

History of Crystallography in the Region of Former Czechoslovakia

Crystallographic milestones, leading figures and groups

Crystallography has long and rich tradition in the region of former Czechoslovakia. It was cultivated in the framework of two principal Czech scientific organizations, Charles University (founded in 1348), and Academy of Sciences (formerly Academy of Sciences and Arts, founded in 1770).



Johannes Kepler, known as a famous astronomer, during his stay in Prague (1600-1612) wrote a paper “On hexagonal snow flake” as a New Year present to his friend and famous diplomat Jan Matouš Wacker von Wackenfels. This paper is the oldest written document of new era crystallography and deals with the outer symmetry seen in morphology of crystals as a reflection of inner symmetry of matter, without any idea about the nature of building elements at that time. Searching an origin of hexagonal symmetry of snow Kepler thought about the closest packing of equal sized solid spheres. He also discussed even more general space orderings and introduced the term coordination number as a number of neighbour spheres, which are in contact with the central one. The trial to explain the shape of snow flakes from building of water particles symmetrically arranged in space can be regarded as an origin of theory of crystal lattice. He also mentioned the constant ratio of angles among equivalent faces and edges of crystals. In 2014, the work was issued by Charles University in Latin-Czech bilingual form (translated from Latin) and by Oxford University press in Latin-English form.



Old Czech family of German chemist Friedrich August Kekulé, later **Kekulé von Stradonitz** (1829-1896), came from a village located near Slaný in Bohemia. He published a paper in French suggesting that the structure of benzene contained a six-membered ring of carbon atoms with alternating single and double bonds. The next year he published a much longer paper in German on the same subject. Kekulé used evidence that had accumulated in the intervening years—namely, that there always appeared to be only one isomer of any monoderivative of benzene, and that there always appeared to be exactly three isomers of every derivative—now understood to correspond to the ortho, meta, and para patterns of arene substitution—to argue

in support of his proposed structure. Kekulé’s symmetrical ring could explain these curious facts, as well as benzene’s 1:1 carbon-hydrogen ratio.



Crystallographer and mineralogist **Bohuslav Ježek** (1877-1950) was a pioneer of “roentgenometry” of crystals. The first Laue patterns he obtained in collaboration with famous physicist Karel Teige and they introduced the first lecture at Faculty of Science, Charles University, Prague in 1922/23 – *Symmetry and roentgenometry of crystals*, followed by *Atomic theory of crystal lattices* and *Individual X-ray works*. He also wrote the first textbook *Outline of Roentgenometry of Crystals* (1923).

Václav Dolejšek (1895-1945) was director of Spectroscopic institute of Charles University. Since 1934 he worked in Physical research of Škoda factory (non-destructive testing, residual stresses, phase analysis of alloys, textures). He also systematically studied X-rays. He discovered X-ray spectral lines of N-series of uranium, thorium and bismuth.



Adéla Kochanovská (1907-1985), one of the students of prof. Dolejšek has enormous importance for the Czechoslovak crystallography and for industrial applications of the X-ray diffraction in particular. She was the head of the X-ray microstructure analysis department in the Research Institute of Physics of Skoda Works since 1935. Several years later this unit was integrated into the Institute of Physics of Czech Academy of Sciences. She continued work there till 1968, and partly also in the Czech Technical University in Prague (Faculty of nuclear sciences and physical engineering). She wrote text books “*Examination of fine structure of materials by Roentgen*

rays” (1943), “*Radiocrystallography*” (1952) and “*Structural crystallography*” (1964). Her influence on growth of new generation of crystallographers in former Czechoslovakia was enormous. Attached figure shows prof. Kochanovská together with the first commercially produced X-ray diffraction unit in our country, generator Mikrometa made by Chirana.

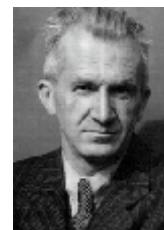
The first independent experiments with **X-rays** were performed in Prague by Ivan Pulyj (Pulyui, 1845-1918), Ukrainian professor of physics and electrical engineering at Prague Technical University, who developed an X-ray emitting device as early as 1881. The device became known as the Pulyui lamp and it was mass-produced for a period.



The name of **Friedrich Reinitzer** (1857- 1927) is connected with the discovery of liquid crystals. Reinitzer came from a Prague-German family and studied chemistry on that time at German technical university in Prague. After active work at the university as a docent he moved to Gratz in Austria. In 1888 he published the paper *Beiträge zur Kenntniss des Cholesterins in Monatshefte für Chemie und verwandte Wissenschaften*. His research was

mainly based on microscopic observations of thermal properties and structural changes.

Jan Böhm (1895-1952), physical chemist, worked in Berlin and Freiburg but later returned to Prague in 1935 to escape from Nazis. He constructed a goniometer later called Weissenberg-Böhm (*Z. Phys.* 39 (1926) 557) based on Weissenberg idea of rotating crystal. He also investigated hydroxides and böhmite was named after him.



Interesting historical data

First dissertations:

Interference of X-Rays (1917, Rudolf Šimůnek)
Crystallographic investigations of some compounds (1920, Anna D. Kašparová)

First monographies:

Roentgen X-Rays (1925, Václav Posejpal)
Roentgenography of metals and alloys (1947, Petr Skulari)

First international conference on the application of X-rays in industry in Czechoslovakia, 28.11.–1.12. 1945.

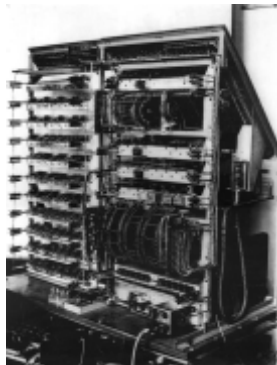


After the break of Habsburg monarchy in 1918, Czechoslovakia was an industrially advanced country and thus X-rays were used intensively for testing of materials in steel production and machinery. X-ray static and mobile instrumentation for medical purposes and for material testing was produced by **CHIRANA** Company founded by Miroslav Vinopal in 1922. The company produced X-ray tubes, generators and powder goniometers, Debye-Scherrer and Guinier cameras for structure research in period 1955-1980. Nowadays, Chirana produces X-ray equipment for medical purposes only.



Allan Línek (1925-1984) from the Institute of Physics of Czech Academy of Sciences in Prague was one of the most active crystallographers in our country after the 2nd world war. His main interest was in structure solution and computerization of crystallographic calculations. Determination of structure of Ethylene-diamine Tartarate Among belongs to his

best achievements. The structural model of this compound was a part of Czechoslovak pavilion on the World Exhibition in Brussels in 1958. His ideas were also most important in construction of the first Czech computer *Eliška* dedicated to structure solution computing. One of the new versions of this computer is now shown in the National Technical Museum in Prague.



Línek was very active in many national and international scientific organizations. From 1959 served as the secretary of the National Committee for Crystallography. He was involved in the IUCr for many years as a member of the Commission on Crystallographic Computing 1963-1966, member of the Executive Committee 1966-1972, Chairman of the Sub-Committee on the Union Calendar 1969-1972, and the Union's representative on the IUPAP Commission on the Structure and Dynamics of Condensed Matter from 1978.

The first crystal structure was solved in Brno in the group of Antonín Šimek. The structure of TeO_2 was published by B. Stehlík and L. Balák (*Chemické zvesti*, 2 (1948)). The **first crystal structure published in international journal** was solved by K. Toman (*The structure of NiSi*, *Acta Cryst.* 4, 1951, 462), the head of the crystallography group in the Institute of Macromolecular Chemistry of the Academy of Sciences of the CR.



His successor in the period 1969–1992, **Karel Huml**, working also in crystal structure analysis, and statistical methods was the president of the European Crystallographic Committee (1991–1994). He was deeply involved in work for computing commission of the IUCr (1971-1997) and chaired of the Summer School of Crystallographic Computing in Praha 1975 (240 participants).



Růžena Bubáková (1917-2005), colleague of Allan Línek, gave the first experimental evidence of the validity of the dynamical X-ray diffraction theory. Publications Bubáková – Drahokoupil – Fingerland (R. Bubáková, J. Drahokoupil, A. Fingerland, Czech. *J. Phys B.*, 11, (1961), 199; 12, (1962), 764) on the theory and applications of the double and triple crystal diffractometers came to be one of the essential pillars of the field known at the present as high resolution X-ray diffraction.

Later she focused her research to the double crystal X-ray diffraction topography and many beam crystal diffraction.



Slavomír Ďurovič (1929) from the Institute of Inorganic Chemistry of Slovak Academy of Sciences in Bratislava, has shown that structure of a large number of materials can be described in terms of stacking of layers of atoms and extensively discussed the ways how to do this and how to describe such structures (OD).

His colleagues, Emil Makovický and

Vlado Kupčík later emigrated and become professors in Copenhagen and Göttingen, respectively.

Boris Gruber, a mathematician from the Faculty of Mathematics and Physics of Charles University in Prague, found the way how to introduce unique primitive cell of a lattice using significant geometrical features based on extremal principles (e.g. *Acta Cryst.* (1989). A45, 123-131).

Vojtěch Kopský (1936-2016) from the Institute of Physics in Prague was famous with his deep insight into the field of subgroups of crystallographic space groups of symmetry, for example sectional layer groups or penetration rod groups.

Fero Hanic (1927), close friend of Línek, was at the same time leading crystallographic person in Slovakia. His interests were very broad, single crystal diffractometry, powder methods, high temperature crystallography, instrumentation, etc.



The attached figure shows his excellent precession chamber which differed from the Buerger model by some patented construction details and was produced commercially.



Milena Polcarová (1931-2008), another scientist of the Institute of Physics in Prague, was internationally recognized expert in the field of X-ray diffraction topography. Her discovery of previously unobserved magnetic domain structures [M. Polcarová, A. R. Lang, *Appl.Phys.Let.*,1 (1962), 13] got into textbooks. The figure illustrates magnetic domains in Fe- 6 at.% Si made by M. Polcarová using the Lang topography method.



Several crystallographic groups appeared from 50s to 70s of the last century working in physics, materials science, chemistry and also biocrystallography

Mineralogy had long tradition in the Czech Republic. **Mineralogical institute of Charles University** was restored after the World War II by **J. Novák** (1902-1971) who worked with V. M. Goldschmidt in Göttingen and with Charles Mauguin in Paris. He was the first representative of Czechoslovakia at the meeting of crystallographers after the World War II in London, where decision on creation of the IUCr was accepted. He was then also the chair of National Committee of the IUCr.

Among other persons of the institute, **Milan Rieder**, should be mentioned, whose main interests for many years were the study of micas and precession diffraction. Mineralogic collection was established already in 1835 by F. X. M. Zippe and significantly improved by **Augustin Ondřej** (1887-1956) in **Institute of Chemical Technology in Prague**. It has 30 250 mineral samples and it is also remarkable by completeness of several mineral collections from different genetic provinces of the World.

Milan Rieder



Chemical crystallography was developed at the **Faculty of Science in Brno** mainly by **Zdirad Žák**, at the **Faculty of Science of Charles University in Prague (J. Loub)**, **Institute of Chemical Technology in Prague (B. Kratochvíl)** and **Faculty of Science in Olomouc (J. Kameníček)**.



Michal Dunaj-Jurčo



Josef Loub

Modern coordination chemistry in Slovakia was developed at the **Chemical Faculty of Slovak Technical University in Bratislava** since 1955 by J. Gažo and main attention was given to Cu complexes. Structural studies were performed mainly by **Ján Garaj** and **Michal Dunaj-Jurčo**.

X-ray structure analysis was one of the basic activities of solid state physics in the **Faculty of Mathematics and Physics, Charles University in Prague** since 1951 and followed the work of A. Kochanovská in microstructure of polycrystalline materials. The group leader **J. Šedivý** established long-time collaboration with the industry of powder metallurgy. His successor, **V. Valvoda**, extended largely the topics studied to deformation electron densities, diffusion, thin films and multilayers, high-temperature superconductors. He was the secretary of the Crystallographic Association and he also wrote textbooks on crystallography and structure analysis.



Václav Valvoda

Another group following the work of A. Kochanovská was at the **Faculty of Nuclear Engineering, Czech Technical University**, which became known first of all by the work in materials research, in particular, residual stresses and by **I. Kraus** who wrote books on this topics as well as fundamental textbooks on crystallography and methods of X-ray analysis. Laboratory of Neutron Diffraction was headed by **S. Vratislav**.



Ivo Kraus

Materials research, stress and microstrain measurements were developed also at the **Faculty of Mechanical Engineering, Technical University of Brno** since 1956 and it was later connected with the name of **Antonín Buchal**.

Zdeněk Weiss (1942-2005), was the main person of crystallography in **Ostrava** where he founded **Institute of Materials Chemistry (Technical University)**. The research was quite broad from fundamental crystallography and mineralogy to materials research with applications in ecology (nanomaterials based on clay minerals used as sorbents) and many industrial branches (construction materials based on nanocomposite polymer-silicate).



History of **neutron diffraction at the Institute of Nuclear Physics, Academy of Sciences in Řež near Prague** began in 1965 (R. Michalec, B. Chalupa, J. Vavřín, J. Vávra). The first programmes focused on diffraction was Diffraction on ferromagnetic perfect single crystals and Neutron diffraction on ultrasound generated vibrating crystals, later study of magnetic properties of uranium compounds. In 1983, the first SANS experiments were performed and in 1986-87 neutron interferometry was developed and diffraction on elastically deformed perfect single crystals



Important contribution of crystallography in Brno was brought into physics. It was developed at the **Institute of Physics, Faculty of Science**. **Martin Černožorský** (later Institute of Physical Metallurgy), elaborated precise procedure for determination of lattice parameters. **Josef Kuběna** oriented the group to study of semiconductors modified by ion implantation, study of defects in single crystals, X-ray topography and diffuse scattering (Václav Holý).



Martin Černožorský



Josef Kuběna

History of industrial applications of X-ray diffraction in **Škoda factory in Pilsen** started in 1943. Main work consisted in analysis of retained austenite in steels, carbides and nitrides, phase analysis of Cu, Al, and Ti alloys, ceramics, glass ceramics, plastics, corrosion products, different coatings, nitrided layers. The main person was for many years **Jaroslav Fiala**.



X-ray laboratory of Faculty of Science, **Palacky University in Olomouc** was established in 1965 and it is connected with the names of **Dagmar Krausová** and **Jiří Kameníček**. Problems were concentrated on rare earth complexes with hydroacids, coordination compounds of transition elements. Interesting works were done in collaboration with forensic medicine, study of gallstones.



Institute of molecular biology, Slovak Academy of Sciences in Bratislava was the first institution in Czechoslovakia working in the field of protein crystallography and determined the **first protein structure** (ribonuclease from *Streptomyces aureofaciens*). The main person there was **Jozef Ševčík**.



Activities of Czech and Slovak crystallographers in the field of international crystallography are also reflected in contributions to **International Tables for Crystallography**:

- Vol.A** (2006), Space group symmetry, Chapter 9.3. **Further properties of lattices, B. Gruber.**
- Vol.C** (2004), Mathematical, physical and chemical tables, Chapter 4.1 **Radiations used in crystallography, V. Valvoda.**
- Vol.C** (2004), Mathematical, physical and chemical tables, Chapter 9.2. **Layer stacking, S. Durovič, ...**
- Vol.D** (2013), Symmetry aspects of phase transitions,.. Chapter 3. **Structural phase transitions, ..., V. Janovec, V. Kopský, J. Přívratská, ...**
- Vol. E: Subperiodic groups** (2002). **V. Kopský** and D. Litvin.

Round Robin Tests (1993-1996): Faculty of Mathematics and Physics, Charles University in Prague, in cooperation with the International Centre for Diffraction Data (namely with R. Jenkins), organized three Round Robin tests on powder diffractometer sensitivity, intensity measurements and quantitative phase analysis in 35 X-ray laboratories in Czech Republic and Slovakia.

Many Czechs and Slovaks has been successfully working abroad for years. A few examples are: Emil Makovický (University of Copenhagen), Radovan Černý (University of Geneva), Jiří Kulda (ILL Grenoble), David Rafaja (Technical University Freiberg), Jan Ilavský (Argonne National Laboratory), Vratislav Langer (Chalmers University of Technology, Göteborg).

Lukáš Palatinus

(Institute of Physics, Academy of Sciences of the Czech Republic) won the second Erwin Felix Lewy Bertaut Prize (ECA-ENSA) in 2009.



Jan Ilavský



Vratislav Langer



Radovan Černý