta_2}}, \quad (1.40)$$

where $n_2$ is a complex refractive index of the core layer, $\delta_2, \delta_3$ are the decrements of the refractive index for the core layer and the bottom cladding layer, respectively (see eq.(1.4)). The resonance occurs then the excited wave period is the integer fraction of the core layer width [11]. Consequently, the knowledge of the structure composition allows to estimate the minimum core layer thickness for the waveguide modes formation. Figure 1.6 shows the electric field intensity distribution in three different Mo-Be-Mo waveguides. As one can see, the degree of the intensity enhancement is depended on the layers thickness.
Figure 1.5 X-ray reflectivity curve and electric field intensity distribution, calculated for the Mo(5 nm)-Be(50 nm)-Mo(50 nm) waveguide at incident beam photon energy 15 keV.
Figure 1.6 Electric field intensity distribution in the core layer of the several Mo-Be-Mo waveguides for the first four excited waveguide modes at incident beam photon energy 13 keV.
References

Appendix B. Mathematical backgrounds of genetic algorithms

Here, mathematical backgrounds, explaining the work of genetic algorithm, will be given. In this thesis a binary representation is used mainly, so the theory will be presented for the finite length strings under the binary alphabet \{‘0’, ‘1’\}.

A schema \cite{1} is a similarity template describing a subset of strings with similarities at certain string positions. To introduce a schema, an additional symbol ‘*’ will be introduced into the alphabet. This symbol has “don’t care” meaning and matches either 0 or 1 at particular position. A schema matches a particular string if at every location in the schema ‘1’ matches a ‘1’ in the string, a ‘0’ matches a ‘0’ and a ‘*’ matches either ‘1’ or ‘0’ in the string. For example, the schema

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describes a subset with four members:

00110, 01110, 10110, 11110.

We consider a population of individuals (strings) \( A_j \), \((j=1, 2, \ldots, n)\) contained in the population \( A(t) \) at generation \( t \) \((t=1, 2, \ldots)\), where the boldface is used to denote the population, and a schema \( H \) taken from the three-letter alphabet \{0,1,*\}.

For alphabet of cardinality \( k \), where are \((k+1)^l\) schemata, where \( l \) is the length of the string. Furthermore, recall that in a string population with \( n \) members there are at most \( n2^l \) schemata contained in a population because each string is itself a representative of \( 2^l \) schemata. These
counting arguments give us some feel for the magnitude of the information being processed by genetic algorithms.

All schemata are not equal. Some are more specific than others. The schema 01*1* is more definite statement about important similarity than the schemata *1***. Furthermore, certain schemata span more of the total string length than others. The schema 1***0 spans a larger portion of the string than the schema 1*0**. To quantify these ideas, two schema properties are introduced: schema order and defining length.

The order of a schema \( H \), denoted by \( o(H) \), is the number of fixed positions (in case of binary string the number of ‘1’-s and ‘0’-s) present in the template. For example, the order of the schema 00*01 is 4, the order of the schema 1***0 is 2.

The defining length of a schema \( H \), denoted by \( \delta(H) \), is the distance between the first and the last specific string positions. For example, the schema 0**2* has defining length 3, because the last specific symbol position is 4 and, consequently, \( \delta(H)=4-1=3 \).

Schemata provide the basic means for analyzing the net effect of reproduction and genetic operators on the building blocks contained within the population. Below the individual and combined effect of reproduction, crossover and mutation on schemata contained within a population of strings will be considered. Suppose that the population \( A(t) \) contains \( m(H,t) \) examples of a particular schema \( H \) at a given generation \( t \). During the reproduction the strings are copied according to their fitness. More precisely a string \( A_i \) gets selected with probability

\[
p_i = \frac{f_i}{\sum_{j=1}^{n} f_j}
\]  \hspace{1cm} (1)
After picking a non overlapping population of size \( n \) with replacement from the population \( A(t) \), \( m(H,t+1) \) representatives of the schema \( H \) is expected to be in the population at generation \( t \) as given by

\[
m(H,t+1) = \frac{m(H,t)nf(H)}{\sum_{j=1}^{n} f_j(t)},
\]

where \( f(H) \) is the average fitness of the strings representing schema \( H \) at generation \( t \). The average fitness of the entire population is defined as

\[
\bar{f} = \frac{1}{n} \sum_{j=1}^{n} f_j.
\]

Thus the reproductive schema growth equation can be rewritten as follows:

\[
m(H,t+1) = m(H,t)\frac{f(H)}{\bar{f}(t)}.
\]

Assuming that \( f(H)/\bar{f} \) remains relatively constant for \( t=1, 2, \ldots \), the preceding equation is a linear difference equation \( x(t+1) = ax(t) \) with constant coefficient, which has a solution \( x(t) = a^t x(t) \). A particular scheme grows a ratio of the average fitness of the schema to the average fitness of the population. Schemata with the witness values above the population average will receive an increasing number of samples in the next generation, while schemata with fitness values below the population average will receive a decreasing number of samples. This behavior is carried out with every schema \( H \) contained in the particular population \( A \) in parallel. In other words, all the schemata in a population grow or decay according to their schema averages under the operation of reproduction alone. Above-average schemata grow and below-average schemata die off.

Suppose that a particular schema \( H \) remains an amount \( c\bar{f} \) above the average with \( c \) a constant. Under this assumption eq.(4) can be rewritten
\[ m(H, t + 1) = m(H, t) \frac{f + cf}{f(t)} = (1 + c)m(H, t). \]  \hspace{1cm} (5)

Starting at \( t=0 \) and assuming the a stationary value of \( c \), one can obtain

\[ m(H, t + 1) = m(H, 0)(1 + c)^t. \]  \hspace{1cm} (6)

This is a geometric progression, which is a discrete analog of the exponential form. Reproduction allocates exponentially increasing (decreasing) numbers of trials to above- (below-) average schemata.

It should be noted, that during the reproduction no new points are explored in the search space, the old structures are copied only. Consequently, there is no new regions exploration in the search space. The new structures are created during the crossover. To see, how the schemata are affected by crossover, a particular string and two schemata will be considered:

\[
A = 0100010 \\
H_1 = **0***0 \\
H_2 = ****0*0
\]

Both the schemata are represented in the string \( A \). It will be assumed, that this string was selected as a mate for crossover. In this string there are six possible positions for the crossing site. Suppose, that the crossing site was selected between third and fourth characters:

\[
A = 010|0010 \\
H_1 = **0|***0 \\
H_2 = ***|*0*0
\]

It is clear, that the schema \( H_1 \) will be broken, unless the mate of the string \( A \) is identical to \( A \) at fixed positions of the schema. The 0 at positions 3 and 7 are on the opposite side of the cross point, consequently they will be placed in different offspring. From another hand, the schema \( H_2 \)
will survive, since all the fixed positions of this schema are on one side of the crossing point and will be carried intact to a single offspring. A defining length of the schema $H_1$ is 5. If the crossing point selected uniformly at random among the possible 6 sites, schema $H_1$ will be destroyed with the probability $p_e = \delta(H)/(l-1)=5/6$ (or it will survive with the probability $p_s=1-p_e=1/6$). Similarly, the schema $H_2$ has defining length 1. Consequently, the probability of its surviving is $p_s=5/6$. More generally, the probability of surviving for the schema $H$ is $p_s=1-\delta(H)/(l-1)$. Now the combined effect of the reproduction and crossover may be considered. Assuming independence of the operations one can obtain [1]:

$$m(H,t+1) = m(H,t) \frac{f(H)}{f} \left(1 - p_c \frac{\delta(H)}{l-1}\right),$$  \hspace{1cm} (7)

where $p_c$ is a probability of the crossover. It follows from (7), that schema $H$ grows or decays depending upon the multiplier, which depends on two things: whether the schema $H$ above or below the population average and whether the schema has relatively short or long defining length.

The last operator to consider is mutation. Mutation is a single alteration of the symbol in the single position with the probability $p_m$. Consequently, the schema $H$ will survive only when all of the specified positions survive themselves. Since each of the mutations is statistically independent, the probability of the schema surviving during mutation is $(1 - p_m)^o(H)$. For the small values of $p_m$ the surviving probability may be approximated $(1 - o(H)p_m)$. Thus, a particular schema $H$ receives an expected number of copies in the next generation under reproduction, crossover and mutation as given by equation:

$$m(H,t+1) = m(H,t) \frac{f(H)}{f} \left(1 - p_c \frac{\delta(H)}{l-1} - o(H)p_m\right).$$  \hspace{1cm} (8)

Now the fundamental theorem of genetic algorithms (Schemata Theorem) can be formulated based on equation (8) [1]: by using the selection, crossover and mutation of the standard genetic
algorithm, then short, low-order and above average schemata receive exponentially increasing trials in subsequent generations.

The short, low order and above average schemata are called building blocks. The fundamental theorem indicates that building blocks are expected to dominate the population. But this theorem does not answer the question, is it good or not, in terms of the original goal of function optimization. Although several studies have been done in which mathematical methods have been used to prove, that genetic algorithms find the best solution, but they were limited to some special cases only. From the practical point of view, many of functions encountered in the real world allow the optimum finding using genetic algorithms. In this thesis the numerically obtained waveguides has a strong waveguide field excited in the core layer compare with the waveguides, which are used now in practical applications. It gives rise to believe in practical value of the obtained results.
References

Appendix C. MS-Access “Multilayer Reflectivity” Database. Types and Procedures description

In this appendix a brief description of the procedures and types, used in the database is presented.

Data structure

All the data are stored in the following tables:

- PeriodicTable
- ScatteringFactor
- Graph
- Layer
- Material
- Materials

**PeriodicTable**

This table contains the information about the chemical elements, which are stored in the following fields:

- NUMBER – the order number of the element in the periodic table;
- NAME – English name of the chemical element;
- SHORTNAME – standard two character notation of the chemical element;
- WEIGHT – atomic weight of the element in atomic units;
- DENSITY – density of the element in its natural form.

An example of the record for helium is presented below.
PeriodicTable

<table>
<thead>
<tr>
<th>NUMBER</th>
<th>NAME</th>
<th>SHORTNAME</th>
<th>WEIGHT</th>
<th>DENSITY</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Helium</td>
<td>He</td>
<td>4.003</td>
<td>1.79E-05</td>
</tr>
</tbody>
</table>

ScatteringFactor

This table contains the tabulated values of the $f_1, f_2$ atomic scattering factors according to Henke et al. The table contains the following fields:

- EnergyValue – energy value in eV for which the data are tabulated.
- ElementID – the number of the chemical element in the periodic table, for which the data are stored.
- $f_1$, $f_2$ – tabulated values for the atomic scattering factors, corresponding to the chemical elements, defining the ElementID value, for energy EnergyValue.
- PrevEnergyValue – previous value of the energy, for which the data are stored. This field is added to simplify the search procedure.

An example of the record, which contains scattering factor values for helium (ElementID=2) and energy 749.928 eV.

<table>
<thead>
<tr>
<th>EnergyValue</th>
<th>ElementID</th>
<th>$f_1$</th>
<th>$f_2$</th>
<th>PrevEnergyValue</th>
</tr>
</thead>
<tbody>
<tr>
<td>748.928</td>
<td>2</td>
<td>2.02165</td>
<td>0.0104593</td>
<td>737.008</td>
</tr>
</tbody>
</table>

Graph

This table is to keep the temporary data of the calculated x-ray reflectivity coefficient. It contains the following fields:

- x – glancing angle, photon energy or wavelength, depending on the choice, that has been done in Multilayer Reflectivity utility;
- s-polarization – reflectivity coefficient for s-polarized beam, corresponding to the x value;
- p-polarization – reflectivity coefficient for p-polarized beam, corresponding to the x value.
An example of the record data:

<table>
<thead>
<tr>
<th>Layer</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0.18</td>
<td>0.982020512409356</td>
<td>0.9820250601106</td>
<td></td>
</tr>
</tbody>
</table>

**Layer**

This table contains the information about the waveguide layer for Multilayer Reflectivity utility. The fields are as follows:

- **layerID** – the global number of the layer in the table. This field is used layer identification.
- **structID** – the order number of the periodic structure, to which the layer belongs.
- **thickness** – the thickness of the layer in angstrom.
- **layerNum** – the order number of the layer in period.
- **density** – layer material density in g/cm³.

The current version of the database operates with the waveguides, which consist of several periods of the one periodic structure. Consequently, this table is temporary of no usage.

**Materials**

This table contains the captions of the materials groups, which are used in the database. The fields are as follows:

- **GroupID** – the global order number of the materials group. This fields is used for the group identification.
- **GroupName** – caption of the group of materials.

An example of the record in this table is presented below.

<table>
<thead>
<tr>
<th>Materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>GroupID</td>
</tr>
<tr>
<td>1</td>
</tr>
</tbody>
</table>

**Material**

This table contains the information about the various materials for further usage in the calculations. The fields of the table are as follows:
✓ MaterialID – the global order number of material in the table for identification purposes.
✓ MaterialName – caption of material. This field can be empty
✓ MaterialChemExp – chemical composition of material. If the composition is a decimal fraction, then the dot ‘.’ is used as a decimal separator. If integer part is zero, then ‘0’ is omitted.
✓ MaterialDensity – density of material in g/cm³.
✓ GroupID – order number of the materials group, material belongs to. Group name is substituted automatically.

An example of the record for Zerodur, which belongs to the ‘Presented at CXRO homepage’ group of materials, is presented below.

<table>
<thead>
<tr>
<th>MaterialID</th>
<th>Name</th>
<th>Chemical Expression</th>
<th>Density</th>
<th>GroupID</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>Zerodur</td>
<td>Si.56Al.5P.16Li.04Ti.02Zr.02Zn.03O2.46</td>
<td>2.53</td>
<td>Presented at CXRO homepage</td>
</tr>
</tbody>
</table>

Types and procedures, used for calculations

Complex numbers
X-ray reflection coefficient calculation implies the treatment of the complex numbers. MS-VBA does not contain the built-in complex number arithmetic, so all the procedures for complex number treatment should be defined manually. Complex numbers are of tComplexN type:

```vba
Public Type tComplexN
    Re As Double
    Im As Double
End Type
```

MyDiv(z1, z2, z3)
Complex number z1 is divided by the complex number z2 and result is stored into the complex number z3.
Sub MyDiv(z1 As tComplexN, z2 As tComplexN, z3 As tComplexN)
    Dim znam As Double
    znam = z2.Re * z2.Re + z2.Im * z2.Im
    z3.Re = (z1.Re * z2.Re + z1.Im * z2.Im) / znam
    z3.Im = (z1.Im * z2.Re - z1.Re * z2.Im) / znam
End Sub

MyExp(z1, z3)
The exponent $e^{z1}$ of the complex number $z1$ is calculated and result is stored into the complex number $z3$.

Sub MyExp(z1 As tComplexN, z3 As tComplexN)
    z3.Re = Exp(z1.Re) * Cos(z1.Im)
    z3.Im = Exp(z1.Re) * Sin(z1.Im)
End Sub

MySqrt(z1, z3)
The square root of the complex number $z1$ is calculated and result is stored into the complex number $z3$.

Sub MySqrt(z1 As tComplexN, z3 As tComplexN)
    Dim a#, b#
    a = z1.Re
    b = z1.Im
    z3.Re = Sqr(Sqr(a * a + b * b) + a) / Sqr(2)
    z3.Im = -Sqr(Sqr(a * a + b * b) - a) / Sqr(2)
End Sub

MySumm(z1, z2, z3)
A sum of the complex numbers $z1$ and $z2$ is calculated and result is stored into the complex number $z3$.

Sub MySumm(z1 As tComplexN, z2 As tComplexN, z3 As tComplexN)
    z3.Re = z1.Re + z2.Re
    z3.Im = z1.Im + z2.Im
End Sub
**MyMult(z1, z2, z3)**

Complex number $z_1$ is multiplied by the complex number $z_2$ and result is stored into the complex number $z_3$.

```vba
Sub MyMult(z1 As tComplexN, z2 As tComplexN, z3 As tComplexN)
    z3.Re = z1.Re * z2.Re - z1.Im * z2.Im
    z3.Im = z1.Re * z2.Im + z1.Im * z2.Re
End Sub
```

**MyMinus(z1, z2, z3)**

Complex number $z_2$ is taken from the complex number $z_1$ and result is stored into the complex number $z_3$.

```vba
Sub MyMinus(z1 As tComplexN, z2 As tComplexN, z3 As tComplexN)
    z3.Re = z1.Re - z2.Re
    z3.Im = z1.Im - z2.Im
End Sub
```

**Refractive index and reflectivity coefficient calculation**

The following types are used for the calculations.

**ElementRecord**

Variables of this type are used to keep the order number of chemical element in periodic table (eAtomNumber) and its fraction in the chemical composition (eAmount).

```vba
Public Type ElementRecord
    eAtomNumber As Byte
    eAmount As Double
End Type
```

**tFormula**

Variables of this type are used to keep the information about the chemical composition of the material, namely amount of the chemical elements in the composition (ElementAcount) and array ChemExpression(), each element of which keeps the information about the fraction of
particular element.

    Public Type tFormula
        ElementAcount As Integer
        ChemExpression() As ElementRecord
    End Type

**LayerData**

Variables of this type are used to keep the parameters of particular layer in the waveguide: width, density, chemical expression (Formula), complex refractive index (beta, delta, n) and factors for recurrent formula (F,a)

    Public Type LayerData
        Width As Double
        Density As Double
        Formula As tFormula
        beta As Double
        delta As Double
        n As tComplexN
        F As tComplexN
        a As tComplexN
    End Type

**LayerInputData**

Variables of this type are used to keep the initial information about the particular layer. Three strings contain the values, which were entered into the input fields of the corresponded utility window. Namely, layer thickness (strWidth), chemical composition (strChemExpression) and density (strDensity).

    Public Type LayerInputData
        strWidth As String
        strDensity As String
        strChemExpression As String
    End Type

**Input data treatment procedure source code**

Sub TransExp(s As String, wForm() As tFormula, errors As Boolean, errortext$)
    Dim works, el As String
    Dim p As Boolean
    Dim j, i, eIN As Integer
Dim rsPeriod As Recordset
Set rsPeriod = CurrentDb.OpenRecordset(“PeriodicTable”)  
rsPeriod.Index = “SHORTNAME”
elN = 0

With wForm(1)
ReDim .ChemExpression(1 To Len(s)) As ElementRecord
While s <> “”
    works = “”
j = 1
p = True
While p
    works = Right(s, j)
    Select Case Asc(Left(works, 1))
        Case 65 To 90
            p = False
        Case Else
            j = j + 1
            If (j > Len(s)) Then p = False
    End Select
Wend
s = Left(s, Len(s) - j)
j = 1
If Len(works) > 1 Then
    Select Case Asc(Mid(works, 2, 1))
        Case 97 To 122
            j = 2
    End Select
End If
el = Left(works, j)
works = Mid(works, j + 1)
Select Case Left(works, 1)
    Case “”
        works = “1”
    Case “,” “.,” “,”
        works = “0” & works
End Select
i = InStr(works, “.”)
If i <> 0 Then works = Left(works, i - 1) & "," & Mid(works, i + 1) 
' inserting
rsPeriod.Seek ",", el
If (rsPeriod.NoMatch) Or (Not (IsNumeric(works))) Then GoTo Error_exit

elN = elN + 1
.ChemExpression(elN).eAtomNumber = rsPeriod![NUMBER]
.ChemExpression(elN).eAmount = CDbI(works)
Wend
ReDim Preserve .ChemExpression(1 To elN) As ElementRecord
.ElementAcount = elN
End With

exit_sub:
rsPeriod.Close
Exit Sub

Error_exit:
errortext = "Incorrect chemical expression!"
errors = True
rsPeriod.Close
End Sub

Optical constants calculation procedure source code
Sub OpticCalc(wForm() As tFormula, ByVal wenerg#, ByVal wdens#, ByRef wdelta#, ByRef wbeta#)
Dim s$, wk%
Dim s1$, s2$, s3$
Dim rsPeriod As Recordset, rsScatFac As Recordset, rsScatFac2 As Recordset
Dim i%, iElementID%
Dim dSumAlfaA#, dAlfa#
Dim dMult#, dPrevEnerg#, dEnerg#
Dim dF1#, dF2#, dPrevF1#, dPrevF2#, f1#, f2#
Dim dN#, dSumN1#, dSumN2#
Dim ws1$, ws2$, ws3$

Set rsPeriod = CurrentDb.OpenRecordset("PeriodicTable")
s1 = "SELECT * FROM [ScatteringFactor] WHERE 
(([ScatteringFactor].[PrevEnergyValue]<" 
s2 = ") AND ([ScatteringFactor].[EnergyValue]>=" 
s3 = ")) ORDER BY [ScatteringFactor].[ElementID]"
ws1 = "SELECT * FROM [ScatteringFactor] WHERE 
(([ScatteringFactor].[EnergyValue]=" 
ws2 = ") AND ([ScatteringFactor].[ElementID]=" 
ws3 = "))"
Dim Re, hc, mc12, pi As Double
Re = 2.81794092E-13
hc = 0.00012398424
mc12 = 1.6605402E-24
pi = 3.14159265358979
dMult = Re / mc12 * hc * hc / pi / 2
'415.72127305
dSumAlfaA = 0
rsPeriod.Index = "PrimaryKey"

With wForm(1)
For i = 1 To .ElementAcount
iElementID = .ChemExpression(i).eAtomNumber
dAlfa = .ChemExpression(i).eAmount
rsPeriod.Seek ",", iElementID
dSumAlfaA = dSumAlfaA + dAlfa * rsPeriod.Fields("WEIGHT")
Next i
dN = wdens / dSumAlfaA

dSumN1 = 0
dSumN2 = 0

For i = 1 To .ElementAcount
iElementID = .ChemExpression(i).eAtomNumber
dAlfa = .ChemExpression(i).eAmount
Set rsScatFac = CurrentDb.OpenRecordset(s1 + Str(wenerg) + s2 + Str(wenerg) + 
ws2 + CStr(iElementID) + ws3)
dPrevEnerg = rsScatFac.Fields("PrevEnergyValue")
dEnerg = rsScatFac.Fields("EnergyValue")
dF1 = rsScatFac.Fields("f1")
dF2 = rsScatFac.Fields("f2")

Set rsScatFac2 = CurrentDb.OpenRecordset(s1 + Str(dPrevEnerg) + s2 +
Str(dPrevEnerg) + ws2 + CStr(iElementID) + ws3)
dPrevF1 = rsScatFac2.Fields("f1")
dPrevF2 = rsScatFac2.Fields("f2")
f1 = (dPrevF1 - dF1) * (wenerg - dPrevEnerg) / (dEnerg - dPrevEnerg) + dPrevF1
f2 = (dPrevF2 - dF2) * (wenerg - dPrevEnerg) / (dEnerg - dPrevEnerg) + dPrevF2
dSumN1 = dSumN1 + dAlfa * f1
dSumN2 = dSumN2 + dAlfa * f2
rsScatFac.Close
rsScatFac2.Close

Next i
End With

wdelta = dMult * dN * dSumN1 / wenerg / wenerg
wbeta = dMult * dN * dSumN2 / wenerg / wenerg

rsPeriod.Close
End Sub

X-ray reflectivity coefficient calculation for s-polarization. Function source code

Function GetIntensRat(ByVal fi#, ByVal lambda#, ByVal alper%, ByVal NPer%,
Pl() As LayerData) As Double

's-polarization!
Dim p#, q#, Azv#, Bzv#
Dim nk As tComplexN, cosFk As tComplexN, fch As tComplexN, fzn As tComplexN
Dim F As tComplexN, R As tComplexN, D As tComplexN, Z As tComplexN
Dim i%, j&, i_pred%, part%
Dim pi#
pi = 4 * Atn(1)
fi = (90 - fi) * pi / 180
'lambda = 12398.424 / energ
For \( j = 2 \) To alper + 2
   With Pl(j)
      fch.Re = .n.Re - Sin(fi)
      fch.Im = .n.Im
      fzn.Re = .n.Re + Sin(fi)
      fzn.Im = .n.Im
      Call MyMult(fch, fzn, nk)
      Call MySqrt(nk, .F)
   End With
Next j
Pl(1).F.Re = Cos(fi): Pl(1).F.Im = 0

For \( j = 2 \) To alper + 1
   ' Pi = 4*Atn(1)
   With Pl(j)
      nk.Re = 0
      nk.Im = -16 * Atn(1) * .Width / lambda
      Call MyMult(nk, .F, fch)
      Call MyExp(fch, .a)
   End With
Next j
Pl(1).a.Re = 1: Pl(1).a.Im = 0
Pl(alper + 2).a.Re = 1: Pl(alper + 2).a.Im = 0

R.Re = 0: R.Im = 0

For \( j = \) alper * NPer + 2 To 2 Step -1
   Select Case j
      Case 2
         i = 2
         i_pred = 1
      Case alper * NPer + 2
         i = alper + 2
         i_pred = alper + 1
      Case Else
         i = ((j - 1) Mod alper) + 1
      If i = 1 Then i = alper + 1
         i_pred = i - 1
      If i_pred = 1 Then i_pred = alper + 1
End Select

Call MyMinus(Pl(i_pred).F, Pl(i).F, fch)
Call MySumm(Pl(i_pred).F, Pl(i).F, fzn)
Call MyDiv(fch, fzn, F)

Call MySumm(F, R, fch)
Call MyMult(F, R, fzn)

fzn.Re = fzn.Re + 1
Call MyDiv(fch, fzn, nk)
Call MyMult(Pl(i_pred).a, nk, R)

Next j
GetIntensRat = R.Re * R.Re + R.Im * R.Im
End Function

X-ray reflectivity coefficient calculation for s-polarization. Function source code

Function GetIntensRatP(ByVal fi#, ByVal lambda#, ByVal alper&, ByVal NPer%, Pl() As LayerData) As Double

' p-polarization!
Dim p#, q#, Azv#, Bzv#
Dim nk As tComplexN, cosFk As tComplexN, fch As tComplexN, fzn As tComplexN
Dim F As tComplexN, R As tComplexN, D As tComplexN, Z As tComplexN
Dim i%, j& , i_pred%
Dim pi#
pi = 4 * Atn(1)
fi = (90 - fi) * pi / 180
'lambda = 12398.424 / energ

For j = 2 To alper + 2
With Pl(j)
    fch.Re = .n.Re - Sin(fi)
fch.lm = .n.lm
fzn.Re = .n.Re + Sin(fi)
fzn.lm = .n.lm
Call MyMult(fch, fzn, nk)
Call MySqrt(nk, fch)
Call MyMult(.n, .n, fzn)
Call MyDiv(fch, fzn, .F)
End With
Next j
Pl(1).F.Re = Cos(fi): Pl(1).F.Im = 0

For j = 2 To alper + 2
' Pi = 4*Atn(1)
With Pl(j)
nk.Re = 0
nk.Im = -16 * Atn(1) * .Width / lambda
Call MyMult(nk, .F, fch)
Call MyMult(fch, .n, fzn)
Call MyMult(fzn, .n, fch)
Call MyExp(fch, .a)
End With
Next j
Pl(1).a.Re = 1: Pl(1).a.Im = 0
Pl(alper + 2).a.Re = 1: Pl(alper + 2).a.Im = 0

R.Re = 0: R.Im = 0
For j = alper * NPer + 2 To 2 Step -1
Select Case j
Case 2
  i = 2
  i_pred = 1
Case alper * NPer + 2
  i = alper + 2
  i_pred = alper + 1
Case Else
  i = ((j - 1) Mod alper) + 1
  If i = 1 Then i = alper + 1
  i_pred = i - 1
  If i_pred = 1 Then i_pred = alper + 1
End Select
Call MyMinus(Pl(i_pred).F, Pl(i).F, fch)
Call MySumm(Pl(i_pred).F, Pl(i).F, fzn)
Call MyDiv(fch, fzn, F)
Call MySumm(F, R, fch)
Call MyMult(F, R, fzn)
fzn.Re = fzn.Re + 1
Call MyDiv(fch, fzn, nk)
Call MyMult(Pl(i_pred).a, nk, R)
Next j
GetIntensRatP = R.Re * R.Re + R.Im * R.Im
End Function