**Name of the course:** “X-Ray Spectroscopy and X-Ray Diffraction”

**Department responsible for the course or equivalent:** Dpt of Chemistry

**Lecturer (name, academic title, e-mail):** Dr. **V.B. Nalbandyan (**[vbn@sfedu.ru](mailto:vbn@sfedu.ru)**), Dr. A.N.Morozov (**[mrzv\_61@mail.ru](mailto:mrzv_61@mail.ru)**)**

**Semester when the course unit is delivered:** 2

**Teaching hours per week:** 4

**Level of course unit:** Master level.

**ECTS credits:** 5

**Admission requirements:**

– basic knowledge of chemistry, physics and mathematics (bachelor level);

– theory of symmetry, part of the preceding course “General Laws in Chemistry”.

**Course objectives (aims):**

X-ray methods play a major role in modern chemistry, physics and materials science, but are usually underrepresented in chemical curricula. This course combines two main branches of X-ray methods. X-ray spectroscopy, besides emission spectroscopy, a major method of elemental analysis (both total and local), includes X-ray absorption spectroscopy (XAS) providing power tools for studying local atomic structure and electron structure of matter. X-ray diffraction (XRD) methods include determination of crystal and molecular structure of solids, phase analysis studies in various fields of science and industry (from cement to pharmaceuticals) and several more specific techniques.

The goals of the course are:

To inform students on the basic principles, current status, actual problems and trends in the development of X-ray instrumentation and techniques;

To make students able to extract structural information from the EXAFS and XANES data;

To make students able to develop the structure of chemical compounds by means of XAS methods and perform original experimental investigations using powder XRD.

**Course contents:**

**Module 1. X-Ray Spectroscopy**

1.1. Ranges of electromagnetic radiation. X-ray tubes. Synchrotron radiation. Advantages and disadvantages of different types of emitters. Synchrotron device. Ondulators and Wiglers.

1.2. Some basic concepts of photoelectrons, interference, diffraction, coherence, luminescence, fluorescence, internal conversion.

1.3. Elastic and inelastic scattering. Coherent x-ray scattering. Compton scattering.

1.4. The photoelectric effect. Auger spectroscopy. A comparative analysis of Auger processes and x-ray fluorescence. Pairing probabilities of both processes.

1.5. X-ray fluorescence.

1.6. Continuous and characteristic X-Ray spectra. Moseley's law.

1.7. Comparative analysis of different kinds of effects of X-ray radiation on the atom of matter. Components of the scattered x-rays.

1.8. X-ray attenuation. Linear and mass absorption coefficients. Their dependence on the X-ray wavelength and atomic number of the absorbing element.

1.9. Atomic absorption of X-ray quantum.

1.10. Physical basis of EXAFS spectroscopy; main limitations of the method.

1.11. The curves of X-ray absorption. K-, L- and M- edges.

1.12. Spin-orbital interaction and its magnitude.

1.13. Energy of absorption edges. Fine structure of K-edge absorption and its nature. EXAFS and XANES ranges.

1.14. Stages of X-ray scattering in EXAFS and XANES. Interference effects.

1.15. EXAFS formula. The concept of the wave vector. Equation for EXAFS-function (k) for S-ionization levels. The characteristic components of the equation. Debye-Waller factor. Model of approximation: muffin-tin (Mt) potential.

1.16. Extracting the structural information from EXAFS spectra of compounds.

1.17. The techniques of the EXAFS experiment.

1.18. Methods of EXAFS-function extracting from the experimental absorption spectrum. Steps of EXAFS function allocation.

1.19. Overview of the Fourier transformation method. Direct and inverse transformation. Types of Fourier transformations. Multidimensional expressions (MDX), discrete, "window" transformation (principle), Fourier series. Sampling frequency. Kotelnikov's theorem. Problems of application of Fourier transformation in the spectral analysis. "Window" conversion. Types of "window" functions and their use in the analysis of a continuous spectrum.

1.20. Radial distribution function.

1.21. Achievements and advantages of EXAFS over other methods.

1.22. Informational content of the method.

1.23. Principles of XANES. Single and multiple scattering. The path of the wave scattered in terms of multiple scattering for four-points fragment of molecules. Historical background on the development of EXAFS and XANES. Ridberg's state of the atom.

1.24. An example of accounting of multiple scattering in a cluster. Problems in the study of multiple scattering: computational and basic ones. Advantages and disadvantages compared with XANES EXAFS.

1.25. Steps of obtaining the experimental data. Basic registration scheme.

1.26. Examples of using EXAFS and XANES spectroscopy: the use of absorption bands' maximum's mobility for measurement of ionic-covalence relationship of chemical bond; the use of EXAFS for identification of sulphur compounds in the analysis of natural hydrocarbons; EXAFS method being used for study of mononuclear coordination compounds: study of intercalates, valence states of metal and coordination mode; EXAFS method for study of binuclear coordination compounds: determination of local structure in binuclear metal-chelates of copper (I) and copper (II); determination of the metal-to-metal distance in the complexes with phosphine based derivatives. Common research tasks of XANES. Dependency types range from valence state of metal and ligand environment. The use of EXAFS and XANES for exploring the catalysts.

**Module 2. Fundamentals of X-Ray Diffraction**

2.1. Two conditions for obtaining the Bragg maximum. Three variants of experimental fulfilling the Bragg condition. Renaissance of the Laue method.

2.2. Film and counter techniques. Point and position-sensitive detectors. Methods of obtaining monochromatic or quasi-monochromatic radiation.

2.3. Rotation and oscillation patterns. Weissenberg and precession methods. Single-crystal diffractometers. Assessment of crystal quality using the Laue method and rocking curves.

2.4. Powder diffraction: Debye, Guinier and Bragg-Brentano geometry.

2.5. Requirements for obtaining reproducible patterns with the Bragg-Brentano scheme: slits, sample area, sample thickness, particle size and crystal orientation. Zero-background holders.

2.6. Random and systematic errors in measuring peak positions. Sample displacement and sample transparency. Elimination of the systematic errors using internal and external standards, extrapolation and auto-correction methods.

2.7. High-temperature and low-temperature attachments.

2.8. Application of XRD phase analysis for studying chemical reactions, phase transitions, phase relations, and for examination of various samples in mineralogy, industry, medicine, health and forensic studies.

2.9. Powder Diffraction File (PDF 2) and its Subfiles. Origins of the diffraction data, estimation of their reliability, data format, typical errors.

2.10. Quantitative phase analysis. Use of internal standards, small additives and relative intensity ratios from the PDF.

2.11. Problem of indexing powder patterns. Indexing with known approximate parameters. Indexing by analogy. Ab initio indexing: manual methods and automatic programs.

2.12. Systematic absences: determination of Bravais cell and possible space groups.

2.13. Verification of indexing: De Wolf and Smith-Snyder figures of merit.

2.14. X-ray and experimental density. Pycnometry and hydrostatic weighing.

2.15. Textures of alignment, deformation and crystallization. Textures in ferroics. Methods of evaluation and reduction of texture in powder XRD.

2.16. Factors affecting peak width. Spectral and instrumental broadening. Broadening due to dislocations, point defects and small size of blocks. Separation of different contributions to the observed peak width.

**Module 3. Structural analysis**

3.1. What is to be determined? Description of a structure in terms of space group, lattice parameters, atomic coordinates, thermal displacement parameters and site occupancies.

3.2. Atomic scattering factors and thermal parameters.

3.3. Structure factors, Fourier synthesis and Fourier maps.

3.4. XRD intensity in single-crystal and powder experiments.

3.5. The phase problem and Patterson function.

3.6. Structure solution using positions of heavy atoms.

3.7. Structure refinement and R-factors.

3.8. Use of anomalous scattering for determination of absolute configurations and discrimination between atoms in different oxidation state (e.g., Fe2+ and Fe3+) with precise adjustment of the wavelength from the synchrotron source.

3.9. X-ray free electron lasers (XFEL) and serial femtosecond crystallography.

3.10. Basic idea of the powder full-profile analysis (the Rietveld method).

3.11. Peak shapes.

3.12. Approximation of the background.

3.13. Le Bail method.

3.14. Profile refinement, R-factors and goodness of fit.

3.15. Refinement with additional limitations (e.g., hard body model)

3.16. Non-X-ray diffraction methods. Comparison of electron, X-ray and neutron diffraction: instrumentation and availability, penetration depth and sample size, possible sample environments, accuracy of the wavelengths, angles and lattice parameters, scattering factors vs. atomic numbers, angular dependence of intensity, sensitivity to the spin structure. Advantages of combined use of different methods.

3.17. Constant wavelength and time-of-flight neutron diffraction.

**Learning outcomes:**

It is expected that a student finally

– will be well informed in the basic principles, current status, actual problems and trends in the development of X-ray instrumentation and techniques;

– will be able to extract structural information from the EXAFS and XANES data;

– will be ready to solve problems and perform original experimental investigations using powder XRD.

**Planned learning activities and teaching methods –** lectures with a variety of examples and practice. Laboratory training includes sample preparation (solid-state or wet or semi-wet method), ion exchange studies and electrical measurements.

Individual work (self-education) includes reading textbooks, monographs and original papers, problem solutions, interpretation of experimental data (e.g., analysis of structural data) and preparing a report on a specific problem (or a phenomenon, method, material or class of materials), to be delivered and defended in a seminar.

**Assessment methods and criteria:** examination